United States Department of Agriculture
Natural Resources Conservation Service
National Soil Survey Center

SOIL SURVEY LABORATORY
METHODS MANUAL

Soil Survey Investigations Report No. 42
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Cover Photos:

Site Description: The typical landscape of the Jerryslu, fine-loamy, mixed, thermic Typic Natridurids. The Jerryslu has a natric horizon at 10 cm and a $CaCO_3$ and silica-cemented duripan beginning at 89 cm.

Pedon Description: Almond orchard in bloom on the Atesh, coarse-loamy, mixed (calcareous), thermic Duric Torriarents. Atesh is a modified Jerryslu soil. Modifications at this site include landleveling, ripping of the duripan, irrigation, and fertilization (including additions of gypsum, manure, and elemental sulfur). These pedons of Atesh and Jerryslu are located in Tulare County, California, approximately 100 m from each other.

Laboratory Characterization: Thin section photomicrograph of the Btkqm2 horizon (107-126 cm) of the Jerryslu pedon under cross-polarized light. Oriented, illuvial clay was initially deposited along channel walls, followed by nearly complete infilling with silica and $CaCO_3$ (Photo width = 2.8 mm).

FOREWORD

The development of laboratory methods for Soil Survey is the cumulative effort of a generation of soil scientists. The need for revision and enhancement of *Procedures for Collecting Soil Samples and Methods of Analysis for Soil Survey*, Soil Survey Investigations Report (SSIR) No. 1 (1984), was recognized by the National Soil Survey Center (NSSC) for some years. The collective efforts of many individuals at the Soil Survey Laboratory (SSL) resulted in a new document, *Soil Survey Laboratory Methods Manual* (SSIR No. 42, Version 1.0, 1989; Version 2, 1992). Mr. Frederick M. Kaisaki, soil scientist, developed a format and initiated descriptions of methods in the chemistry section. Mr. Laurence E. Brown, former Analytical Staff Leader at the SSL, with the support of Dr. E.G. Knox, former National Leader, Soil Survey Investigations, actively encouraged, supported, and managed the effort to describe all the methods currently in use in the new comprehensive format. Mr. Brown emphasized that the descriptions should specify the methods as actually used in enough detail for other workers to apply the method consistently. Other major contributors to the method descriptions include Dr. Michael A. Wilson, Dr. Thomas G. Reinsch, Benny R. Brasher, Leo C. Klameth, and Lea Ann Pytlik. Dr. W. Dennis Nettleton wrote the description and interpretation of soil micromorphology as seen in thin sections. The discussion of identification and significance of minerals, microcrystalline aggregates, and amorphous substances in optical studies of grain mounts was modified by Dr. Warren C. Lynn from material prepared by Dr. John G. Cady. Soil Survey Laboratory technicians also made important contributions to the method descriptions and appendices.

Since 1992, the SSL has undergone many technological changes as the result of improvements in analytical instrumentation and development of analytical methods. In 1995, a revised version (Version 3.0) of the SSIR No. 42 was initiated by Dr. M. Dewayne Mays, Head, Soil Survey Laboratory, to reflect these many changes. Many of the contributors to the earlier versions participated in the review and update of this revised version of *Soil Survey Laboratory Methods Manual*. In addition, Dr. Lynn has included in this version a more comprehensive description of the SSL field sampling procedures which is not found in the earlier versions.

Dr. Rebecca Burt, author of the *Soil Survey Laboratory Information Manual* (SSIR No. 45, 1995), served as technical editor for all versions of the SSIR No. 42. Her contribution is significant in scope; she wrote several methods and appendices, is responsible for additions, corrections, and consistency of the other methods, and provided leadership in the assemblage of this document.

PREFACE

The methods described in this manual are those used by the laboratory at the National Soil Survey Center (NSSC). They are documented by method codes and linked with analytical results that are stored in the NSSC laboratory database.

The methods in current use at this laboratory are described in enough detail that they can be performed in many laboratories without reference to other sources. An introduction to each group of related methods describes common characteristics. However, some repetition is included in order to make the method descriptions complete in themselves and to minimize reference to other parts of the manual. The appendix describes the operation of the instruments that are used in the laboratory procedures. Laboratory preparation and mineralogy codes are also included.

Some analytical results in the NSSC Soil Survey Laboratory (SSL) national database were obtained using procedures that are no longer used at the SSL. Descriptions for these procedures are located in a section following the appendix. Information is not available to describe these procedures in the same detail as used to describe the current methods in the laboratory.

The purpose of this manual is to document methodology and to serve as a reference for the laboratory analyst. The manual replaces *Procedures for Collecting Soil Samples and Methods of Analysis for Soil Survey,* Soil Survey Investigations Report (SSIR) No. 1. (1984) as a reference for laboratory methods used at the NSSC. We expect that development and adoption of additional methods will lead to revisions of this document. The *Soil Survey Laboratory Methods Manual* also serves as the primary document from which a companion manual, *Soil Survey Laboratory Information Manual* (SSIR No. 45, 1995), has been developed. The SSIR No. 45 describes in greater detail the application of SSL laboratory data.

Trade names are used in the manual solely for the purpose of providing specific information. Mention of a trade name does not constitute a guarantee of the product by the U.S. Department of Agriculture nor does it imply an endorsement by the Department of Agriculture.

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[1]Methods marked with an asterisk are not being used at the present time. These methods are included because many of the published laboratory data have been determined by these methods.

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SAMPLE COLLECTION AND PREPARATION
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PEDON SAMPLING (1A2)

1. APPLICATION

The United States National Cooperative Soil Survey (NCSS) Program has prepared soil maps for much of the country. Both field and laboratory data are used to design map units and provide supporting information for scientific documentation and predictions of soil behavior. A soil map delineates areas occupied by different kinds of soil, each of which has a unique set of interrelated properties characteristic of the material from which it is formed, its environment, and its history (Soil Survey Division Staff, 1993). The soils mapped by the NCSS are identified by names that serve as references to a national system of soil taxonomy (Soil Survey Staff, 1994). Coordination of mapping, sampling site selection, and sample collection in this program contributes to the quality assurance process for laboratory characterization. Requisites to successful laboratory analysis of soils occur long before the sample is analyzed (Soil Conservation Service, 1984). In the field, these requisites include site selection, descriptions of site and soil pedon, and careful sample collection. A complete description of the sampling site not only provides a context for the various soil properties determined but it is also a useful tool in the evaluation and interpretation of the soil analytical results (Canadian Soil Science, 1993). Landscape, landform, and pedon documentation of the sampling site serves as a link in a continuum of analytical data, sampled horizon, pedon, landscape, and overall soil survey area.

The objectives of a project or study form the basis for designing the sampling strategy. A carefully designed sampling plan is required to provide reliable samples for the purpose of sampling. The plan needs to address the site selection, depth of sampling, type and number of samples, details of collection, and sampling and subsampling procedures to be followed. The Soil Survey Laboratory (SSL) primarily serves the NCSS, which is conducted jointly by USDA Natural Resources Conservation Service (NRCS), the Bureau of Land Management (BLM), Forest Service, and representatives of U.S. Universities and Agricultural Experiment Stations. In this context, the primary objective of SSL sampling programs has been to select sites and pedons that are representative of a soil series and to collect samples that are representative of horizons within the pedon.

There are various kinds of sampling plans, e.g., intuitive and statistical, and many types of samples, e.g., representative, systematic, random, and composite. In the field, the SSL has more routinely used intuitive sampling plans to obtain representative samples. The intuitive sampling plan is one based on the judgment of the sampler, wherein general knowledge of similar materials, past experience, and present information about the universe of concern, ranging from knowledge to guesses, are used (Taylor, 1988). A representative sample is one that is considered to be typical of the universe of concern and whose composition can be used to characterize the universe with respect to the parameter measured (Taylor, 1988).

In the laboratory, the primary objectives of sample collection and preparation are to homogenize and obtain a representative soil sample to be used in chemical, physical, and mineralogical analyses (procedure 1B). The analyst and the reviewer of data assume that the sample is representative of the soil horizon being characterized. Concerted effort is made to keep analytical variability small. Precise laboratory work means that the principal variability in characterization data resides in sample variability, i.e., sampling is the precision-limiting variable. As a result, site-selection and sample collection and preparation are critical to successful soil analysis.

2. SUMMARY OF METHOD

In the U.S. Soil Survey Program, field data (e.g., transects and pedon descriptions) combined with laboratory data are used to define map unit components, establish ranges of component properties, establish or modify property ranges for soil series, and answer taxonomic and interpretive questions (Wilson et al., 1994).

A site is selected that meets the objectives of the laboratory sampling. The site and soil pedon are described and georeferenced. These descriptions include observations of specific soil properties such as texture, color, slope, and depth. Descriptions may also include inferences of soil quality (soil erodibility and productivity) as well as soil-forming factors (climate, topography, vegetation, and geologic material).

SAMPLE COLLECTION AND PREPARATION
FIELD SAMPLING (1A)
SITE SELECTION (1A1)
PEDON SAMPLING (1A2)

A soil pit is often excavated with a back-hoe. Depth and breadth of pit depend on the soil material and objectives of sampling. Soil horizons or zones of uniform morphological characteristics are identified for sampling.

The variable nature or special problems of the soil itself, e.g., Vertisols, Histosols, or permafrost-affected soils, may require the use of specific excavation and sampling techniques. For example, the shear failure that forms slickensides in Vertisols also disrupts the soil to the point that conventional soil horizons do not adequately describe the morphology.

Representative samples are collected and mixed for chemical, physical, and mineralogical analyses. A representative sample is collected using the boundaries of the horizon to define the vertical limits and the observed short-range variability to define the lateral limits. The tag on the sample bag is labelled to identify the site, pedon, and soil horizon for the sample.

In the field, the 20- to 75-mm fraction is generally sieved, weighed, and discarded. In the laboratory, the <20-mm fraction is sieved and weighed. The SSL estimates weight percentages of the >2-mm fractions from volume estimates of the >20-mm fractions and weight determinations of the <20-mm fractions by procedure 3B1b.

Undisturbed clods are collected for bulk density and micromorphological analysis. Clods are obtained in the same part of the pit as the mixed, representative sample. Bulk density clods are used for water retention data; to convert from a weight to volume basis; to determine the coefficient of linear extensibility (COLE); to estimate saturated hydraulic conductivity; and to identify compacted horizons. Microscope slides of soil prepared for micromorphology are used to identify fabric types, skeleton grains, weathering intensity, illuviation of argillans, and to investigate genesis of soil or pedological features.

3. INTERFERENCES

In the process of sampling, a number of obstacles may arise from external sources, e.g., weather, accessibility, steep terrain, wet terrain, insects, and large rock fragments. Sometimes pits have to be hand-excavated. Common sense and the guidelines for obtaining representative samples are applied to the extent possible.

4. SAFETY

Sampling pits deeper than 125 cm (5 feet) need to be shored to meet U.S. Dept. of Labor Occupational Safety and Health Administration (OSHA) standards, or one side has to be opened and sloped upward to prevent entrapment. Acetone used in the saran mix is flammable and should be used down wind from a site to keep fumes from collecting in the bottom of the pit. Take precautions when operating or in the proximity of machinery, e.g., backhoe, drill rig, or hydraulic probe, and when lifting sample bags.

5. EQUIPMENT
5.1 Plastic bags, for mixed samples
5.2 Tags, for mixed samples
5.3 Plastic bags, for bulk density and thin section clods
5.4 Aluminum case, for shipping clod boxes
5.5 Shipping bags (canvas, leather, or burlap) for mixed samples
5.6 Clod boxes, cardboard with dividers
5.7 Core boxes, to transport cores from drill rig or hydraulic probe)
5.8 Stapler
5.9 Staples
5.10 Hair nets
5.11 Rope
5.12 Clothes pins
5.13 Felt markers, permanent
5.14 Sampling pans

5.15 Sampling knives
5.16 Measuring tape
5.17 Photo tape
5.18 Sieves (3-inch and 20-mm)
5.19 Plastic sheets
5.20 Canvas tarp

6. REAGENTS
6.1 Acetone
6.2 Water, in spray bottle
6.3 Dow Saran F-310 Resin. Available from Dow Chemical Company.

7. PROCEDURE

Project and Sampling Objectives

The number and types of samples collected from a site are governed in part by the objectives of the information needed. Sampling schemes can be divided into three general project categories based on project needs.

Reference Projects: These projects are designed to answer specific questions on mapping or soil classification, provide data for transect of a mapping unit, or for collection of calibration standards. Samples are typically collected from specific horizons in 3 to 5 locations that relate to the question or are representative of the map unit. A limited number of analyses, specific to the questions asked, are performed on these samples.

If a transect is used to test map unit composition, an appropriate sample from each transect point may be collected for analyses that are critical to distinguishing between map unit components. Also, samples may be collected as standards for the survey project for texture, organic carbon, or for calibration of field office analyses such as base saturation.

Characterization Projects: These projects are designed to obtain comprehensive soil characterization data for a representative pedon of a map unit or a pedon which is included in a research study. Samples collected from each horizon include bulk samples of approximately 3 kg, as well as clods of natural fabric for bulk density and micromorphology. A standard suite of laboratory analyses are performed on each horizon. In addition, specific analyses, such as mineralogy or andic properties, may be requested to provide more complete information on the specific pedon sampled.

Geomorphology and Stratigraphy Projects: These projects are designed to study relationships between soils, landforms, and/or the stratigraphy of their parent materials. For example, a specific project may be designed to study the relationships between a catena of soils, their morphological properties, e.g., redoximorphic features, and the hydrology of the area. Another study may be designed to determine the lateral extent of stratigraphic breaks. Site or pedon selection is governed by the objectives of the study but often is selected to represent typical segments of the landform. Sampling and analytical requests may be similar to the scheme used in a characterization or reference project. Often, core samples may be collected to several meters in depth through the use of a hydraulic probe.

Pedon Sampling Techniques

Excavated Pits: A pit may be excavated by hand or with a backhoe. Hand-digging may be necessary depending on site location, type of soil material, or availability of a backhoe. Pedons are generally excavated through the solum and into the parent material, or to a maximum depth of 2 meters. When using a backhoe, dig the pit in the form of an arc with a minimum working face deeper than about 150 cm (5 ft). Slope the pit upward toward the backhoe for an escape route. The pit can also be modified from the back side to form a T with the back of the trench opened and widened for an escape route. If this is not practical, shoring is required to meet OSHA standards if the pit is deeper than 125 cm (5 ft).

SAMPLE COLLECTION AND PREPARATION
FIELD SAMPLING (1A)
SITE SELECTION (1A1)
PEDON SAMPLING (1A2)

The sampling procedure is the same for hand-dug and backhoe pits. Mark horizons or zones to be sampled. Take a representative sample from boundary to boundary of a horizon and for a lateral extent to include the observed short-range variability. Unless the soil exhibits little short range variability, the best procedure is to place 4 to 5 kg soil on the plastic sheet or canvas tarp, mix thoroughly by rolling action, and place a representative subsample, minimum of 3 kg (3 qt), in a plastic sample bag. Label a tag with soil name, soil survey number, horizon (zone), and depth (as a minimum). Double fold the top of the plastic bag (forward and reverse) and staple the top of the tag under the folds. The sampling may be extended deeper by bucket auger or hydraulic probe as appropriate to meet the objectives of the project. If the soil has rock fragments in one or more horizons, the soil and coarse fragments need to be sieved and weighed as described below.

Collect 3 bulk density clods from each horizon. Two clods are used in the primary analysis. The third clod is reserved for a rerun, if needed. Clods should be roughly fist-sized and should fit into the cell (8 x 6 x 6 cm) of a clod box fairly snugly. Take the clods in the same vicinity of the pit as the mixed sample. Carve out a working section in the pit wall to remove an undisturbed block. Break the block into fist-sized pieces and pare into a ovoid (egg-shaped) clod. Place the clod in a hair net. If the clod is dry, mist the clod with water just until the surface glistens to inhibit saran penetration of the clod. Dip once, briefly, in saran mix to coat the clod, and hang from a rope with a clothes pin to dry. Clods can be dipped and then hung, or can be hung and then dipped by raising the container up to immerse the clod, briefly. Keep the saran container covered except when dipping clods to prevent acetone evaporation. Coat only once in the field. Additional coats are applied in the laboratory. When the clod is dry (bottom is not sticky to the touch), place the clod in a plastic bag, and put into a cell of a clod box. Label the appropriate cell on the inside of the lid of the box to identify the soil survey number and horizon (zone) for the clod. Clod boxes are designed to identify sequences of 3 clods per horizon.

Collect 2 clods from each horizon for preparation of thin sections and micromorphological examination. Place a staple in the top of each clod for orientation. Clods should be roughly fist size, but kept unmodified otherwise. If the soil fabric is fragile, the clod can be placed in a hairnet and dipped briefly in saran as described above. Place the clod in a plastic bag and put into a cell of a clod box. The sampler should make special note of any features to be studied by thin section. Label the appropriate cell on the inside of the lid of the box to identify the soil survey number and horizon (zone) for the clod.

If the material is too sandy and/or too dry to hold together in a clod, bulk density samples can be collected with an aluminum moisture can or other small can of known volume. Sampling is easier if the can has a small hole in the bottom to allow air to escape as the can is inserted. Smooth a planar area in the pit face, or, if sampling from the top down, smooth a planar horizontal area. In either case, choose an area that appears representative of the horizon. With the palm of the hand, gently push the can into the smoothed area until the bottom of the can is flush with the wall or until resistance stops you. In this case, lay a board across the bottom of the can and tap lightly with a hammer or geology pick until the bottom of the can is flush with the pit wall. Then dig out the sampling can plus extra sample and, with a knife blade, smooth off the sample flush with the top of the can. Empty the contents of the can into a plastic bag, tie the top of the bag in a single knot and put into a cell in a clod box. Label the appropriate cell on the inside of the lid of the box to identify the soil survey number and horizon (zone) for the sample. Collect two samples per horizon. Indicate the volume of the sampling can in the sampling notes. It is assumed that there is no volume change with moisture content in sandy soils. Therefore, one density is representative for all moisture contents of coarse-textured soils.

Avoid leaving empty cells in a clod box. Fill empty cells with a wadded paper. This prevents clods from shifting in transit. Tape down the top of a filled clod box with nylon filament tape (one short piece on each end and two short pieces in front). Label the top of the box to identify type of sample (bulk density or thin section) and appropriate soil survey numbers and horizons (zones) for the samples. Place six clod boxes in an aluminum case for shipment. Single clod boxes also ship well.

SAMPLE COLLECTION AND PREPARATION
FIELD SAMPLING (1A)
SITE SELECTION (1A1)
PEDON SAMPLING (1A2)

Hand Probe: Remove surface if it is not suitable for coring. Remove core sections and lay in order on plastic sheet. Measure core length against depth in hole to determine if the core has been compressed. Mark horizon breaks on the plastic. Mix the horizon or zone to be sampled. Place sample in a plastic bag and label with soil survey number, horizon (zone), and depth for the core. Samples need to be a minimum of 500 g (1 pt), and are generally suitable for a limited number of analyses only.

Hydraulic probe: Remove surface if it is not suitable for coring. Remove core sections and lay in order on plastic sheet. With a sharp knife trim the exterior to remove any oil and contaminating soil material. Split one core open to mark horizons, describe and then sample. Measure core length against depth in hole to determine if the core has been compressed. Mark horizon breaks on the plastic. Mix the horizon or zone to be sampled. Place in a plastic bag and label with soil survey number, horizon (zone), and depth for the core. Obtain a minimum of 500 g (1 pt) for a reference sample or 3 kg (3 qt) for a characterization sample.

If the core has not been compressed, and the core diameter is 3 inches or more, samples for bulk density can be taken from a second core. Mark a segment 8-cm long on an undisturbed section and slice a cylindrical segment. Measurements of core diameter and length can be used to calculate volume and density at the field state moisture content. Core segments can be placed in a hair net, dipped once briefly in saran mix to coat the clod, hung from a rope with a clothes pin to dry, placed in a plastic bag and then put into a cell of a clod box.

Rotary drill (hollow stem): Remove drill core sections and lay in order on plastic sheet. Measure core length against depth in hole to determine if the core has been compressed. Mark horizon breaks on the plastic. Mix the horizon or zone to be sampled. Place in a plastic bag and label with soil survey number, horizon (zone), and depth for the core. Obtain a minimum of 500 g (1 pt) for a reference sample or 3 kg (3 qt) for a characterization sample.

If the core has not been compressed, and the core diameter is 3 inches or more, samples for bulk density can be taken from the core. Mark a segment 8 cm long on an undisturbed section and slice a cylindrical segment. Note the core diameter and length in the soil description. Place the core segment in a plastic bag and place bag into a bulk density (clod) box for shipment. Measurements of core diameter and length can be used to calculate volume and density at the field state moisture content. Core segments can be placed in a hair net, dipped once, briefly in saran mix to coat the clod, hung from a rope with a clothes pin to dry, placed in a plastic bag and then put into a cell of a clod box. Label the appropriate cell number on the inside of the box lid to identify the site, pedon, and horizon.

A core segment can be taken for thin section. Place a staple in the top of the core, place the core in a plastic bag and put the bag into a cell in a clod box. Label the appropriate cell number on the inside of the box lid to identify the site, pedon, and horizon.

Bucket Auger: Remove surface if it is not suitable for auguring. Remove auger loads and lay in order on plastic sheet. When horizon breaks are detected, measure depth in hole and mark it on the plastic. Mix the horizon or zone to be sampled. Place in a plastic bag and label with soil survey number, horizon (zone), and depth for the sample. Obtain a minimum of 500 g (1 pt) for a reference sample or 3 kg (3 qt) for a characterization sample. Sampling depth in a pit can be extended by the use of an auger in the pit bottom.

Specific Sampling Techniques

Soils with Rock Fragments: If coarse fragments up to 75 mm (3 in) in diameter are to be weighed in the field, place excavated sample in a bucket of known weight (tare) and weigh. Sieve the sample through both a 75-mm and 20-mm sieve (3/4 in) onto a canvas tarp which can be suspended from a scale. Estimate the coarse fragment volume percent of both the 75 to 250 mm (10 in) fraction and > 250-mm fraction, and record these values in the description or sampling notes. Weigh the 20 to 75 mm and the <20 mm fractions in pounds or kilograms, and record these weights. Weights are calculated to an oven-dry base in the laboratory. Place a minimum of 4 kg (1 gal) in a plastic bag, double fold the bag, and staple. The moisture content is determined on the sample in the laboratory. If

the 20 to 75-mm fraction is not weighed in the field, estimate the volume percent and record in the sampling notes or description.

Organic Soils: If the soils are drained or the natural water table is below the surface, obtain samples of upper layers from a pit. If the hydraulic conductivity is slow enough, dig and remove samples below the water table as far as practical with due haste and place on a plastic sheet in an orderly fashion for describing and processing. If undisturbed blocks can be removed for bulk density, carve out cubes of known dimension (e.g., 5 cm on a side), place the block in a plastic bag and tie the top in a knot. Place in a second plastic bag if soil is saturated, tie the top in a knot. Put the double bagged sample in a clod box and label the appropriate cell on the inside of the lid to identify the soil survey number and horizon (zone) for the sample. Note the sample dimensions in the sampling notes.

Collect samples from below the water table with a Macaulay peat sampler. If the samples appear undisturbed, mark 10-cm segments, slice with a knife, and place a single segment in a plastic bag. Tie the top in a knot and place in a second plastic bag and tie the top of that bag in a knot. Put the double bagged sample in a clod box and label the appropriate cell on the inside of the lid to identify the soil survey number and horizon (zone) for the sample. Note the sampler diameter and length of core in sampling notes. The sample shape is a half-cylinder. As an alternative, carve a block to fit snugly in a tared moisture can. Place lid on can, put can in a plastic bag, tie the top, and put in a clod box. Identify can number, depth in sampling notes along with the tare weight. Take replicate samples for the mixed sample, as necessary.

Larger samples can be taken below the water table by removing the surface mat with a spade and sampling lower layers with a post-hole digger. Place samples of each layer on plastic for examination. Transfer samples to small plastic bags, knead to remove air. Put two small bags of sample into one large plastic bag, fold top, staple, and tag.

Permafrost Affected Soils: Soils with permafrost present two special sampling problems. The permafrost is very resistant to excavation and the cryoturbation disrupts horizon morphology. In many cases the surface layers are organic materials. The following sampling approach is suggested.

Test the depth to the frost table with a small (1 to 2 mm) diameter steel rod.. Excavate a small pit (about 0.7 by 1.3 m) to leave about 10 cm of unfrozen material over the permafrost. If a cyclic pattern (up to a few meters) is evident in the surface topography, extend the pit through at least one cycle. The organic layers can be carved out with a sharp knife or shovel in many cases and removed. Save the large chunks, if possible.

The objective is to record the morphology of the unfrozen soil before the permafrost is disturbed. Examine the surface and designate horizons. If the soil is disrupted to the extent that lateral horizons do not represent the morphology, impose a grid over the pit face and sketch the morphology on graph paper. Describe the soil down to the frost table. When the description of the unfrozen material is complete, remove all unfrozen material to examine the conformation of the frost table. Note on graph paper if necessary and photograph.

Frozen earth can be removed in successive steps with a gasoline-powered jackhammer. Place pieces from each step on a separate plastic sheet. Examine pieces and describe the morphology as they are removed. Note thickness of segregated ice lenses and make a visual estimate of relative volume of segregated ice. Place representative pieces into a water-tight container so that the sample can be weighed, dried, and weighed again to calculate the amount of water and volume of ice. Excavate to a depth of 30 to 50 cm below the frost table, if practical. Clean off the pit face and be ready to photograph immediately. Sample each horizon or zone for mixed sample, bulk density, and thin section as is practical.

Vertisols: The shear failure that forms slickensides in Vertisols also disrupts the soil to the point that conventional horizons do not adequately describe the morphology. A gilgai surface topography is reflected in the subsurface by bowl-shaped lows and highs. One convention is to sample pedons out of the low and the high areas which represent extremes in the cyclic morphology.

SAMPLE COLLECTION AND PREPARATION
FIELD SAMPLING (1A)
SITE SELECTION (1A1)
PEDON SAMPLING (1A2)

In order to examine morphology and associated soil properties in more spatial detail, the following procedure is suggested: Dig a trench long enough to cover two or three cycles of morphological expression. From the bottom of the pit remove soil from the non-work face so it slopes up and away. Use nails and string to outline boundaries of morphological cells. Assign a number and a horizon designation to each cell.

Construct a level line about one meter below the highest point on the surface. Hammer a spike into the wall at one end of the pit. Tie a loop in string, place the loop over the spike, and run the string to the far end of the pit. Place a line level on the string, tie another loop in the string, place a second spike through the loop, pull the string taut, raise or lower the spike until the string is level, and hammer the spike into the pit face.

Place a marker at each meter along the string from one end to the other. Transfer the morphology outlined by the string to graph paper by measuring the x-coordinate along the string and the y-coordinate above or below the string, both in centimeters. Use a level or a plumb bob to make the y measurement vertical.

Sample each cell for characterization analysis as described above. The sampling scheme can include traditional pedon sequences by sampling vertical sequences of cells at low, high, and intermediate positions along the cycle.

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SAMPLE COLLECTION AND PREPARATION
LABORATORY PREPARATION OF SOIL SAMPLES (1B)

INTRODUCTION

The purpose of any soil sample is to obtain information about a particular soil and its characteristics. Sampling provides a means to estimate the parameters of these soil characteristics with an acceptable accuracy at the lowest possible cost. Subsampling also may be used as it permits the estimation of some characteristics of the larger sampling unit without the necessity of measurement of the entire unit. Subsampling reduces the cost of the investigation, but usually decreases the precision with which the soil characteristics are estimated. Efficient use of subsampling depends on a balance between cost and precision (Petersen and Calvin, 1986).

Soil variability and sample size are interferences to sample collection and preparation. At each stage of sampling, an additional component of variability, the variability within the larger units, is added to the sampling error (Petersen and Calvin, 1986). Soil material needs to be adequate in amount and thoroughly mixed in order to obtain a representative sample.

The objective of laboratory preparation is to homogenize the soil samples used in chemical, physical, and mineralogical analyses. These analyses are generally determined on the fine-earth (<2-mm) fraction that has been air-dried (30 to 35°C) to a constant weight. Drying generally requires 3 to 7 days. The standard air-dry preparation is procedure 1B1. Other procedures for laboratory preparation include Field Moist, 1B2; Coarse Fragments (2 to 20 mm), 1B5; Whole Soil, 1B6; and Organic Material, 1B7. In addition to laboratory preparation for bulk samples, undisturbed soil clods that are used to determine some physical properties, e.g., bulk density, also are processed.

The following procedural steps are not repeated in each of the methods for laboratory preparation as they are generally applicable to all methods.

1. Assign a lab identification number and preparation code to samples. Preparation code depends on properties of the sample and on the requested analyses.

2. Assign clods and natural fabrics (NF) with a lab identification number corresponding to the respective bulk sample. In the field, place a pin or staple in the top of sample to ensure proper orientation, if requested.

3. Prepare a 480-mL (pint) container of fine-earth fraction for laboratory analyses. Prepare an additional 480-mL (pint) container for saturation paste when salt analyses are requested. For comprehensive sampling projects, prepare two 480-mL (2-pint) containers of fine-earth material and a NF sample and store in a sample bank. If an NF sample was not selected in the field, select one from bulk sample. Generally, do not select NF samples for reference projects.

4. Check soil samples for presence of carbonates. Reference samples (knowns) are available for comparisons. Place 1 g of <2-mm soil in porcelain spot plate, add distilled water, and stir to remove entrapped air. Add 1 N HCl to soil, observe amount of effervescence, and record as follows:

None (0)

Trace (T) - Bubbles rise at a few points in the sample and consistently appear at the same point in either a steady stream of tiny bubbles or in a slower stream of larger bubbles. Do not mistake trapped air bubbles for a positive test. Generally, these air bubbles appear immediately after the addition of 1 N HCl.

Weak (W) - More small bubbles, and possibly a few larger bubbles, appear throughout the sample than with a trace reaction.

Medium (M) - More large bubbles are evident than with a weak reaction. Often the reaction is violent at first and then quickly decreases to a reaction that produces many small bubbles.

Strong (S) - The sample effervesces violently. Many large bubbles appear to burst from the spot plate.

5. Sterilize soils from quarantined areas in an oven for 15 h at 150°C or in a steam sterilizer for 30 min. at 105°C and 22 psi before discarding. Do not exceed 5-cm depth for sterilized residues. Also sterilize containers of regulated material before discarding. When regulated samples are requested, only send to laboratories that are authorized to handle this material. Stamp "STERILIZE BEFORE DISCARDING" on each container before sending.

REFERENCES
Petersen, R.G., and L.D. Calvin. 1986. Sampling. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:33-51.

SAMPLE COLLECTION AND PREPARATION
LABORATORY PREPARATION OF SOIL SAMPLES (1B)
STANDARD AIR-DRY (1B1)

1. APPLICATION

Air-dry soil is used for most standard analyses. This is generally the optimum moisture content to handle and to process soil. In addition, the weight of air-dry soil remains relatively constant, and biological activity is low during storage. The preparation codes for this procedure are "S", "SP", and "N". Refer to Appendix I, Laboratory Preparation Codes. The "S" preparation code is used when the data for the >2-mm fractions are recorded, and the analytical results are reported on the <2-mm basis. The "SP" code is used when clod parameters are reported on the whole soil basis. The "SP" preparation code is generally used when the coarse fragments are porous, e.g., cinders. The "N" preparation code is used when the data for the >2-mm fractions are not recorded, and the analytical results are reported on the <2-mm basis.

2. SUMMARY OF METHOD

The field sample is air-dried, crushed, and sieved. Weight measurements are made on the 20- to 75-mm, 5- to 20-mm, and 2- to 5-mm fractions. The <2-mm material is saved for chemical, physical, and mineralogical analysis.

3. INTERFERENCES

Soil variability and sample size are interferences to sample collection and preparation. At each stage of sampling, an additional component of variability, the variability among smaller elements within the larger units, is added to the sampling error (Petersen and Calvin, 1986). Soil material needs to be in adequate amount and thoroughly mixed to obtain a representative sample.

Soil is mixed by moving it from the corners to the middle of processing area and then by redistributing the material. This process is repeated four times. Enough soil material needs to be sieved and weighed to obtain statistically accurate rock fragment content. In order to accurately measure rock fragments with a maximum particle diameter of 20 mm, the minimum specimen size ("dry" weight) that needs to be sieved and weighed is 1.0 kg. Refer to ASTM method D 2487 (American Society for Testing and Materials, 1993).

4. SAFETY

Dust from sample processing is a nuisance. A mask should be worn in order to avoid breathing dust. Keep clothing and hands away from the crusher and pulverizer when these machines are in use. Use face shield and goggles when operating the jaw crusher. Use goggles when operating the air compressor. The HCl used to check carbonates can destroy clothing and irritate skin. Immediately rinse acid with water from clothing or skin and seek professional medical help, if needed.

5. EQUIPMENT

5.1 Electronic Balance,$\pm$1-g sensitivity and 15-kg capacity
5.2 Cardboard trays for sample storage
5.3 Trays, plastic, tared
5.4 Sieves, square-hole
5.4.1 80 mesh, 180 μm
5.4.2 10 mesh, 2 mm
5.4.3 4 mesh, 4.75 mm
5.4.4 19 mm, 3/4 in
5.4.5 76 mm, 3 in
5.5 Sieves, round-hole
5.5.1 2 mm
5.6 Mechanical shaker with 10-mesh and 4-mesh sieves
5.7 Pulverizer
5.8 Wooden rolling pin
5.9 Rubber roller

5.10 Retsch laboratory jaw crusher, Model BB2/A, Brinkmann Instruments Inc., Des Plaines, IL.

5.11 Metal plate, 76 x 76 x 0.5 cm

5.12 Aluminum foil dishes, 57-mm diameter x 15-mm deep, with lifting tab

5.13 Paper containers, 480 mL (pint), with lids

5.14 Brown kraft paper

5.15 Air compressor, Cast-iron Series, SpeedAire, Campbell Hausfeld Mfg. Co., Harrison, OH.

5.16 Mixer/Mill, Spex 8000, Edison, N.J. Fine-grind, 80-mesh.

5.17 Vial rotator, Sampletex, Model 200, Lincoln, NE. Fine-grind, 80 mesh.

6. REAGENTS

6.1 Distilled water

6.2 1 N HCl

6.3 Sodium hexametaphosphate solution. Dissolve 35.7 g of sodium hexametaphosphate ($Na_4P_2O_7$) and 7.94 g of sodium carbonate (Na_2CO_3) in 1 L of distilled water.

7. PROCEDURE

7.1 Distribute field sample on a plastic tray. Weigh material and record moist weight. Air-dry, weigh, and record weight of soil material.

7.2 Roll soil material with wooden rolling pin to crush clods to pass a 2-mm sieve. For samples with easily crushed coarse fragments, substitute a rubber roller for a wooden rolling pin. Roll and sieve until only the coarse fragments that do not slake in sodium metaphosphate solution remain on sieve. Crush soils that contain no coarse fragments in a laboratory jaw crusher. Sieve clayey soils that contain many coarse fragments in the mechanical shaker.

7.3 Process air-dry soil on a flat, metal plate that is covered with brown kraft paper. Thoroughly mix material by moving the soil from the corners to the middle of the processing area and then by redistributing the material. Repeat process four times.

7.4 If more sample is received than is needed for processing, select subsample for preparation. Weigh subsample and record weight.

7.5 Weigh soil material with diameters of 2 to 5 mm. Soak in sodium hexametaphosphate solution for 12 h. Air-dry, weigh the material that does not slake, record weight, and discard. Weigh, record weight, and discard coarse fragments with diameters of 20 to 75 mm and 5 to 20 mm.

7.6 Place the <2-mm, air-dry material in a 480-mL (pint) container and store until it is used for chemical, physical, or mineralogical analysis. Also place <2-mm, air-dry material into two aluminum foil dishes for AD/OD (air-dry/oven-dry ratio) and 15-bar analysis. Use a fine-ground (<80-mesh), air-dry subsample when total S, C, and N analyses are requested.

Square-hole 2-mm sieve (1B1a)

7a. Procedure
7a.1 Pass sample through a square-hole, 2-mm sieve. This procedure is the standard method.

Round-hole 2-mm sieve (1B1b)

7b. Procedure
7b.1 Pass sample through a round-hole 2-mm sieve.

8. CALCULATIONS
Calculations for coarse fragments are reported in procedure 3B.

9. REPORT
9.1 Weight (g) of field moist soil sample
9.2 Weight (g) of air-dry soil sample
9.3 Weight (g) of air-dry soil processed sample
9.4 Weight (g) of 20- to 75-mm fraction
9.5 Weight (g) of 5- to 20-mm fraction
9.6 Weight (g) of 2- to 5-mm fraction
9.7 Weight (g) of subsample of 2- to 5-mm fraction before slaking
9.8 Weight (g) of subsample of 2- to 5-mm fraction after slaking
9.9 Effervescence with HCl (S = strong; M = medium; W = weak; T = trace; 0 = none)

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
American Society for Testing and Materials. 1993. Annual book of ASTM standards. Construction.
Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.
Petersen, R.G., and L.D. Calvin. 1986. Sampling. *In* A. Klute (ed.) Methods of soil analysis. Part 1.
Physical and mineralogical methods. 2nd ed. Agronomy 9:33-51.

SAMPLE COLLECTION AND PREPARATION
LABORATORY PREPARATION OF SOIL SAMPLES (1B)
FIELD MOIST (1B2)

1. APPLICATION

When the physical properties of a soil are irreversibly altered by air drying, a field-moist soil sample is used for analysis. Analyses that may require field moist material are physical properties, e.g., water retention, particle-size analysis, and plasticity index for Andisols and Spodosols. The preparation code for this procedure is "M". Refer to Appendix I, Laboratory Preparation Codes. The data are recorded, and the analytical results are reported on the <2-mm basis.

2. SUMMARY OF METHOD

A subsample of field moist material is forced through a 2-mm screen by hand or with a large, rubber stopper. The moist sample is stored in 120-mL (4-oz) and/or 240-mL (8-oz), sealed, polypropylene containers. Moist samples may be used for 15-bar water content, particle-size analysis, Atterberg Limits, salts, cation exchange capacity, and other chemical properties. The remaining sample is air-dried and sieved (<2 mm). Weight measurements are made on the 20- to 75-mm, 5- to 20-mm, and 2- to 5-mm fractions. The <2-mm, air-dry material is also saved for the chemical, physical, and mineralogical analysis that do not require a field moist sample.

3. INTERFERENCES

Soil variability and sample size are interferences to sample collection and preparation. At each stage of sampling, an additional component of variability, the variability among smaller elements within the larger units, is added to the sampling error (Petersen and Calvin, 1986). Soil material needs to be in adequate amount and thoroughly mixed in order to obtain a representative sample.

The moist material is distributed on a plastic tray and thoroughly mixed. Soil is selected from at least five separate areas on the tray and forced through a 2-mm sieve. The air-dry soil is also thoroughly mixed by moving the soil from the corners to the middle of the processing area and then by redistributing the material. This process is repeated four times. Enough soil material needs to be sieved and weighed to obtain statistically accurate rock fragment content. In order to accurately measure rock fragments with a maximum particle diameter of 20 mm, the minimum specimen size ("dry" weight) that needs to be sieved and weighed is 1.0 kg. An homogenized soil sample is more readily obtained from air-dry material than from field moist material. Whenever possible, "moist" samples or materials should have weights two to four times larger than for "dry" specimens (American Society for Testing and Materials, 1993). Refer to ASTM method D 2487 (American Society for Testing and Materials, 1993).

4. SAFETY

Dust from sample processing is a nuisance. A mask should be worn in order to avoid breathing dust. Keep clothing and hands away from the crusher and pulverizer when these machines are in use. Use face shield and goggles when operating the jaw crusher. Use goggles when operating the air compressor. The HCl used to check carbonates can destroy clothing and irritate skin. Immediately rinse acid with water from clothing or skin and seek professional medical help, if needed.

5. EQUIPMENT
5.1 Electronic Balance, ±1-g sensitivity and 15-kg capacity
5.2 Cardboard trays for sample storage
5.3 Trays, plastic, tared
5.4 Sieves, square-hole
5.4.1 80 mesh, 180 μm
5.4.2 10 mesh, 2 mm
5.4.3 4 mesh, 4.75 mm
5.4.4 19 mm, 3/4 in
5.4.5 76 mm, 3 in
5.6 Wooden rolling pin
5.7 Rubber roller

5.8 Metal plate, 76 x 76 x 0.5 cm

5.9 Aluminum foil dishes, 57-mm diameter x 15-mm deep, with lifting tab

5.10 Paper containers, 480 mL (pint), with lids

5.11 Brown kraft paper

5.12 Polyproylene containers, 120 mL (4 fl. oz.) or 240 mL (8 fl. oz.), with lids

5.13 Retsch laboratory jaw crusher, Model BB2/A, Brinkmann Instruments Inc., Des Plaines, IL.

5.14 Air compressor, Cast-iron Series, SpeedAire, Campbell Hausfeld Mfg. Co., Harrison, Ohio.

5.15 Mixer/Mill, Spex 8000, Edison, N.J. Fine-grind, 80-mesh.

5.16 Vial rotator, Sampletex, Model 200, Lincoln, NE. Fine-grind, 80-mesh.

6. REAGENTS

6.1 Distilled water

6.2 1 *N* HCl

6.3 Sodium hexametaphosphate solution. Dissolve 35.7 g of sodium hexametaphosphate ($Na_4P_2O_7$) and 7.94 g of sodium carbonate (Na_2CO_3) in 1 L of distilled water.

7. PROCEDURE

7.1 Distribute field sample on a plastic tray. Thoroughly mix material. Select a representative subsample from at least five different areas on the plastic tray and force through a 2-mm sieve. If only moist 15 bar is requested, sieve enough material to fill a 120-mL (4-oz), polypropylene container. If moist material is requested for 15 bar as well as particle-size analysis, sieve enough material to fill an 240-mL (8-oz), polypropylene container. If moist material is also requested for Atterberg Limits, prepare additional material in an 240-mL (8-oz), polypropylene container. Seal container with lid and store.

7.2 Roll soil material with wooden rolling pin to crush clods to pass a 2-mm sieve. For samples with easily crushed coarse fragments, substitute a rubber roller for a wooden rolling pin. Roll and sieve until only the coarse fragments that do not slake in sodium hexametaphosphate solution remain on sieve.

7.3 Weigh remaining field sample on the plastic tray and record moist weight. Air-dry, weigh, and record weight of soil material. Process air-dry soil on a flat, metal plate that is covered with brown kraft paper. Thoroughly mix material by moving the soil from the corners to the middle of the processing area and then by redistributing the material. Repeat process four times.

7.4 If more sample is received than is needed for processing, select a subsample for preparation. Weigh subsample and record weight.

7.5 Weigh soil material with diameters of 2 to 5 mm. Soak in sodium pyrophosphate solution for 12 h. Air-dry, weigh, record weight, and discard the material that does not slake. Weigh, record, and discard coarse fragments with diameters of 20 to 75 mm and 5 to 20 mm.

7.6 Place <2-mm, air-dry material in a 480-mL (pint) container and store until it is used for chemical, physical, or mineralogical analysis. Also place air-dry material in two aluminum foil dishes for AD/OD (air-dry/oven-dry ratio) and for dry 15-bar moisture analysis. Use a fine-ground (<80-mesh), air-dry subsample when total S, C, and N analyses are requested.

8. CALCULATIONS

Calculations for coarse fragments are reported in procedure 3B.

9. REPORT

9.1 Weight (g) of field moist soil sample
9.2 Weight (g) of air-dry soil sample
9.3 Weight (g) of air-dry soil processed sample
9.4 Weight (g) of 20- to 75-mm fraction
9.5 Weight (g) of 5- to 20-mm fraction
9.6 Weight (g) of 2- to 5-mm fraction
9.7 Weight (g) of subsample 2- to 5-mm fraction before slaking
9.8 Weight (g) of subsample 2- to 5-mm fraction after slaking
9.9 Effervescence with HCl (S = strong; M = medium; W = weak; T = trace; 0 = none)

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
American Society for Testing and Materials. 1993. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

Petersen, R.G., and L.D. Calvin. 1986. Sampling. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:33-51.

SAMPLE COLLECTION AND PREPARATION
LABORATORY PREPARATION OF SOIL SAMPLES (1B)
COARSE FRAGMENTS (2-20 mm) (1B5)

1. APPLICATION

This procedure is used for soils containing coarse fragments with carbonate-indurated or gypsum-indurated material. The 2- to 20-mm fractions are separated for analysis. The preparation codes are "SK" and "SR". Refer to Appendix I, Laboratory Preparation Codes. The "SK" preparation code (procedure 1B5a) is used when the 2- to 20-mm fractions are crushed to <2 mm. These analytical results are reported on the 2- to 20-mm basis. The "SR" preparation (procedure 1B5b) is rarely requested and is used when the 2- to 20-mm fractions are recombined with the <2-mm fraction. These analytical results are reported on the <20-mm basis or are calculated to the <2-mm basis. If carbonate or gypsum accumulations are soft and easily pass a 2-mm sieve, the standard air-dry (1B1) method is requested.

2. SUMMARY OF METHOD

The field sample is air-dried and sieved. Weight measurements are made on the 20- to 75-mm, 5 to 20-mm, and 2 to 5-mm fractions. The <2-mm material is saved for chemical, physical, and mineralogical analysis. The 5- to 20-mm and 2- to 5-mm fractions are recombined after their respective weights are recorded. The recombined, 2- to 20-mm, material is crushed to <2 mm in a laboratory jaw crusher.

3. INTERFERENCES

Soil variability and sample size are interferences to sample collection and preparation. At each stage of sampling, an additional component of variability, the variability among smaller elements within the larger units, is added to the sampling error (Petersen and Calvin, 1986). Soil material needs to be adequate in amount and thoroughly mixed to obtain a representative sample.

Soil is mixed by moving it from the corners to the middle of processing area and then by redistributing the material. This process is repeated four times. Enough material is sieved to obtain statistically accurate data to determine the content of coarse fragments. In order to accurately measure rock fragments with a maximum particle diameter of 20 mm, the minimum specimen size ("dry" weight) that needs to be sieved and weighed is 1.0 kg. Refer to ASTM method D 2487 (American Society for Testing and Materials, 1993).

4. SAFETY

Dust from sample processing is a nuisance. A mask should be worn in order to avoid breathing dust. Keep clothing and hands away from the crusher and pulverizer when these machines are in use. Use face shield and goggles when operating the jaw crusher. Use goggles when operating the air compressor. The HCl used to check carbonates can destroy clothing and irritate skin. Immediately rinse acid with water from clothing or skin and seek professional medical help, if needed.

5. EQUIPMENT

5.1 Electronic balance, $\pm$1-g sensitivity and 15-kg capacity
5.2 Cardboard trays for sample storage
5.3 Trays, plastic, tared
5.4 Sieves, square-hole
5.4.1 10 mesh, 2 mm
5.4.2 4 mesh, 4.75 mm
5.4.3 19 mm, 3/4 in
5.4.4 76 mm, 3 in
5.5 Wooden rolling pin
5.6 Rubber roller
5.7 Retsch laboratory jaw crusher, Model BB2/A, Brinkmann Instruments Inc., Des Plaines, IL.
5.8 Metal Plate, 76 x 76 x 0.5 cm
5.9 Aluminum foil dishes, 57-mm diameter x 15-mm deep, with lifting tabs

5.10 Paper containers, 480 mL (pint), with lids
5.11 Sample splitter
5.12 Brown kraft paper
5.13 Air compressor, Cast-iron Series, SpeedAire, Campbell Hausfeld Mfg. Co., Harrison, Ohio.

6. REAGENTS
6.1 1 *N* HCl

7. PROCEDURE

7.1 Distribute field sample on a plastic tray. Weigh material and record moist weight. Air-dry, weigh, and record weight of soil material.

7.2 Roll material with wooden rolling pin to crush clods to pass a 2-mm sieve. For samples with easily crushed coarse fragments, substitute rubber roller for wooden rolling pin.

7.3 Process air-dry soil on a flat, metal plate that is covered with brown kraft paper. Thoroughly mix material by moving the soil from the corners to the middle of processing area and then by redistributing the material. Repeat process four times.

7.4 If more sample is received than is needed for processing, select subsample for preparation. Weigh subsample and record weight.

7.5 Weigh and record coarse fragments with diameters of 20 to 75 mm, 5 to 20 mm, and 2 to 5 mm. Discard 20 to 75 mm fragments. Recombine the 5- to 20-mm and 2- to 5-mm fractions and crush to <2-mm in a laboratory jaw crusher.

SK Preparation (1B5a)

7a. Procedure
7a.1 Place <2-mm, air-dry material in a 480-mL (pint) container and store until it is used for chemical, physical, or mineralogical analysis. Place <2-mm, air-dry material in two aluminum foil dishes for AD/OD (air-dry/oven-dry ratio) and for 15-bar moisture analysis.

7a.2 Place 2- to 20-mm, air-dry, crushed material in a 240-mL (1/2 pint) container and store for calcium carbonate or gypsum analysis.

SR Preparation (1B5b)

7b. Procedure
7b.1 Use a sample splitter, recombine the 2- to 20-mm, air-dry, crushed material with the <2-mm, air-dry, material. Store material until it is used for chemical, physical, or mineralogical analysis. Also place some of the recombined material in two aluminum foil dishes for AD/OD (air-dry/oven-dry ratio) and for 15-bar moisture analysis.

8. CALCULATIONS
Calculations for coarse fragments, <20-mm carbonate, and <20-mm gypsum are reported in procedures 3B, 6E4, and 6F4, respectively. In procedure 1B5a (SK code preparation), all analytical results of the 2- to 20-mm fraction are reported on the 2- to 20-mm basis, and all other analytical results are reported on the <2-mm basis. In procedure 1B5b (SR preparation code), all analytical results are reported on the <20-mm basis.

SAMPLE COLLECTION AND PREPARATION
LABORATORY PREPARATION OF SOIL SAMPLES (1B)
COARSE FRAGMENTS (2-20 mm) (1B5)

9. REPORT

9.1 Weight (g) of field moist soil sample

9.2 Weight (g) of air-dry soil sample

9.3 Weight (g) of air-dry processed soil sample

9.4 Weight (g) of 20- to 75-mm fraction

9.5 Weight (g) of 5- to 20-mm fraction

9.6 Weight (g) of 2- to 5-mm fraction

9.7 Effervescence with HCl (S = strong; M = medium; W = weak; T = trace; 0 = none)

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

American Society for Testing and Materials. 1993. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

Petersen, R.G., and L.D. Calvin. 1986. Sampling. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:33-51.

SAMPLE COLLECTION AND PREPARATION
LABORATORY PREPARATION OF SOIL SAMPLES (1B)
WHOLE SOIL (1B6)

1. APPLICATION

Coarse fragments and fine-earth material are homogenized so that analyses can be made on the whole soil basis. The preparation code for this procedure is "GP". Refer to Appendix I, Laboratory Preparation Codes. Entire sample is crushed to <2 mm, and analytical results are reported on whole soil basis. This method is used mainly to prepare samples from the Cr or R horizons.

2. SUMMARY OF METHOD

The field sample is air-dried and passed through a laboratory jaw crusher to reduce all material to pass a 2-mm sieve. The processed sample is saved for chemical, physical, and mineralogical analysis.

3. INTERFERENCES

Soil variability and sample size are interferences to sample collection and preparation. At each stage of sampling, an additional component of variability, the variability among smaller elements within the larger units, is added to the sampling error (Petersen and Calvin, 1986). Soil material needs to be in adequate amount and thoroughly mixed to obtain a representative sample. Soil is mixed by moving it from the corners to the middle of the processing area and then by redistributing the material. This process is repeated four times.

4. SAFETY

Dust from sample processing is a nuisance. A mask should be worn in order to avoid breathing dust. Keep clothing and hands away from the crusher and pulverizer when these machines are in use. Use face shield and goggles when operating the jaw crusher. Use goggles when operating the air compressor. The HCl used to check carbonates can destroy clothing and irritate skin. Immediately rinse acid with water from clothing or skin and seek professional medical help, if needed.

5. EQUIPMENT
5.1 Electronic balance, $\pm$1-g sensitivity and 15-kg capacity
5.2 Trays, plastic, tared
5.3 Sieve, square-hole
5.3.1 10-mesh, 2-mm
5.4 Retsch laboratory jaw crusher, Model BB2/A, Brinkmann Instruments Inc., Des Plaines, IL.
5.5 Aluminum foil dishes, 57-mm diameter x 15-mm deep, with lifting tab
5.6 Metal plate, 76 x 76 x 0.5 cm
5.7 Paper containers, 480 mL (pint), with lids
5.8 Brown kraft paper
5.9 Air compressor, Cast-iron Series, SpeedAire, Campbell Hausfeld Mfg. Co., Harrison, Ohio.

6. REAGENTS
6.1 1 *N* HCl

7. PROCEDURE

7.1 Distribute field sample on a plastic tray. Weigh material and record moist weight. Air-dry, weigh, and record weight of soil material. Crush material to <2-mm in a laboratory jaw crusher.

7.2 Process air-dry material on a flat, metal plate that is covered with brown kraft paper. Thoroughly mix material by moving soil from the corners to the middle of processing area and then by redistributing the material. Repeat process four times.

7.3 Place representative sample in a 480-mL (pint) container until it is used for chemical, physical, or mineralogical analysis. Also place air-dry material in two aluminum foil dishes for AD/OD (air-dry/oven-dry ratio) and for 15-bar moisture analysis.

8. CALCULATIONS
      None

9. REPORT
9.1 Weight (g) of field moist soil sample
9.2 Weight (g) of air-dry soil sample
9.3 Effervescence with HCl (S = strong; M = medium; W = weak; T = trace; 0 = none)

10. PRECISION
      Precision data are not available for this procedure.

11. REFERENCES
      Petersen, R.G., and L.D. Calvin. 1986. Sampling. *In* A. Klute (ed.) Methods of soil analysis. Part 1.
            Physical and mineralogical methods. 2nd ed. Agronomy 9:33-51.

SAMPLE COLLECTION AND PREPARATION
LABORATORY PREPARATION OF SOIL SAMPLES (1B)
ORGANIC MATERIAL (1B7)

1. APPLICATION

Both air-dry and field moist material are processed for analysis. This method is used to prepare samples from organic soil horizons. The preparation code for this procedure is "H". Refer to Appendix I, Laboratory Preparation Codes. Field moist samples are used for moist 15 bar (4B2b) water content, mineral content (8F1), fiber volume (8G1), and pyrophosphate color (8H). Fine-ground (<80-mesh), air-dry material is used for lab analyses. The <2-mm, air-dry material is used for 15- 1/10- and 2-bar water content (4B1a) and for the AD/OD (4B5). Analytical results are reported on the <2-mm basis except fabric.

2. SUMMARY OF METHOD

A subsample of field moist material is selected and placed in a 120-mL (4-oz), polypropylene container. The subsample is stored for future analysis. The remaining sample is air-dried and sieved. Weight measurements are made on the 20- to 75-mm, 5- to 20-mm, and 2- to 5-mm fractions. The <2-mm, air-dry material is finely ground (<80-mesh) and saved for the chemical analyses that do not require a field moist sample. The <2-mm, air-dry material is used for dry 15 bar.

3. INTERFERENCES

Soil variability and sample size are interferences to sample collection and preparation. At each stage of sampling, an additional component of variability, the variation among smaller elements within the larger units, is added to the sampling error (Petersen and Calvin, 1986). Soil material needs to be in adequate amount and thoroughly mixed to obtain a representative sample.

The moist material is distributed on a plastic tray and thoroughly mixed. Soil is selected from at least five separate areas and placed in a 120-mL (4-oz), polypropylene container. The air-dry soil is also thoroughly mixed by moving the soil from the corners to the middle of the processing area and then by redistributing the material. This process is repeated four times. For those few organic samples with rock fragments, enough soil material needs to be sieved and weighed to obtain statistically accurate rock fragment content. In order to accurately measure rock fragments with a maximum particle diameter of 20 mm, the minimum specimen size ("dry" weight) that needs to be sieved and weighed is 1.0 kg. Whenever possible, "moist" samples or materials should have weights two to four times larger than for "dry" specimens (American Society for Testing and Materials, 1993). An homogenized soil sample is more readily obtained from air-dry material than from field moist material.

4. SAFETY

Dust from sample processing is a nuisance. A mask should be worn in order to avoid breathing dust. Keep clothing and hands away from the crusher and pulverizer when these machines are in use. Use face shield and goggles when operating the jaw crusher. Use goggles when operating the air compressor. The HCl used to check carbonates can destroy clothing and irritate skin. Immediately rinse acid with water from clothing or skin and seek professional medical help, if needed.

5. EQUIPMENT
5.1 Electronic balance, ±1-g sensitivity and 15-kg capacity
5.2 Cardboard trays for sample storage
5.3 Trays, plastic, tared
5.4 Sieves, square-hole
5.4.1 80 mesh, 180 μm
5.4.2 10 mesh, 2 mm
5.4.3 4 mesh, 4.75 mm
5.4.4 19 mm, 3/4 in
5.4.5 76 mm, 3 in
5.5 Pulverizer
5.6 Wooden rolling pin

5.7 Rubber roller
5.8 Metal plate, 76 x 76 x 0.5 cm
5.9 Aluminum foil dishes, 57-mm diameter x 15-mm deep, with lifting tab
5.10 Paper containers, 480 mL (pint), with lids
5.11 Polypropylene containers, 120 mL (4 fl. oz.), with lids
5.12 Air compressor, Cast-iron Series, SpeedAire, Campbell Hausfeld Mfg. Co., Harrison, Ohio.
5.13 Cross-beater mill, Retsch Laboratory, Type SK-1, Brinkmann Instruments Inc., Des Plaines, IL.
Fine-grind, 80-mesh.

6. REAGENTS
6.1 1 *N* HCl

7. PROCEDURE

7.1 Distribute field sample on a plastic tray. Thoroughly mix material. Select a representative subsample from at least five different areas on the plastic tray and place into a 120-mL (4-oz), polypropylene container. Seal and store container.

7.2 Weigh remaining soil on the plastic tray and record moist weight. Air-dry, weigh, and record weight of soil material. Process air-dry soil on a flat, metal plate that is covered with brown kraft paper. Thoroughly mix material by moving the soil from the 8 Tf048 7 1ı Desdmplefon the Proceovint arh, ar.

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CONVENTIONS
SIZE-FRACTION BASE FOR REPORTING DATA (2A)
PARTICLES <2 mm (2A1)

Unless otherwise specified, report all data on the basis of the <2-mm material.

CONVENTIONS
SIZE-FRACTION BASE FOR REPORTING DATA (2A)
PARTICLES <Specified Size>2mm (2A2)

The maximum coarse-fragment size for the >2-mm base varies. The base usually includes those fragments as large as 75 mm (3 in), if present in the soil. The maximum size for fragments >75 mm, commonly termed whole soil, includes boulders with maximum horizontal dimensions less than those of the pedon.

Record the maximum particle-size set in the parentheses in the column heading. The base with which to calculate the reported >2-mm percentages includes all material in the sample smaller than the particle size recorded in the column heading.

CONVENTIONS
DATA SHEET SYMBOLS (2B)

The following symbols are used or have been used for trace or zero quantities and for samples not tested.

tr, Tr, TR Trace, either is not measurable by quantitative procedure used or is less than reported amount.

tr(s) Trace, detected only by qualitative procedure more sensitive than quantitative procedure used.

- Analysis run but none detected.

-- Analysis run but none detected.

-(s) None detected by sensitive qualitative test.

blank Analysis not run.

nd Not determined, analysis not run.

< Either none is present or amount is less than reported amount, e.g., <0.1 is in fact <0.05 since 0.05 to 0.1 is reported as 0.1.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)

INTRODUCTION

Particle-size analysis for the <2-mm fraction is one of the most requested analysis in soil characterization because soil texture and particle-size distribution can be related to many other soil properties. The Kilmer and Alexander (1949) pipet method was chosen by the Soil Conservation Service because it is reproducible in a wide range of soils. Refer to Appendix II for the Shaw (1932) pipet rack. The standard procedure for analysis of particles with <2-mm diameters is the air-dry method (procedure 3A1). For soils that irreversibly harden when dried, moist particle-size analysis (procedure 3A2) may be requested by project coordinator. Procedures with either a 3A1 or 3A2 in code refer to air-dry or moist samples, respectively.

In addition to standard or moist particle-size analysis, other analyses that may be performed include fine clay (procedures 3A1b and 3A2b); water dispersible clay (procedures 3A1c and 3A2c); carbonate and noncarbonate clay (procedures 3A1d and 3A2d); and special pretreatment and dispersion procedures. Fine clay is the <0.2-μm fraction and is determined from a soil suspension from standard air-dry or moist particle-size analysis. Water dispersible clay is determined from a soil suspension without the oxidation of organic matter or the removal of soluble salts or the addition of chemical dispersant. Carbonate and noncarbonate clay II are determined from the clay residue (<2 μm) from standard air-dry or moist particle-size analysis. Chemical pretreatments to remove cementing agents that often prevent complete dispersion are removal of carbonates with 1 *N* NaOAc buffered at pH 5 (procedures 3A1e and 3A2e); removal of Fe with sodium dithionite-citrate solution (procedures 3A1f and 3A2f); and removal of Si with 0.1 *N* NaOH (procedures 3A1g and 3A2g). Dispersion using ultrasonic probe (procedures 3A1h and 3A2h) can be used with soils that do not completely disperse with standard particle-size analysis. These special pretreatment and dispersion procedures are used upon request by project coordinator.

REFERENCES

Kilmer, V.J., and L.T. Alexander. 1949. Methods of making mechanical analyses of soils. Soil Sci. 68:15-24.

Shaw, T.M. 1932. New aliquot and filter devices for analytical laboratories. Ind. Eng. Chem. Anal. Ed. 4:409.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)

1. APPLICATION

Particle-size analysis (PSA) is one of the most requested analysis in soil characterization because soil texture and the particle-size distribution can be related to many other soil properties. Particle-size distribution is also used as a tool to help explain soil genesis and to quantify soil classification. The Kilmer and Alexander (1949) pipet method was chosen by the Soil Conservation Service because it is reproducible in a wide range of soils.

2. SUMMARY OF METHOD

A 10-g sample of <2-mm, air-dry soil is pretreated to remove organic matter and soluble salts. The sample is dried in the oven to obtain the initial weight, dispersed with a sodium hexametaphosphate solution, and mechanically shaken. The sand fraction is removed from the suspension by wet sieving and then fractionated by dry sieving. The clay and fine silt fractions are determined using the suspension remaining from the wet sieving process. This suspension is diluted to 1 L in a sedimentation cylinder, stirred, and 25-mL aliquots removed with a pipet at calculated, predetermined intervals based on Stokes' law (Kilmer and Alexander, 1949). The aliquots are dried at 105°C and weighed. Coarse silt is the difference between 100% and the sum of the sand, clay, and fine silt percentages.

3. INTERFERENCES

The sedimentation equation that is used to measure the settling rates of particles of different sizes is as follows:

$$v \ = \ 2r^2 g(\rho_s - \rho_l)/(9\eta)$$

where:

v = velocity of fall
r = particle radius
g = acceleration due to gravity
ρ_s = particle density
ρ_l = liquid density
η = fluid viscosity

This formula results from an application of Stokes' law and is referred to as Stokes' law. Assumptions used in applying Stokes' law to soil sedimentation measurements are as follows:

1. Terminal velocity is attained as soon as settling begins.

2. Settling and resistance are entirely due to the viscosity of the fluid.

3. Particles are smooth and spherical.

4. There is no interaction between individual particles in the solution (Gee and Bauder, 1986).

Since soil particles are not smooth and spherical, the radius of the particle is considered an equivalent rather than an actual radius. In this method, particle density is assumed to be 2.65 g cc^{-1}.
The PSA results are dependent on the pretreatments used to disperse the soil. The presence of cementing agents such as calcium carbonate, Fe, and Si often prevent complete dispersion. Chemical pretreatments to remove cementing agents can be requested by project coordinators. Coded

procedures are removal of carbonates with 1 N NaOAc buffered at pH 5 (3A1e); removal of Fe with a sodium dithionite-citrate solution (3A1f); and removal of Si with 0.1 N NaOH (3A1g).

Gypsum interferes with PSA by causing flocculation of particles. Gypsum is removed by stirring and washing the soil with distilled water. This procedure is effective if the soil contains <25% gypsum.

Partial flocculation may occur in some soils if excess H_2O_2 is not removed from the soil after its use in organic matter oxidation.

Treatment of micaceous soils with H_2O_2 causes exfoliation of the mica plates and a matting of particles when dried in the oven. Since exfoliation occurs in these soils, a true measurement of fractions is uncertain (Drosdoff and Miles, 1938).

Soils that irreversibly harden when dried are difficult to disperse. The PSA for these soils can be determined on moist samples (procedure 3A2) upon the request of project coordinator.

4. SAFETY

Use rubber gloves and a face shield when handling acid and H_2O_2. Mix acids in ventilated fume hoods. Heat samples for removal of organic matter or cementing agents in ventilation hoods. Handle heated samples with leather gloves. Never add water to dry phosphorous pentoxide.

5. EQUIPMENT

5.1 Fleakers, 300 mL, tared to 1 mg

5.2 Ceramic filter candles, .3μm absolute retention

5.3 Rack to hold ceramic filter candle and sample container.

5.4 Mechanical shaker, horizontal, 120 oscillations min^{-1}

5.5 Cylinders, 1 L, white line fused onto glass at 1-L mark

5.6 Oven, 105°C

5.7 Hot plate, 100°C

5.8 Vacuum, 0.8 bars (80kPa)

5.9 Thermometer, 0 to 100°C

5.10 Desiccator

5.11 Motor driven stirrer, (Kilmer and Mullins, 1954)

5.12 Hand stirrer, perforated disk fastened to a rod

5.13 Adjustable pipet rack (Shaw, 1932)

5.14 Lowy pipets, 25 mL, with overflow bulb

5.15 Polyurethane foam, pipe insulation that fits snugly around cylinder.

5.16 Sieve shaker with 12.7-mm (1/2 in) vertical and lateral movement at 500 oscillations min^{-1}. Accommodates a nest of 76-mm (3 in) sieves.

5.17 Weighing bottles, 90 mL, with screw caps, tared to 1 mg

5.18 Weighing bottles, 90 mL, tared to 1 mg

5.19 Timer or clock with second hand

5.20 Electronic balance, ±0.1-mg sensitivity

5.21 Electronic balance, ±1-mg sensitivity

5.22 Watch glass, 50- and 65-mm diameters

5.23 Evaporating dish, porcelain, 160-mm diameter, 31-mm height, with lip

5.24 Set of 76-mm (3 in) sieves, square weave phosphor bronze wire cloth except 300 mesh which is twilled weave. U.S. series and Tyler Screen Scale equivalent designations are as follows:

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)

Sand Size	Opening (mm)	U.S. No.	Tyler Mesh Size
VCS	1.0	18	16
CS	0.5	35	32
MS	0.25	60	60
FS	0.105	140	150
VFS	0.047	300	300

6. REAGENTS
6.1 Distilled water
6.2 Hydrogen peroxide (H_2O_2), 30 to 35%
6.3 Sodium hexametaphosphate ($(NaPO_3)_6$), reagent grade
6.4 Sodium carbonate (Na_2CO_3), reagent grade
6.5 Sodium hexametaphosphate solution. Dissolve 35.7 g of $(NaPO_3)_6$ and 7.94 g of Na_2CO_3 in 1 L of distilled water.
6.6 Ethyl alcohol
6.7 Phosphorous pentoxide (P_2O_5), calcium sulfate (anhydrous), or equivalent desiccant

7. PROCEDURE

7.1 Weigh 10 g of <2-mm, air-dry soil to nearest mg on an electronic balance and place into a numbered, tared 300-mL, fleaker. Wash and tare these fleakers once every two months.

7.2 Add $\approx$ 50 mL of distilled water and 5 mL of H_2O_2 to the soil sample at ambient temperature. Cover the soil sample with a 50-mm watch glass. Allow initial oxidation of organic matter to complete and then place sample on hot plate. If the froth from the reaction exceeds the capacity of the fleaker, transfer the sample to a larger beaker.

7.3 Place the sample on a hot plate and heat to 90°C. Add 5-mL increments of H_2O_2 at 30-min intervals until the oxidation has completed or until 30 mL of H_2O_2 have been added. Heat the sample for an additional 45 min to decompose excess H_2O_2. If the reaction is violent, add small increments of ethyl alcohol to the sample or remove the sample from the hot plate to slow the reaction or transfer sample to a 1000-mL beaker. Record any unusual sample reactions.

7.4 Place the sample on the filter rack. Add 150 mL of distilled water. Insert a filter candle, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Wash the sample four additional times with $\approx$ 150 mL of distilled water. If the sample contain gypsum and flocculates, then the following additional washings may be used. If the sample contains 1 to 5% gypsum, stir the sample with a magnetic stirrer for 5 min and wash 5 times with $\approx$ 250 mL of distilled water each time. If the sample contains >5% gypsum, stir the sample with a magnetic stirrer for 5 min then wash 5 times with $\approx$ 750 mL of distilled water each time to remove soluble gypsum.

7.5 Place sample in oven. Dry the sample overnight at 105°C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.6 Record the total weight (TW) of the sample to the nearest mg.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)

7.7 Add 10 mL of sodium hexametaphosphate solution, equivalent to 0.4408 g of sodium hexametaphosphate, to each sample. Subtract the weight of the sodium hexametaphosphate (DW) that is contained in the extracted aliquot from the silt and clay weights to calculate silt and clay percentages. Determine the exact volume of sodium hexametaphosphate to add to each sample by regressing the volume of sodium hexametaphosphate against the dry residue weight of sodium hexametaphosphate and then by predicting the volume needed to dispense 0.4408 g of sodium hexametaphosphate into each sample. Let stand until sample is completely moistened by sodium hexametaphosphate. Add $\approx$ 175 mL of distilled water.

7.8 Place the sample in a horizontal shaker set at 120 oscillations min^{-1} and shake for 15 h (overnight).

7.9 Remove the sample from the shaker and pour through a 300-mesh (0.047-mm) sieve mounted on a ring stand. Place a funnel below the sieve and a 1-L cylinder below the funnel. Collect the silt and clay in the 1-L cylinder. Avoid using jets of water in washing the sample. Wash and rub all particles from the fleaker into the sieve. Continue to wash until the suspension volume in the cylinder is $\approx$ 800 mL. Sand and some of the coarse silt remain on the sieve. Rinse all <20-μm particles into the cylinder. Fill the cylinder to 1 L and cover with a 65-mm watch glass. Prepare a distilled water blank to measure temperature fluctuations. Allow the cylinder to stand overnight to equilibrate the suspension with the room temperature. Wash the sand into an evaporation dish and dry the sand at 105°C overnight.

7.10 Transfer the dried sand to a nest of sieves that has a top-to-bottom order of 1.0, 0.5, 0.25, 0.1, and 0.047 mm. Shake the sand for 3 min on a shaker that has 1.3-cm vertical and lateral movements and oscillates at 500 strokes min^{-1}. Record the weight of each separate sand fraction (SW$_i$) to the nearest mg. If optical analysis is requested, place the very fine sand and fine sand fractions in gelatin capsules and the remaining sand fractions in a labelled vial. Store capsules in the labelled vial. Wash sand dishes after every use.

7.11 Determine the percentage of fine silt and clay gravimetrically by removing an aliquot from the suspension in the 1-L cylinder with a Lowy, 25-mL pipet. Periodically, gravimetrically calibrate the delivery volume of the pipet by weighing the amount of distilled water dispensed from the pipet. Record the delivery volume (DV) and use the value to calculate the results. Regulate the vacuum such that the pipet fills in $\approx$12 s. Record temperature (T$_1$) of blank. Mount the pipet on an adjustable pipet rack (Shaw, 1932). Stir the silt and clay suspension with mechanical stirrer for 6 min or for 8 min, if the suspension has stood for >24 h (Kilmer and Mullins, 1954). Place pipe insulation around sample and blank cylinders to prevent rapid changes in temperatures. Place the cylinder on a stable, vibrationless table and stir with a hand stirrer in an up-and-down motion for 30 s. Timing is started upon completion of the stirring. Record the time that stirring is stopped. For the <20-μm fraction, slowly lower the closed pipet to a 10-cm depth in the suspension, turn on the vacuum, and withdraw an aliquot at the calculated time (Table 1). Dispense the aliquot into a tared and numbered, 90-mL weighing bottle. Rinse the pipet twice with distilled water and dispense into the tared, weighing bottle with the aliquot. For the <2-μm fraction, pipet after a time of 4.5, 5, 5.5, or 6.5 h. Record temperature (T$_2$) of blank. Use the average of T$_1$ and T$_2$ and adjust the pipet depth in the suspension as indicated in Table 2. Repeat the procedure described for the <20-μm fraction. If determination of carbonate is required, use weighing bottle with screw threads. Dry the aliquots at 105°C overnight and cool in a desiccator that contains P$_2$O$_5$ or an equivalent desiccant. Record the weight of the residue (RW) to the nearest 0.1 mg.

7.12 Use the 90-mL, round-bottomed, weighing bottles for the <20-μm aliquots. Wash and tare after every fourth use. Use the 90-mL, square-bottomed, weighing bottles for the <2-μm aliquots. Wash and tare after every use.

7.13 If fine clay analyses are requested, use the remaining suspension and follow procedure 3A1b. If necessary, save the sediment for optical mineralogy.

7.14 If optical mineralogy is requested, decant the suspension and transfer the sediment to a 400-mL beaker. Fill the beaker to a 5.5-cm height. Stir the sediment and allow to settle for 5 min. Discard the supernatant. Refill the beaker to 5.5-cm height. Stir again, allow to settle for 3 min, and then decant. Repeat the filling and the stirring; allow to settle for 2 min; and then decant until top half of suspension is clear. Transfer the sediment, which is dominantly 20 to 50μm, to a labelled drying dish. Wash with ethanol, air-dry, and save in the drying dish for optical mineralogy.

8. CALCULATIONS

8.1 Clay % = 100 x ((RW_2 - DW) x (CF/TW))

where:
RW_2 = residue weight (g), <2-μm fraction
DW   = dispersing agent weight (g) = (0.4408/CF)
CF   = 1000 mL/DV
DV   = dispensed pipet volume
TW   = total weight (g), H_2O_2-treated, oven-dry sample

8.2 Fine Silt % = 100 x ((RW_{20}-DW) x (CF/TW)) - Clay %

where:
RW_{20} = residue weight (g) of <20-μm fraction

8.3 Sand % = $\sum$ (SW/TW) x 100

where:
i = 1.0, 0.5, 0.25, 0.1, and 0.047-mm sand fractions

8.4 Coarse silt % = 100 - (Clay + Fine Silt + Sand %)

9. REPORT
Report percentages of each particle size.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is included in every batch of 24 samples for PSA determinations. The number of observations, mean, standard deviation, and C.V. for the quality control check sample for the sand, silt, and clay fractions are as follows:

Size	n	Mean	Std. Dev.	C.V.
Sand	257	7.8	2.68	34.1
Silt	257	70.1	2.88	4.1
Clay	257	22.1	1.31	5.9

11. REFERENCES

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Table 1. Sampling times at 10-cm sampling depth,
0.4408 g L^{-1} NaHMP solution, and 2.65 g cc^{-1} particle
density.[1]

Temp (°C)	20 μm		5 μm	
	min	s	min	s
18.00	4	53	78	10
19.00	4	45	76	7
20.00	4	38	74	13
20.25	4	36	73	46
20.50	4	34	73	19
20.75	4	33	72	52
21.00	4	31	72	26
21.25	4	30	72	0
21.50	4	28	71	34
21.75	4	26	71	8
22.00	4	25	70	43
22.25	4	23	70	18
22.50	4	22	69	53
22.75	4	20	69	28
23.00	4	19	69	4
23.25	4	17	68	39
23.50	4	15	68	15
23.75	4	14	67	52
24.00	4	13	67	28
24.25	4	11	67	5
24.50	4	10	66	41
24.75	4	8	66	18
25.00	4	7	65	56
25.25	4	5	65	33
25.50	4	4	65	11
25.75	4	3	64	49
26.00	4	1	64	27
26.25	4	0	64	5
26.50	3	59	63	43
26.75	3	57	63	22
27.00	3	56	63	1
27.25	3	55	62	40
27.50	3	53	62	19
27.75	3	52	61	59
28.00	3	51	61	38
28.25	3	49	61	18
28.50	3	48	60	58
28.75	3	47	60	38
29.00	3	46	60	18
29.25	3	44	59	59
29.50	3	43	59	39
29.75	3	42	59	20
30.00	3	41	59	1

[1]Use this table with procedures 3A1, 3A2, 3A1h,
and 3A2h.

Table 2. Sampling depths (cm) for 2-μm clay, 0.4408 g L^{-1} NaHMP solution, and 2.65 g cc^{-1} particle density.[1]

Temp (°C)	Time (h)				
	4.5	5.0	5.5	6.0	6.5
18.00	5.53	6.14	6.75	7.37	7.98
19.00	5.67	6.31	6.94	7.57	8.20
20.00	5.82	6.47	7.11	7.76	8.41
20.25	5.86	6.51	7.16	7.81	8.46
20.50	5.89	6.55	7.20	7.86	8.51
20.75	5.93	6.59	7.24	7.90	8.56
21.00	5.96	6.63	7.29	7.95	8.61
21.25	6.00	6.67	7.33	8.00	8.67
21.50	6.04	6.71	7.38	8.05	8.72
21.75	6.07	6.75	7.42	8.10	8.77
22.00	6.11	6.79	7.47	8.14	8.82
22.25	6.14	6.83	7.51	8.19	8.88
22.50	6.18	6.87	7.55	8.24	8.93
22.75	6.22	6.91	7.60	8.29	8.98
23.00	6.25	6.95	7.64	8.34	9.03
23.25	6.29	6.99	7.69	8.39	9.09
23.50	6.33	7.03	7.73	8.44	9.14
23.75	6.37	7.07	7.78	8.49	9.19
24.00	6.40	7.11	7.83	8.54	9.25
24.25	6.44	7.16	7.87	8.59	9.30
24.50	6.48	7.20	7.92	8.64	9.36
24.75	6.51	7.24	7.96	8.69	9.41
25.00	6.55	7.28	8.01	8.74	9.46
25.25	6.59	7.32	8.05	8.79	9.52
25.50	6.63	7.36	8.10	8.84	9.57
25.75	6.66	7.41	8.15	8.89	9.63
26.00	6.70	7.45	8.19	8.94	9.68
26.25	6.74	7.49	8.24	8.99	9.74
26.50	6.78	7.53	8.28	9.04	9.79
26.75	6.82	7.57	8.33	9.09	9.85
27.00	6.85	7.62	8.38	9.14	9.90
27.25	6.89	7.66	8.42	9.19	9.96
27.50	6.93	7.70	8.47	9.24	10.01
27.75	6.97	7.74	8.52	9.29	10.07
28.00	7.01	7.79	8.57	9.34	10.12
28.25	7.05	7.83	8.61	9.40	10.18
28.50	7.09	7.87	8.66	9.45	10.23
28.75	7.12	7.92	8.71	9.50	10.29
29.00	7.16	7.96	8.75	9.55	10.35
29.25	7.20	8.00	8.80	9.60	10.40
29.50	7.24	8.05	8.85	9.65	10.46
29.75	7.28	8.09	8.90	9.71	10.52
30.00	7.32	8.13	8.95	9.76	10.57

[1]Use this table with procedures 3A1, 3A2, 3A1h, and 3A2h.

PARTICLE-SIZE ANALYSIS
PARTICLES <2mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
FINE CLAY (<0.2 μm) (3A1b)

1. APPLICATION

The fine clay fraction is mineral soil particles with an effective diameter of <0.2 μm. The percentage fine clay is determined for soils that are suspected of having illuviated clay. Fine clay data can be used to determine the presence of argillic horizons or as a tool to help explain soil genesis.

2. SUMMARY OF METHOD

A soil suspension from the air-dry PSA procedure (3A1) is stirred, poured into a centrifuge bottle, and centrifuged at 1500 rpm. A 25-mL aliquot is withdrawn with a pipet. The aliquot is dried in the oven, weighed, and the percentage of fine clay is calculated based on the total sample weight. The time of centrifugation is determined from the following equation modified from Stokes' law (Jackson, 1969).

$$t_m = (63.0 \times 10^8 \eta \, \log \, (rs^{-1})) \, (N_m^2 \, D\mu^2 \, \Delta\rho)^{-1}$$

where:

t_m = time in minutes

η = viscosity in poises

r = radius in cm from center of rotation to sampling depth (3 cm + s)

s = radius in cm from center of rotation to surface of suspension

N_m = rpm (1500)

$D\mu$ = particle diameter in microns (0.2 μm)

$\Delta\rho$ = difference in specific gravity between solvated particles and suspension liquid

3. INTERFERENCES

Assumptions used in applying Stokes' law to soil sedimentation measurements are as follows:

1. Terminal velocity is attained as soon as settling begins.

2. Settling and resistance are entirely due to the viscosity of the fluid.

3. Particles are smooth and spherical.

4. There is no interaction between individual particles in the solution (Gee and Bauder, 1986).

The distance from the center of rotation to the surface of the suspension must be constant for each centrifuge bottle. The particle density of the fine clay is assumed to be 2.5 g cc^{-1}. The suspension temperature must be used to enter the correct liquid viscosity in the equation. Position the bottle under pipet without sudden movement of the centrifuge rotor which causes disturbance of solution. The withdrawal rate with pipet should be constant.

4. SAFETY

Users should be familiar with centrifuge operation. Opposite centrifuge bottles need to be balanced. Centrifuge should not be opened until centrifuge rotor has completely stopped.

5. EQUIPMENT
5.1 Motor driven stirrer, (Kilmer and Mullins, 1954)
5.2 Hand stirrer, perforated disk fastened to a rod
5.3 Centrifuge, International No. 11, with No. 949 rotor head, International Equip. Co., Boston, MA
5.4 Centrifuge bottle, 500 mL

PARTICLE-SIZE ANALYSIS
PARTICLES <2mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
FINE CLAY (<0.2 μm) (3A1b)

5.5 Lowy pipet, 25 mL, with overflow bulb
5.6 Adjustable pipet rack (Shaw, 1932)
5.7 Weighing bottles, 90 mL, tared to 0.1 mg
5.8 Electronic balance, ±0.1-mg sensitivity
5.9 Torsion balance
5.10 Timer or clock with second hand
5.11 Thermometer, 0 to 100°C
5.12 Oven, 105°C

6. REAGENTS
    None

7. PROCEDURE

7.1 After the completion of procedure 3A1, stir the silt and clay suspension with mechanical stirrer for 5 min. Remove sample from mechanical stirrer and place on table. Stir with the hand stirrer in an up-and-down motion for 30 s and allow the suspension to settle for 15 min.

7.2 Pour the suspension into a centrifuge bottle and fill to the line marked on the bottle. The line on each bottle is 13 cm which is the distance from the center of rotation to the surface of the suspension. Stopper and shake well to mix the suspension.

7.3 Balance opposite centrifuge loads, which consist of centrifuge bottle, trunnion carrier and bucket. Place loads on a torsion balance and add water to the lighter bucket until both loads weigh the same.

7.4 Read the temperature of the suspension.

7.5 Centrifuge at 1500 rpm. Vary the centrifuge time according to the temperature as follows:

Temp (°C)	Viscosity η	Density $\Delta\rho$	Time Min
19	0.01047	1.499	38.7
20	0.01021	1.499	37.7
21	0.00997	1.499	36.8
22	0.00973	1.499	36.0
23	0.00950	1.500	35.1
24	0.00928	1.500	34.3
25	0.00907	1.500	33.5
26	0.00887	1.500	32.8
27	0.00868	1.501	32.0
28	0.00848	1.501	31.3
29	0.00830	1.501	30.7
30	0.00812	1.502	30.0

where:
s = 15 cm

PARTICLE-SIZE ANALYSIS
PARTICLES <2mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
FINE CLAY (<0.2 μm) (3A1b)

r   = 18 cm
N_m = 1500 rpm.

7.6 After centrifuging, lower the pipet to a 3-cm depth in the suspension. Withdraw a 25-mL aliquot at a rate of $\approx$ 12 s. Avoid turbulence. Transfer the aliquot to a weighing bottle

7.7 Place weighing bottle with aliquot in oven. Dry overnight at 105°C. Remove sample from oven, place in desiccator with P_2O_5 or equivalent desiccant, and cool to ambient temperature.

7.8 Weigh residue weight (RW) to nearest 0.1 mg.

7.9 Use the 90-mL, round-bottomed, weighing bottles for the <0.2μm aliquots. Wash and tare after every fourth use.

8. CALCULATIONS

Fine Clay (%) = 100 x ((RW-DW) x (CF/TW))

where:
RW = residue weight (g) of <0.2 μm fraction
DW = dispersing agent weight (g) = (0.4364/CF)
CF   = 1000 mL/DV
DV   = dispensed pipet volume
TW   = total weight of H_2O_2-treated, oven-dry sample (procedure 3A1)

9. REPORT
Report the percentage of fine clay.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is included in every batch of 24 samples for PSA determination. The fine clay of the quality control check sample is determined only when fine clay analysis is requested. The number of observations, mean, standard deviation, and C.V. for the fine clay fraction are 122, 9.5, 1.79 and 19%, respectively.

11. REFERENCES
Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. *In* A. Klute (ed.) Methods of soil analysis.
    Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:383-411.
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Kilmer, V. J., and J.F. Mullins. 1954. Improved stirring and pipetting apparatus for mechanical
    analysis of soils. Soil Sci. 77:437-441.
Shaw, T. M. 1932. New aliquot and filter devices for analytical laboratories. Ind. Eng. Chem. Anal.
    Ed. 4:409.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
WATER DISPERSIBLE CLAY (3A1c)

1. APPLICATION

Water dispersible clay provides a means of evaluating the susceptibility of a soil to water erosion. The degree to which a soil disperses without the oxidation of organic matter or the removal of soluble salts, or the addition of a chemical dispersant may be compared with results from chemical dispersion (Bouyoucos, 1929).

2. SUMMARY OF METHOD

A 10-g sample of <2-mm, air-dry soil is mechanically shaken overnight in distilled water. The sand fraction is removed from the suspension by wet sieving and then fractionated by dry sieving. The clay and fine silt fractions are determined using the solution remaining from the wet sieving process. This solution is diluted to 1 L in a sedimentation cylinder, stirred, and 25-mL aliquots removed with a pipet at calculated, predetermined intervals based on Stokes' law (Kilmer and Alexander, 1949). The aliquots are dried at 105°C and weighed. Coarse silt is the difference between 100% and the sum of the sand, clay, and fine silt percentages.

3. INTERFERENCES

Assumptions used in applying Stokes' law to soil sedimentation measurements are as follows:

1. Terminal velocity is attained as soon as settling begins.

2. Settling and resistance are entirely due to the viscosity of the fluid.

3. Particles are smooth and spherical.

4. There is no interaction between individual particles in the solution (Gee and Bauder, 1986).

Since soil particles are not smooth and spherical, the radius of the particle is considered an equivalent rather than an actual radius. In this method, particle density is assumed to be 2.65 g cc^{-1}.

Hydrophobic soils may not completely saturate when water is added to the soil. When the soils are hydrophobic, a few mL of ethyl alcohol are added to wet the sample, and the procedure is continued. The addition of ethyl alcohol to reduce surface tension is assumed to have no effect on mineral structure.

4. SAFETY

No special precautions are specified.

5. EQUIPMENT
5.1 Fleakers, 300 mL, tared to 1 mg
5.2 Mechanical shaker, horizontal, 120 oscillations min^{-1}
5.3 Cylinders, 1 L, white line fused onto glass at 1-L mark
5.4 Oven, 105°C
5.5 Desiccator
5.6 Thermometer, 0 to 100°C
5.7 Motor driven stirrer, (Kilmer and Mullins, 1954)
5.8 Hand stirrer, perforated disk fastened to a rod
5.9 Adjustable pipet rack (Shaw, 1932)
5.10 Lowy pipets, 25 mL, with overflow bulb
5.11 Polyurethane foam, pipe insulation that fits snugly around cylinder.

5.12 Sieve shaker with 12.7-mm (1/2 in) vertical and lateral movement at 500 oscillations min^{-1}.
Accommodates a nest of 76-mm (3 in) sieves.
5.13 Weighing bottles, 90 mL, with screw caps, tared to 1 mg
5.14 Weighing bottles, 90 mL, tared to 1 mg
5.15 Timer or clock with second hand
5.16 Electronic balance, ±0.1-mg sensitivity
5.17 Electronic balance, ±1-mg sensitivity
5.18 Watch glass, 50- and 65-mm diameters
5.19 Evaporating dish, porcelain, 160-mm diameter, 31-mm height, with lip
5.20 Set of 76-mm (3 in) sieves, square weave phosphor bronze wire cloth except 300 mesh which is
twilled weave. U.S. series and Tyler Screen Scale equivalent designations are as follows:

```
Sand      Opening    U.S.     Tyler
Size       (mm)      No.      Mesh
                              Size


VCS       1.0         18        16
CS        0.5         35        32
MS        0.25        60        60
FS        0.105      140       150
VFS       0.047      300       300
```

6. REAGENTS
6.1 Distilled water
6.2 Ethyl alcohol

7. PROCEDURE

7.1 Weigh 10 g of <2-mm, air-dry soil to nearest mg on an electronic balance and place into a numbered, tared 300-mL, fleaker. Wash and tare these fleakers once every two months.

7.2 Dry the sample in an oven at 105°C overnight. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.3 Record the total weight (TW) of the sample to the nearest mg.

7.4 Add ≈ 175 mL of distilled water to sample. Place the sample in a horizontal shaker set at 120 oscillations min^{-1} and shake for 15 h (overnight).

7.5 Remove the sample from the shaker and pour through a 300-mesh (0.047-mm) sieve mounted on a ring stand. Place a funnel below the sieve and a 1-L cylinder below the funnel. Collect the silt and clay in the 1-L cylinder. Avoid using jets of water in washing the sample. Wash and rub all particles from the fleaker into the sieve. Continue to wash until the suspension volume in the cylinder is ≈ 800 mL. Sand and some of the coarse silt remain on the sieve. Rinse all <20-μm particles into the cylinder. Fill the cylinder to 1 L and cover with a 65-mm watch glass. Prepare a distilled water blank to measure temperature fluctuations. Allow the cylinder to stand overnight to equilibrate the suspension with the room temperature. Wash the sand into an evaporation dish and dry the sand at 105°C overnight.

7.6 Transfer the dried sand to a nest of sieves that has a top-to-bottom order of 1.0, 0.5, 0.25, 0.1, and 0.047 mm. Shake the sand for 3 min on a shaker that has 1.3-cm vertical and lateral movements and oscillates at 500 strokes min^{-1}. Record the weight of each separate sand fraction (SW_i) to the nearest mg. If optical analysis is requested, place the very fine sand and fine sand fractions in gelatin capsules and the remaining sand fractions in a labelled vial. Store capsules in the labelled vial. Wash sand dishes after every use.

7.7 Determine the percentage of fine silt and clay gravimetrically by removing an aliquot from the suspension in the 1-L cylinder with a Lowy, 25-mL pipet. Periodically, gravimetrically calibrate the delivery volume of the pipet by weighing the amount of distilled water dispensed from the pipet. Record the delivery volume (DV) and use the value to calculate the results. Regulate the vacuum such that the pipet fills in $\approx$ 12 s. Record temperature (T_1) of blank. Mount the pipet on an adjustable pipet rack (Shaw, 1932). Stir the silt and clay suspension with mechanical stirrer for 6 min or for 8 min, if the suspension has stood for >24 h (Kilmer and Mullins, 1954). Place pipe insulation around sample and blank cylinders to prevent rapid changes in temperatures. Place the cylinder on a stable, vibrationless table and stir with a hand stirrer in an up-and-down motion for 30 s. Timing is started upon completion of the stirring. Record the time that stirring is stopped. For the <20-μm fraction, slowly lower the closed pipet to a 10-cm depth in the suspension, open the pipet, turn on the vacuum, and withdraw an aliquot at the calculated time (Table 1). Dispense the aliquot into a tared and numbered, 90-mL weighing bottle. Rinse the pipet twice with distilled water and dispense into the tared, weighing bottle with aliquot. For the <2-μm fraction, pipet after a time of 4.5, 5, 5.5, or 6.5 h. Record temperature (T_2) of blank. Use the average of T_1 and T_2 and adjust the pipet depth in the suspension as indicated in Table 2. Repeat the procedure described for the <20-μm fraction.

7.8 Dry the aliquots at 105°C overnight and cool in a desiccator that contains phosphorous pentoxide (P_2O_5) or an equivalent desiccant.

7.9 Record the residue weight (RW) to the nearest 0.1 mg.

7.10 Use the 90-mL, round-bottomed, weighing bottles for the <20-μm aliquots. Wash and tare after every fourth use. Use the 90-mL, square-bottomed, weighing bottles for the <2-μm aliquots. Wash and tare after every use.

7.11 If fine clay analyses are requested, use the remaining suspension and follow procedure 3A1b. If necessary, save the sediment for optical mineralogy.

7.12 If optical mineralogy is requested, decant the suspension and transfer the sediment to a 400-ml beaker. Fill the beaker to a 5.5-cm height. Stir the sediment and allow to settle for 5 min. Discard the supernatant. Refill the beaker to 5.5-cm height. Stir again, allow to settle for 3 min, and then decant. Repeat the filling and the stirring; allow to settle for 2 min; and then decant until top half of suspension is clear. Transfer the sediment, which is dominantly 20 to 50 μm, to a labelled drying dish. Wash with ethanol, air-dry, and save in the drying dish for optical mineralogy.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
WATER DISPERSIBLE CLAY (3A1c)

8. CALCULATIONS

8.1 Clay % = 100 x ((RW_2 x CF)/TW)

where:
RW_2 = residue weight (g), <2-μm fraction
CF = 1000 mL/DV
DV = dispensed pipet volume
TW = total weight (g), H_2O_2-treated, oven-dry sample

8.2 Fine Silt % = (100 x (RW_{20} x CF)/TW)) - Clay %

where:
RW_{20} = residue weight (g) of <20-μm fraction

8.3 Sand % = $\sum$ (SW /TW) x 100

where:
i = 1.0, 0.5, 0.25, 0.1, and 0.047-mm sand fractions

8.4 Coarse silt % = 100 - (Clay + Fine Silt + Sand %)

9. REPORT
Report percentages of each particle size and specify procedure 3A1c..

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Bouyoucos, G.B. 1929. The ultimate natural structure of the soil. Soil Sci. 28:27-37.
Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:383-411.
Kilmer, V.J., and L.T. Alexander. 1949. Methods of making mechanical analyses of soils. Soil Sci. 68:15-24.
Kilmer, V.J., and J.F. Mullins. 1954. Improved stirring and pipetting apparatus for mechanical analysis of soils. Soil Sci. 77:437-441.
Shaw, T. M. 1932. New aliquot and filter devices for analytical laboratories. Ind. Eng. Chem. Anal. Ed. 4:409.

Table 1. Sampling times at 10-cm sampling depths and
         2.65 g cc^{-1} particle density.[1]

Temp (°C)	20 μm		5 μm	
	min	s	min	s
18.00	4	52	78	0
19.00	4	45	76	7
20.00	4	38	74	13
20.25	4	36	73	46
20.50	4	34	73	19
20.75	4	33	72	52
21.00	4	31	72	26
21.25	4	30	72	0
21.50	4	28	71	34
21.75	4	26	71	8
22.00	4	25	70	43
22.25	4	23	70	18
22.50	4	22	69	53
22.75	4	20	69	28
23.00	4	19	69	4
23.25	4	17	68	39
23.50	4	15	68	15
23.75	4	14	67	52
24.00	4	13	67	28
24.25	4	11	67	5
24.50	4	10	66	41
24.75	4	8	66	18
25.00	4	7	65	56
25.25	4	5	65	33
25.50	4	4	65	11
25.75	4	3	64	49
26.00	4	1	64	27
26.25	4	0	64	5
26.50	3	59	63	43
26.75	3	57	63	22
27.00	3	56	63	1
27.25	3	55	62	40
27.50	3	53	62	19
27.75	3	52	61	59
28.00	3	51	61	38
28.25	3	49	61	18
28.50	3	48	60	58
28.75	3	47	60	38
29.00	3	46	60	18
29.25	3	44	59	59
29.50	3	43	59	39
29.75	3	42	59	20
30.00	3	41	59	1

[1]Use this table with procedures 3A1c and 3A2c.

Table 2. Sampling depths (cm) for 2-μm clay and 2.65 g cc^{-1} particle density.[1]

Temp (°C)	Time (h)				
	4.5	5.0	5.5	6.0	6.5
18.00	5.54	6.15	6.77	7.38	8.00
19.00	5.67	6.31	6.94	7.57	8.20
20.00	5.82	6.47	7.11	7.76	8.41
20.25	5.86	6.51	7.16	7.81	8.46
20.50	5.89	6.55	7.20	7.86	8.51
20.75	5.93	6.59	7.24	7.90	8.56
21.00	5.96	6.63	7.29	7.95	8.61
21.25	6.00	6.67	7.33	8.00	8.67
21.50	6.04	6.71	7.38	8.05	8.72
21.75	6.07	6.75	7.42	8.10	8.77
22.00	6.11	6.79	7.47	8.14	8.82
22.25	6.14	6.83	7.51	8.19	8.88
22.50	6.18	6.87	7.55	8.24	8.93
22.75	6.22	6.91	7.60	8.29	8.98
23.00	6.25	6.95	7.64	8.34	9.03
23.25	6.29	6.99	7.69	8.39	9.09
23.50	6.33	7.03	7.73	8.44	9.14
23.75	6.37	7.07	7.78	8.49	9.19
24.00	6.40	7.11	7.83	8.54	9.25
24.25	6.44	7.16	7.87	8.59	9.30
24.50	6.48	7.20	7.92	8.64	9.36
24.75	6.51	7.24	7.96	8.69	9.41
25.00	6.55	7.28	8.01	8.74	9.46
25.25	6.59	7.32	8.05	8.79	9.52
25.50	6.63	7.36	8.10	8.84	9.57
25.75	6.66	7.41	8.15	8.89	9.63
26.00	6.70	7.45	8.19	8.94	9.68
26.25	6.74	7.49	8.24	8.99	9.74
26.50	6.78	7.53	8.28	9.04	9.79
26.75	6.82	7.57	8.33	9.09	9.85
27.00	6.85	7.62	8.38	9.14	9.90
27.25	6.89	7.66	8.42	9.19	9.96
27.50	6.93	7.70	8.47	9.24	10.01
27.75	6.97	7.74	8.52	9.29	10.07
28.00	7.01	7.79	8.57	9.34	10.12
28.25	7.05	7.83	8.61	9.40	10.18
28.50	7.09	7.87	8.66	9.45	10.23
28.75	7.12	7.92	8.71	9.50	10.29
29.00	7.16	7.96	8.75	9.55	10.35
29.25	7.20	8.00	8.80	9.60	10.40
29.50	7.24	8.05	8.85	9.65	10.46
29.75	7.28	8.09	8.90	9.71	10.52
30.00	7.32	8.13	8.95	9.76	10.57

[1]Use this table with procedures 3A1c and 3A2c.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
CARBONATE AND NONCARBONATE CLAY II (3A1d)
(II = electronic manometer with pressure sensor)

1. APPLICATION

Carbonate clay is considered important in PSA because clay-size carbonate particles have properties that are different from noncarbonate clay. The cation exchange capacity of carbonate clay is very low compared to noncarbonate clay. Water holding capacity of carbonate clay is $\approx$ two thirds that of noncarbonate clay. Since carbonate clay is a diluent, it is often subtracted from the total clay in order to make inferences about soil genesis and clay activities.

2. SUMMARY OF METHOD

Clay residue from air-dry PSA (procedure 3A1) is treated with acid in a closed system. The pressure of the evolved gas is measured. The pressure is related linearly to the CO_2 content in the carbonates. A manometer is used to measure the pressure.

3. INTERFERENCES

The method is semi-quantitative. It is assumed that all of the carbonates are converted to CO_2. This method measures all forms of carbonates. In addition to Ca, the carbonates of Mg, Na, and K also react with the acid. Analytical interferences may be caused by temperature changes within the reaction vessel. The analyst should not touch the glass of the vessel when reading the pressure. When sealing the vessel, the analyst should not hold onto the vessel any longer than necessary to tighten the cap. The internal pressure must be equalized with the atmosphere. Approximately 3 to 5 s are required to equalize the internal pressure of the bottle when piercing the septa with a needle. The analyst should replace septa at regular intervals. The septa develop leaks after extensive use.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when handling acids. Use the fume hood when diluting concentrated HCl. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Perform the transfer of acid to gelatin capsules near a sink in case of leakage or spills.

5. EQUIPMENT
5.1 Manometer, hand-held gauge and differential pressure, PCL-200 Series, Omega Engineering, Stamford, CT.
5.2 Gelatin capsules, 5 mL
5.3 Threaded weighing bottles, 90 mL.
5.4 Machined PVC caps for threaded 90-mL weighing bottles, 3.2-cm (1 1/4 in) diameter with 1.1-cm (7/16 in) diameter hole drilled in center, O-ring seal.
5.5 O-rings, 3.2 x 38.1 mm (1/8 x 1 1/2 in)
5.6 Septa, rubber, 7.9-mm (5/16 in) diameter. Place in machined cap.
5.7 Hypodermic needle, 25.4 mm (1 in), 23 gauge.
5.8 Oven, 105°C
5.9 Electronic balance, ±0.1-mg sensitivity.

6. REAGENTS
6.1 Distilled water
6.2 Hydrochloric acid (HCl), 6 *N*, technical grade. Dilute 1 L of concentrated HCl with 1 L of distilled water.
6.3 Sodium carbonate (Na_2CO_3) reagent. Dissolve 10.6 g Na_2CO_3 in distilled water and make to 1 L (10 mg $CaCO_3$ mL^{-1}).
6.4 Glycerine, USP. Put Glycerine in small squeeze bottle.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
CARBONATE AND NONCARBONATE CLAY II (3A1d)
(II = electronic manometer with pressure sensor)

7. PROCEDURE

Manometer Calibration

7.1 Calibrate the manometer quarterly or whenever equipment changes. Calibrate by placing 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 mL of the Na_2CO_3 reagent into tared, 90-mL weighing bottles. Dry the standard samples in the oven overnight at 105°C. Remove samples from oven, place in desiccator and cool to ambient temperature. Record the weight of the standard samples to nearest 0.1 mg.

7.2 Lubricate the lip of the 90-mL, weighing bottle that contains the Na_2CO_3 with a thin film of glycerine. Dispense 3 mL of 6 *N* HCl into a gelatin capsule and place the top on the capsule. If HCl leaks from the capsule, discard the capsule. Place the capsule into the glass bottle and immediately cap the bottle. Release pressure in the bottle by piercing the septa with a hypodermic needle which is not connected to the manometer. Allow 3 to 5 s for internal pressure in bottle to equalize.

7.3 After the gelatin capsule has dissolved (several minutes), slowly tip the bottle and rotate it to saturate the standard sample adhering to the sides of the bottle. Avoid changing the temperature of the container by only handling the cap. Allow sample to stand for at least 30 min.

7.4 Adjust the manometer to zero before taking measurements. Insert the hypodermic needle in the septa stopper which is connected to the transducer. Measure the pressure inside the weighing bottle. Record the manometer readings using the rounding-up procedure.

7.5 Calculate the linear regression equation, i.e., the dependent variable is the Na_2CO_3 weights (regressed or predicted values) and the independent variable is the corresponding manometer readings.

Carbonate Determination

7.6 Determine the presence of carbonates in <2-mm soil by placing soil on a spot plate and adding two or three drops of 1 *N* HCl. The rate of CO_2 evolution indicates the relative amount of carbonates (procedure 1B).

7.7 If the soil contains more than a trace amount of carbonates, determine the amount of carbonate clay in the <2-μm dry residue (procedure 3A2).

7.8 With a thin film of glycerine, lubricate the lip of the 90-mL, weighing bottle that contains the <2-μm residue. In each analysis batch, include an empty weighing bottle as a blank. Dispense 3 mL of 6 *N* HCl into a gelatin capsule and place the top on the capsule. If HCl leaks from the capsule, discard the capsule. Place the capsule into the glass bottle and immediately cap the bottle. Release any pressure in the bottle by piercing the septa with a hypodermic needle that is not connected to the manometer. Approximately 3 to 5 s are required to equalize the internal pressure of the bottle.

7.9 After the gelatin capsule has dissolved (several minutes), slowly tip the bottle and rotate it to saturate the clay adhering to the sides of the bottle. Handle only the cap to avoid changing the temperature of the container. Allow sample to stand for at least 30 min.

7.10 Turn on the manometer at least 30 min before use. Adjust the manometer to zero before taking measurements. Insert the hypodermic needle in septa stopper which is connected to the transducer. Measure the pressure inside the weighing bottle and record the manometer readings (MR). Begin readings with the blank (BR).

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
CARBONATE AND NONCARBONATE CLAY II (3A1d)
(II = electronic manometer with pressure sensor)

7.11 Compare the sample readings with those of a standard curve prepared by measuring CO_2 evolved from a series of Na_2CO_3 aliquots with a range 0 to 35 mg.

7.12 Use the 90-mL, square-bottomed, weighing bottles for the <2-μm aliquots and carbonate determination. Wash and tare after every use.

8. CALCULATIONS

8.1 Calculate the linear regression equation, i.e., the dependent variable is the Na_2CO_3 weights (regressed or predicted values) and the independent variable is the corresponding manometer readings.

8.2 Correct the manometer reading as follows:

$$CR = (MR - BR)$$

where:
CR = corrected reading
MR = manometer reading
BR = blank reading

8.3 Use the calculated linear regression equation and the CR for the standard samples to estimate the g of $CaCO_3$ in sample.

8.4 Carbonate Clay Equivalent (<2 μm) (%) = ((g $CaCO_3$) x 100 x CF)/TW

where:
CF = 1000 mL/dispensed pipet volume (mL)
TW = total weight of H_2O_2-treated oven-dry sample (procedure 3A1)

8.5 Noncarbonate Clay (<2 μm) (%) = Total Clay (%) - Carbonate Clay Equivalent (%)

9. REPORT
Report percentages of carbonate and noncarbonate clay.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Shields, L.G., and M.W. Meyer. 1964. Carbonate clay: measurement and relationship to clay distribution and cation exchange capacity. Soil Sci. Soc. Am. Proc. 28:416-419.
Williams, D.E. 1948. A rapid manometric method for the determination of carbonate in soils. Soil Sci. Soc. Am. Proc. 13:127-129.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
PRETREATMENT TO REMOVE CARBONATES (with pH 5 NaOAc) (3A1e)

1. APPLICATION

Soils high in carbonate content do not readily disperse. Pretreatment of these soils with acid destroys the carbonates (Grossman and Millet, 1961; Jackson, 1969; Gee and Bauder, 1986). This method may be requested by project coordinators to determine the particle-size distribution after pretreatment to remove carbonates. This determination is used primarily for studies of soil genesis and parent material.

2. SUMMARY OF METHOD

Carbonates are destroyed with NaOAc solution buffered to pH 5. The NaOAc solution is added to sample until carbonate bubbles no longer evolve. The NaOAc solution is then washed from the sample. After destruction of carbonates, the standard PSA (procedure 3A1) is followed.

3. INTERFERENCES

Acidification can destroy primary mineral structure of clay (Gee and Bauder, 1986).

4. SAFETY

Use rubber gloves and a face shield when handling acids. Mix acids in ventilated fume hoods. Never add water to acid.

5. EQUIPMENT
5.1 Fleaker, 300 mL, tared to 1 mg
5.2 Rubber policeman
5.3 Stirring rod
5.4 Ceramic filter candles, .3μm absolute retention
5.5 Watch glass, 50-mm diameter
5.6 Hot plate, 100°C.
5.7 Vacuum, 0.8 bars (80 kPa)

6. REAGENTS
6.1 Distilled water
6.2 1 *N* sodium acetate (NaOAc) solution, buffered to pH 5. Dissolve 680 g of NaOAc in 4 L of distilled water. Add ≈ 250 mL of acetic acid. Make to 5-L volume with distilled water.
6.3 Ethyl alcohol
6.4 Hydrogen peroxide (H_2O_2), 30 to 35%

7. PROCEDURE

7.1 Weigh sufficient sample to yield 10 g of <2-mm, air-dry carbonate-free soil sample, e.g. if the sample contains 50% carbonates, weigh 20 g of soil. Place the <2-mm, air-dry sample into a 300-mL, tared, fleaker.

7.2 Add ≈ 200 mL of the 1 *N* NaOAc solution to the sample, mix with a stirring rod, and cover with a watch glass. Allow the sample to stand overnight.

7.3 Place the sample on the hot plate and heat to ≈ 90°C until bubbles are no longer evident. Do not boil. Heating accelerates reaction. Decant the solution and add more 1 *N* NaOAc solution. If a reaction occurs, repeat the heating procedure. Continue to decant, add NaOAc solution, and heat until all the carbonates are removed. The speed of dissolution can be increased by lowering the pH of the 1 *N* NaOAc solution (Rabenhorst and Wilding, 1984).

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
PRETREATMENT TO REMOVE CARBONATES (with pH 5 NaOAc) (3A1e)

7.4 When no more carbonate bubbles are observed, insert the ceramic filter candle into the solution. Apply vacuum and candle the sample to dryness. Rinse once with 200 mL of distilled water.

7.5 Add ≈ 50 mL of distilled water and 5 mL of H_2O_2 to the soil sample at ambient temperature. Cover the soil sample with 50-mm watch glass. Allow initial oxidation of organic matter to complete and then place sample on hot plate. If the froth from the reaction exceeds the capacity of the fleakers, transfer the samples to larger beakers.

7.6 Place the sample on the hot plate and heat to ≈ 90°C. Add 5-mL increments of H_2O_2 at 45-min intervals until oxidation has completed or until 30 mL of H_2O_2 have been added. Heat the sample for an additional 45 min to decompose excess H_2O_2. If the reaction is violent, add small increments of ethyl alcohol to the sample or remove the sample from the hot plate to slow the reaction.

7.7 Place the sample on the filter rack. Add 150 mL of distilled water. Insert filter candle, connect to the vacuum trap assembly with tubing, and turn on vacuum. Wash the sample four additional times with ≈ 150 mL of distilled water. If the sample contain gypsum and flocculates, then the following additional washings may be used. If the sample contains 1 to 5% gypsum, stir the sample with a magnetic stirrer for 5 min and wash 5 times with ≈ 250 mL of distilled water each time. If the sample contains >5% gypsum, stir the sample with a magnetic stirrer for 5 min then wash 5 times with ≈ 750 mL of distilled water each time to remove soluble gypsum.

7.8 Place the sample in the oven and dry overnight at 105°C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.9 Record the total weight (TW) of the sample to the nearest mg.

7.10 Proceed with standard PSA (procedure 3A1).

8. CALCULATIONS
Calculations are reported in procedure 3A1.

9. REPORT
Report as carbonate-free PSA data and specify procedure 3A1e.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:383-411.

Grossman, R.B., and J.L. Millet. 1961. Carbonate removal from soils by a modification of the acetate buffer method. Soil Sci. Soc. Am. Proc. 25:325-326.

Jackson, M.L. 1969. Soil chemical analysis--advanced course. 2nd ed. Univ. Wisconsin, Madison.

Rabenhorst, M.C., and L.P. Wilding. 1984. Rapid method to obtain carbonate-free residues from limestone and petrocalcic materials. Soil Sci. Soc. Am. J. 48:216-219.

PARTICLE-SIZE ANALYSIS
PARTICLES <2-mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
PRETREATMENT TO REMOVE IRON (3A1f)
(with sodium dithionite-citrate)

1. APPLICATION

Iron and other oxides coat and bind clay, silt and sand particles to form aggregates. Soils with iron cementation do not readily disperse. The iron oxides are removed using bicarbonate-buffered, sodium dithionite-citrate solution (Mehra and Jackson, 1960; Gee and Bauder, 1986). This chemical pretreatment is used when requested by the project coordinator.

2. SUMMARY OF METHOD

Soil samples are pretreated with H_2O_2 to remove organic matter. Iron oxides are removed with bicarbonate-buffered, sodium dithionite-citrate solution and heated until the sample color changes to a grayish color. The suspension is flocculated with saturated NaCl solution and filtered to remove soluble salts. After iron oxide removal, standard PSA (3A1) is followed.

3. INTERFERENCES

If the temperature of the water bath exceeds 80°C, elemental sulfur will precipitate (Mehra and Jackson, 1960). This pretreatment destroys primary mineral grains in the clay fraction (El-Swaify, 1980).

4. SAFETY

Use rubber gloves and a face shield when handling acid and H_2O_2. Mix acids in ventilated fume hoods. Heat samples for removal of organic matter or cementing agents in ventilation hoods. Handle heated samples with leather gloves.

5. EQUIPMENT

5.1 Ceramic filter candles, .3μm absolute retention
5.2 Electronic balance, ±1-mg sensitivity
5.3 Fleaker, 300 mL, tared to 1 mg
5.4 Rubber policeman
5.5 Calibrated scoop, 1 g
5.6 Glass stirring rod
5.7 Thermometer, 0 to 100°C
5.8 Timer or clock with second hand
5.9 Water bath, 80°C
5.10 Centrifuge
5.11 Vacuum, 0.8 bars (80 kPa)

6. REAGENTS

6.1 Sodium citrate solution, 0.3 M $Na_3C_6H_5O_7 \cdot 2H_2O$ (88.4 g L^{-1})
6.2 Sodium bicarbonate buffer solution, 1 M $NaHCO_3$ (84 g L^{-1})
6.3 Sodium dithionite ($Na_2S_2O_4$ - hydrosulphite)
6.4 Saturated NaCl solution (solubility at 20°C; 360 g L^{-1})
6.5 Ethyl alcohol
6.6 Hydrogen peroxide (H_2O_2), 30 to 35%

7. PROCEDURE

7.1 A maximum of ~ 0.5 g of Fe_2O_3 can be dissolved in 40 mL of the citrate solution. Adjust the weight of the <2-mm, air-dry soil sample so that any one fleaker does not contain more than 0.5 g of Fe_2O_3. Split the sample into different fleakers if necessary. Total sample weight after dissolution should be ≈ 10 g. Place the sample into a tared, labelled, 300-mL fleaker.

PARTICLE-SIZE ANALYSIS
PARTICLES <2-mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
PRETREATMENT TO REMOVE IRON (3A1f)
(with sodium dithionite-citrate)

7.2 Add $\approx$ 50 mL of distilled water and 5 mL of H_2O_2 to the soil sample at ambient temperature. Cover the soil sample with a 50-mm watch glass. Allow initial oxidation of organic matter to complete, and then place sample on hot plate. If the froth from the reaction exceeds the capacity of the fleaker, transfer the sample to a larger beaker.

7.3 Place the sample on a hot plate and heat to 90°C. Add 5-mL increments of H_2O_2 at 45-min intervals until oxidation has completed or until 30 mL of H_2O_2 have been added. Heat the sample for an additional 45 min to decompose excess H_2O_2. If the reaction is violent, add small increments of ethyl alcohol to the sample or remove the sample from the hot plate to slow the reaction.

7.4 Add 40 mL of the citrate solution and 5 mL of the sodium bicarbonate. Heat to 80°C in a water bath, but do not exceed 80°C. Add 1 g of sodium dithionite powder with a calibrated scoop. Stir constantly with a glass rod for 1 min and then occasionally for 15 min. Add 10 mL of saturated NaCl solution and mix.

7.5 Centrifuge or candle the sample to remove the dissolved Fe_2O_3. Combine the split samples into fewer fleakers.

7.6 If the sample contains less than 0.5 g of Fe_2O_3, repeat the dissolution treatment. For samples with more than 0.5 g of Fe_2O_3, repeat the dissolution treatment two more times.

7.7 Place the sample on the filter rack. Add 150 mL of distilled water. Insert a filter candle, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Wash the sample four additional times with $\approx$ 150 mL of distilled water. If the sample contains gypsum and flocculates, then the following additional washings may be used. If the sample contains 1 to 5% gypsum, stir the sample with a magnetic stirrer for 5 min and wash 5 times with $\approx$ 250 mL of distilled water each time. If the sample contains >5% gypsum, stir the sample with a magnetic stirrer for 5 min then wash 5 times with $\approx$ 750 mL of distilled water each time to remove soluble gypsum.

7.8 Place the sample in the oven and dry overnight at 105°C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.9 Record the total weight (TW) of the sample to the nearest mg.

7.10 Proceed with standard PSA (procedure 3A1).

8. CALCULATIONS

Calculations are reported in procedure 3A1.

9. REPORT

Report as iron-free PSA data and specify procedure 3A1f.

10. PRECISION

Precision data are not available for this procedure.

PARTICLE-SIZE ANALYSIS
PARTICLES <2-mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
PRETREATMENT TO REMOVE IRON (3A1f)
(with sodium dithionite-citrate)

11. REFERENCES

El-Swaify, S.A. 1980. Physical and mechanical properties of Oxisols. p. 303-324. *In* B.K.G. Theng (ed.) Soils with variable charge. N.Z. Soc. Soil Sci., Lower Hutt, N.Z.

Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:383-411.

Mehra, O.P., and M.L. Jackson. 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. p. 237-317. *In* Clays and clay minerals. Proc. 7th Conf. Natl. Acad. Sci. Natl. Res. Counc. Pub., Washington, DC.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
PRETREATMENT TO REMOVE SILICA (with NaOH) (3A1g)

1. APPLICATION

Soils that are cemented by Si do not completely disperse with hydrogen peroxide pretreatment and sodium hexametaphosphate. A pretreatment with a weak base dissolves the Si bridges and coats and increases the soil dispersion. This method is experimental and can be used when requested by project coordinators. The determination is used for soil parent material and genesis studies.

2. SUMMARY OF METHOD

Soils are pretreated with H_2O_2 to remove organic matter. Soils with Si cementation or coatings are pretreated with a weak NaOH solution overnight. After removal of siliceous cementing agents, standard PSA (procedure 3A1) is followed.

3. INTERFERENCES

The effects of this pretreatment on clay minerals and particle size distribution are unknown.

4. SAFETY

Use rubber gloves and a face shield when handling bases. Mix bases in ventilated fume hoods.

5. EQUIPMENT
5.1 Fleakers, 300 mL, tared to 1 mg
5.2 Ceramic filter candles, .3μm absolute retention
5.3 Vacuum, 0.8 bars (80 kPa)
5.4 Electronic balance, ±1-mg sensitivity
5.5 Watch glass, 50-mm diameter

6. REAGENTS
6.1 Distilled water
6.2 Hydrogen peroxide (H_2O_2), 30 to 35%
6.3 Sodium hydroxide solution (NaOH), 0.1 N. Dissolve 4 g NaOH pellets in 1 L of distilled water.
6.4 Ethyl alcohol

7. PROCEDURE

7.1 Weigh 10 g of <2-mm, air-dry soil to nearest mg on an electronic balance and place in a 300-mL, tared fleaker.

7.2 Add ≈ 50 mL of distilled water and 5 mL of H_2O_2 to soil sample at ambient temperature. Cover the soil sample with 50-mm watch glass. Allow initial oxidation of organic matter to complete, and then place sample on hot plate. If the froth from the reaction exceeds the capacity of the fleaker, transfer the sample to a larger beaker.

7.3 Place the sample on a hot plate and heat to 90°C. Add 5-mL increments of H_2O_2 at 45-min intervals until oxidation has completed or until 30 mL of H_2O_2 have been added. Heat the sample for an additional 45 min to decompose excess H_2O_2. If the reaction is violent, add small increments of ethyl alcohol to the sample or remove the sample from the hot plate to slow the reaction.

7.4 Soak the sample overnight in 100 mL of 0.1 N NaOH.

7.5 Place the sample on the filter rack. Add 150 mL of distilled water. Insert a filter candle, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Wash the sample four additional times with ≈ 150 mL of distilled water. If the sample contains gypsum and flocculates, then the following

additional washings may be used. If the samples contain 1 to 5% gypsum, stir the samples with a magnetic stirrer for 5 min and wash 5 times with ≈ 250 mL of distilled water each time. If the sample contains >5% gypsum, stir the sample with a magnetic stirrer for 5 min then wash 5 times with ≈ 750 mL of distilled water each time to remove soluble gypsum.

7.6 Place the sample in the oven and dry overnight at 105°C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.7 Record the total weight (TW) of the sample to the nearest mg.

7.8 Proceed with standard PSA in procedure 3A1.

8. CALCULATIONS
Calculations are reported in procedure 3A1.

9. REPORT
Report as Si-free PSA data and specify procedure 3A1g.

10. PRECISION
Precision data are not available for this procedure.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
DISPERSION USING ULTRASONIC PROBE (3A1h)

1. APPLICATION

Soils that do not completely disperse with standard PSA can be dispersed using ultrasonic dispersion (Gee and Bauder, 1986). Pretreatments coupled with ultrasonic dispersion yield maximum clay concentrations (Mikhail and Briner, 1978). This is a developmental procedure as no standard method has been adopted using ultrasonic dispersion. This method is used when requested by project coordinators.

2. SUMMARY OF METHOD

A 10-g sample of <2-mm, air-dry soil is pretreated to remove organic matter and soluble salts. The sample is dried in the oven and weighed to obtain the initial weight. Sodium hexametaphosphate solution is added to the sample and then made to 100-mL volume with distilled water. The sample is subjected to ultrasonic vibration for 5 min. The sand fraction is removed by wet sieving and then fractionated by dry sieving. The clay and fine silt fractions are determined using the suspension remaining from the wet sieving process. This suspension is diluted to 1 L in a sedimentation cylinder, stirred, and 25-mL aliquots removed with a pipet at calculated, predetermined intervals based on Stokes' law (Kilmer and Alexander, 1949). The aliquots are dried at 105°C and weighed. Coarse silt is the difference between 100% and the sum of the sand, clay, and fine silt percentages.

3. INTERFERENCES

Ultrasonic dispersion has been reported to destroy primary soil particles. Watson (1971) summarized studies that reported the destruction of biotite and breakdown of microaggregates by ultrasonic dispersion. However, Saly (1967) reported that ultrasonic vibration did not cause the destruction of the clay crystalline lattice or the breakdown of primary grains. The samples ranged from sandy to clayey soils. The cementing agents represented humus, carbonates, and hydroxides of Fe and Al. No standard procedures have been adopted using ultrasonic dispersion.

4. SAFETY

Use rubber gloves and a face shield when handling acid and H_2O_2. Mix acids in ventilated fume hoods. Heat samples for removal of organic matter or cementing agents in ventilation hoods. Handle heated samples with leather gloves. Never add water to dce ne nuil in hydrooveDɪ˝(eardardtestruc and)Tjɪ˝T*ɪ˝-0.001 Tel

5.17 Sieve shaker with 12.7-mm (1/2 in) vertical and lateral movement at 500 oscillations min^{-1}. Accommodates a nest of 76-mm (3 in) sieves.
5.18 Weighing bottles, 90 mL, with screw caps, tared to 1 mg
5.19 Weighing bottles, 90 mL, tared to 1 mg
5.20 Timer or clock with second hand
5.21 Electronic balance, ±0.1-mg sensitivity
5.22 Electronic balance, ±1-mg sensitivity
5.23 Watch glass, 50- and 65-mm diameters
5.24 Evaporating dish, porcelain, 160-mm diameter, 31-mm height, with lip
5.25 Set of 76-mm (3 in) sieves, square weave phosphor bronze wire cloth except 300 mesh which is twilled weave. U.S. series and Tyler Screen Scale equivalent designations are as follows:

```
Sand      Opening    U.S.      Tyler
Size       (mm)      No.       Mesh
                               Size


VCS        1.0         18        16
CS         0.5         35        32
MS         0.25        60        60
FS         0.105      140       150
VFS        0.047      300       300
```

6. REAGENTS
6.1 Distilled water
6.2 Hydrogen peroxide (H_2O_2), 30 to 35%
6.3 Sodium hexametaphosphate (($NaPO_3)_6$), reagent grade
6.4 Sodium carbonate (Na_2CO_3), reagent grade
6.5 Sodium hexametaphosphate solution. Dissolve 35.7 g ($NaPO_3)_6$ and 7.94 g Na_2CO_3 per L of distilled water.
6.6 Ethyl alcohol
6.7 Phosphorous pentoxide (P_2O_5), calcium sulfate (anhydrous), or equivalent desiccant

7. PROCEDURE

7.1 Weigh 10 g of <2-mm, air-dry soil to nearest mg on an electronic balance and place into a numbered, tared, 300-mL, fleaker. Wash and tare these fleakers once every two months.

7.2 Add ≈ 50 mL of distilled water and 5 mL of H_2O_2 to the soil sample at ambient temperature. Cover the soil sample with a 50-mm watch glass. Allow initial oxidation of organic matter to complete and then place sample on hot plate. If the froth from the reaction exceeds the capacity of the fleaker, transfer the sample to a larger beaker.

7.3 Place the sample on a hot plate and heat to 90°C. Add 5-mL increments of H_2O_2 at 30-min intervals until the oxidation has completed or until 30 mL of H_2O_2 have been added. Heat the sample for an additional 45 min to decompose excess H_2O_2. If the reaction is violent, add small increments of ethyl alcohol to the sample or remove the sample from the hot plate to slow the reaction or transfer sample to a 1000-mL beaker. Record any unusual sample reactions.

7.4 Place the sample on the filter rack. Add 150 mL of distilled water. Insert a filter candle, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Wash the sample four additional times

with ≈ 150 mL of distilled water. If the sample contains gypsum and flocculates, then the following additional washings may be used. If the sample contains 1 to 5% gypsum, stir the sample ewith a magnetic stirrer for 5 min and wash 5 times with ≈ 250 mL of distilled water each time. If the sample contains >5% gypsum, stir the sample with a magnetic stirrer for 5 min then wash 5 times with ≈ 750 mL of distilled water each time to remove soluble gypsum.

7.5 Place sample in oven. Dry the sample overnight at 105°C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.6 Record the total weight (TW) of the sample to the nearest mg.

7.7 Add ≈ 100 mL of distilled water and 10 mL of sodium hexametaphosphate solution, equivalent to 0.4408 g of NaHMP, to each sample. Subtract the weight of the sodium hexametaphosphate (D) contained in the extracted aliquot from the silt and clay weights in the calculation of results. Determine the exact volume of sodium hexametaphosphate to add to each sample by regressing the volume of sodium hexametaphosphate against the dry residue weight of sodium hexametaphosphate and then by predicting the volume needed to dispense 0.4408 g of sodium hexametaphosphate into each sample.

7.8 Disperse the suspension with ultrasonic vibrations. Ensure the power supply is properly tuned. Consult the instruction manual. Immerse the probe in the suspension to a 3-cm depth. Set timer to 5 min. Press start button. Adjust output control as required. Between samples, clean the probe by placing it in water or alcohol and energizing it for a few seconds.

7.9 After ultrasonic dispersion, pour the suspension through a 300-mesh (0.047-mm) sieve mounted on a ring stand. Place a funnel below the sieve and a 1-L cylinder below the funnel. Collect the silt and clay in the 1-L cylinder. Avoid using jets of water in washing the sample. Wash and rub all particles from the fleaker into the sieve. Continue to wash until the suspension volume in the cylinder is ≈ 800 mL. Sand and some of the coarse silt remain on the sieve. Rinse all <20-μm particles into the cylinder. Fill the cylinder to 1 L and cover with a 65-mm watch glass. Prepare a distilled water blank to measure temperature fluctuations. Allow the cylinder to stand overnight to equilibrate the suspension with the room temperature. Wash the sand into an evaporation dish and dry the sand at 105°C overnight.

7.10 Transfer the dried sand to a nest of sieves that has a top-to-bottom order of 1.0, 0.5, 0.25, 0.1, and 0.047 mm. Shake the sand for 3 min on a shaker that has 1.3-cm vertical and lateral movements and oscillates at 500 strokes min^{-1}. Record the weight of each separate sand fraction (SW$_i$) to the nearest mg. If optical analysis is requested, place the very fine sand and fine sand fractions in gelatin capsules and the remaining sand fractions in a labelled vial. Store capsules in the labelled vial. Wash sand dishes after every use.

7.11 Determine the percentage of fine silt and clay gravimetrically by removing an aliquot from the suspension in the 1-L cylinder with a Lowy, 25-mL pipet. Periodically, gravimetrically calibrate the delivery volume of the pipet by weighing the amount of distilled water dispensed from the pipet. Record the delivery volume (DV) and use the value to calculate the results. Regulate the vacuum so that the pipet fills in ≈ 12 s. Record temperature (T$_1$) of blank. Mount the pipet on an adjustable pipet rack (Shaw, 1932). Stir the silt and clay suspension with mechanical stirrer for 6 min or for 8 min, if suspension has stood more than 24 h. (Kilmer and Mullins, 1954). Place pipe insulation on sample and blank cylinders to prevent rapid changes in temperatures. Place the cylinder on a stable, vibrationless table and stir with a hand stirrer in an up-and-down motion for 30 s. Timing is started upon completion of the stirring. Record the time when stirring is stopped. For the <20-μm fraction, slowly lower the closed pipet to a 10-cm depth in suspension, turn on the vacuum, open the pipet, and withdraw an aliquot at the

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
AIR-DRY SAMPLES (3A1)
DISPERSION USING ULTRASONIC PROBE (3A1h)

calculated time (Table 1). Dispense the aliquot into a tared and numbered, 90-mL weighing bottle. Rinse the pipet with distilled water and dispense into the tared, weighing bottle with aliquot. For the <2-μm fraction, pipet after a time of 4.5, 5, 5.5, or 6.5 h. Record temperature (T_2) of blank. Use the average of T_1 and T_2 and adjust the pipet depth in the suspension as indicated in Table 2. Repeat the procedure described for the <20-μm fraction. If determination of carbonate clay is required, use weighing bottle with screw threads.

7.12 Place the aliquots and weighing bottles in an oven. Dry the aliquots at 105°C overnight and cool to ambient temperature in a desiccator that contains P_2O_5 or an equivalent desiccant.

7.13 Record the weight of the residue (RW) to the nearest 0.1 mg.

7.14 Use the 90-mL, round-bottomed, weighing bottles for the <20-μm aliquots. Wash and tare after every fourth use. Use the 90-mL, square-bottomed, weighing bottles for the <2-μm aliquots. Wash and tare after every use.

7.15 If fine clay analyses are requested, use the remaining suspension and follow procedure 3A1b. If necessary, save the sediment for optical mineralogy.

7.16 If optical mineralogy is requested, decant the suspension and transfer the sediment to a 400-mL beaker. Fill the beaker to a 5.5-cm height. Stir the sediment and allow to settle for 5 min. Discard the supernatant. Refill the beaker to 5.5-cm height. Stir again, allow to settle for 3 min, and then decant. Repeat the filling and the stirring; allow to settle for 2 min; and then decant until top half of suspension is clear. Transfer the sediment, which is dominantly 20 to 50 μm, to a labelled, drying dish. Wash with ethanol, air-dry, and save in the drying dish for optical mineralogy.

8. CALCULATIONS

8.1 Clay % = 100 x ((RW_2 - DW) x (CF/TW))

where:
RW_2 = residue weight (g), <2-μm fraction
DW   = dispersing agent weight (g) = (0.4408/CF)
CF   = 1000 mL/DV
DV   = dispensed pipet volume
TW   = total weight (g), H_2O_2-treated, oven-dry sample

8.2 Fine Silt % = 100 x ((RW_{20}-DW) x (CF/TW)) - Clay %

where:
RW_{20} = residue weight (g) of <20-μm fraction

8.3 Sand % = Σ (SW/TW) x 100

where:
i = 1.0, 0.5, 0.25, 0.1, and 0.047-mm sand fractions

8.4 Coarse silt % = 100 - (Clay + Fine Silt + Sand %)

9. REPORT

Report percentages of each particle size and specify procedure 3A1h.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods 2nd ed. Agronomy 9:383-411.

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PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)

1. APPLICATION

Particle-size analysis (PSA) is one of the most requested analysis in soil characterization because soil texture and the particle-size distribution can be related to many other soil properties. Particle-size distribution is also used as a tool to help explain soil genesis and to quantify soil classification. The Kilmer and Alexander (1949) pipet method was chosen by the Soil Conservation Service because it is reproducible in a wide range of soils.

2. SUMMARY OF METHOD

Two 10-g samples of <2-mm, moist soil are pretreated to remove organic matter and soluble salts. One sample is dried in the oven to obtain the oven-dry weight. The other sample is dispersed with a sodium hexametaphosphate solution, and mechanically shaken. The sand fraction is removed from the suspension by wet sieving and then fractionated by dry sieving. The clay and fine silt fractions are determined using the suspension remaining from the wet sieving process. This suspension is diluted to 1 L in a sedimentation cylinder, stirred, and 25-mL aliquots removed with a pipet at calculated, predetermined intervals based on Stokes' law (Kilmer and Alexander, 1949). The aliquots are dried at 105°C and weighed. Coarse silt is the difference between 100% and the sum of the sand, clay, and fine silt percentages.

3. INTERFERENCES

The sedimentation equation that is used to measure the settling rates of particles of different sizes is as follows:

$$\nu = 2r^2 g(\rho_s - \rho_l)/(9\eta)$$

where:

ν = velocity of fall
r = particle radius
g = acceleration due to gravity
ρ_s = particle density
ρ_l = liquid density
η = fluid viscosity

This formula results from an application of Stokes'law and is referred to as Stokes' law. Assumptions used in applying Stokes' law to soil sedimentation measurements are as follows:

1. Terminal velocity is attained as soon as settling begins.

2. Settling and resistance are entirely due to the viscosity of the fluid.

3. Particles are smooth and spherical.

4. There is no interaction between individual particles in the solution (Gee and Bauder, 1986).

Since soil particles are not smooth and spherical, the radius of the particle is considered an equivalent rather than an actual radius. In this method, particle density is assumed to be 2.65 g cc^{-1}.

The PSA results are dependent on the pretreatments used to disperse the soil. The presence of cementing agents such as calcium carbonate, Fe, and Si often prevent complete dispersion. Chemical pretreatments to remove cementing agents can be requested by project coordinators. Coded

procedures are removal of carbonates with 1 N NaOAc buffered at pH 5 (3A1e); removal of Fe with a sodium dithionite-citrate solution (3A1f); and removal of Si with 0.1 N NaOH (3A1g).

Gypsum interferes with PSA by causing flocculation of particles. Gypsum is removed by stirring and washing the soil with distilled water. This procedure is effective if the soil contains <25% gypsum.

Partial flocculation may occur in some soils if excess H_2O_2 is not removed from the soil after its use in organic matter oxidation.

Treatment of micaceous soils with H_2O_2 causes exfoliation of the mica plates and a matting of particles when dried in the oven. Since exfoliation occurs in these soils, a true measurement of fractions is uncertain (Drosdoff and Miles, 1938).

Soils that irreversibly harden when dried are difficult to disperse. The PSA for these soils can be determined on moist samples (procedure 3A2) upon the request of project coordinator.

4. SAFETY

Use rubber gloves and a face shield when handling acid and H_2O_2. Mix acids in ventilated fume hoods. Heat samples for removal of organic matter or cementing agents in ventilation hoods. Handle heated samples with leather gloves. Never add water to dry phosphorous pentoxide.

5. EQUIPMENT
5.1 Fleakers, 300 mL, tared to 1 mg
5.2 Ceramic filter candles, .3μm absolute retention
5.3 Rack to hold ceramic filter candle and sample container.
5.4 Mechanical shaker, horizontal, 120 oscillations min^{-1}
5.5 Cylinders, 1 L, white line fused onto glass at 1-L mark
5.6 Oven, 105°C
5.7 Hot plate, 100°C
5.8 Vacuum, 0.8 bars (80kPa)
5.9 Thermometer, 0 to 100°C
5.10 Desiccator
5.11 Motor driven stirrer, (Kilmer and Mullins, 1954)
5.12 Hand stirrer, perforated disk fastened to a rod
5.13 Adjustable pipet rack (Shaw, 1932)
5.14 Lowy pipets, 25 mL, with overflow bulb
5.15 Polyurethane foam, pipe insulation that fits snugly around
cylinder.
5.16 Sieve shaker with 12.7-mm (1/2 in) vertical and lateral movement at 500 oscillations min^{-1}.
Accommodates a nest of 76-mm (3 in) sieves.
5.17 Weighing bottles, 90 mL, with screw caps, tared to 1 mg
5.18 Weighing bottles, 90 mL, tared to 1 mg
5.19 Timer or clock with second hand
5.20 Electronic balance, ±0.1-mg sensitivity
5.21 Electronic balance, ±1-mg sensitivity
5.22 Watch glass, 50- and 65-mm diameters
5.23 Evaporating dish, porcelain, 160-mm diameter, 31-mm height, with lip
5.24 Set of 76-mm (3 in) sieves, square weave phosphor bronze wire cloth except 300 mesh which is twilled weave. U.S. series and Tyler Screen Scale equivalent designations are as follows:

Sand Size	Opening (mm)	U.S. No.	Tyler Mesh Size
VCS	1.0	18	16
CS	0.5	35	32
MS	0.25	60	60
FS	0.105	140	150
VFS	0.047	300	300

6. REAGENTS

6.1 Distilled water

6.2 Hydrogen peroxide (H_2O_2), 30 to 35%

6.3 Sodium hexametaphosphate (($NaPO_3)_6$), reagent grade

6.4 Sodium carbonate (Na_2CO_3), reagent grade

6.5 Sodium hexametaphosphate solution. Dissolve 35.7 g of ($NaPO_3)_6$ and 7.94 g of Na_2CO_3 in 1 L of distilled water.

6.6 Ethyl alcohol

6.7 Phosphorous pentoxide (P_2O_5), calcium sulfate (anhydrous), or equivalent desiccant

7. PROCEDURE

7.1 Weigh two 10-g samples of <2-mm, moist soil to nearest mg on an electronic balance and place into numbered, tared, 300-mL, tared fleakers. Wash and tare these fleakers once every two months.

7.2 Add ≈ 50 mL of distilled water and 5 mL of H_2O_2 to both soil subsamples at ambient temperature. Cover the soil samples with a 50-mm watch glass. Allow initial oxidation of organic matter to complete and then place sample on hot plate. If the froth from the reaction exceeds the capacity of the fleaker, transfer the sample to a larger beaker.

7.3 Place the samples on the hot plate and heat to 90°C. Add 5-mL increments of H_2O_2 at 30-min intervals until the oxidation has completed or until 30 mL of H_2O_2 have been added. Heat the samples for an additional 45 min to decompose excess H_2O_2. If the reaction is violent, add small increments of ethyl alcohol to the samples or remove the samples from the hot plate to slow the reaction or transfer samples to 1000-mL beakers. Record any unusual sample reactions.

7.4 Place the samples on a filter rack. Add 150 mL of distilled water. Insert a filter candle, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Wash the samples four additional times with ≈ 150 mL of distilled water. If the samples contain gypsum and flocculates, then the following additional washings may be used. If the samples contain 1 to 5% gypsum, stir the samples with a magnetic stirrer for 5 min and wash 5 times with ≈ 250 mL of distilled water each time. If the samples contain >5% gypsum, stir the samples with a magnetic stirrer for 5 min then wash 5 times with ≈ 750 mL of distilled water each time to remove soluble gypsum.

7.5 Place one of the samples in the oven and dry overnight at 105°C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.6 Record the total weight (TW) of the H_2O_2-treated, oven-dry sample to the nearest mg. The H_2O_2-treated, oven-dry sample is not used in the remaining PSA procedural steps. Use the H_2O_2-treated sample that was not dried in oven for all of the following PSA procedural steps.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)

7.7 Add 10 mL of sodium hexametaphosphate solution, equivalent to 0.4408 g of sodium hexametaphosphate, to each sample. Subtract the weight of the sodium hexametaphosphate (D) that is contained in the extracted aliquot from the silt and clay weights in the calculation of silt and clay percentages. Determine the exact volume of sodium hexametaphosphate to add to each sample by regressing the volume of sodium hexametaphosphate against the dry residue weight of sodium hexametaphosphate and then by predicting the volume needed to dispense 0.4408 g of sodium hexametaphosphate into each sample. Let stand until sample is completely moistened by sodium hexametaphosphate. Add ≈ 175 mL of distilled water.

7.8 Place the sample in a horizontal shaker set at 120 oscillations min^{-1} and shake for 15 h (overnight).

7.9 Remove the sample from the shaker and pour through a 300-mesh (0.047-mm) sieve mounted on a ring stand. Place a funnel below the sieve and a 1-L cylinder below the funnel. Collect the silt and clay in the 1-L cylinder. Avoid using jets of water in washing the sample. Wash and rub all particles from the fleaker into the sieve. Continue to wash until the suspension volume in the cylinder is ≈ 800 mL. Sand and some of the coarse silt remain on the sieve. Rinse all <20-μm particles into the cylinder. Fill the cylinder to 1 L and cover with a 65-mm watch glass. Prepare a distilled water blank to measure temperature fluctuations. Allow the cylinder to stand overnight to equilibrate the suspension with the room temperature. Wash the sand into an evaporation dish and dry the sand at 105°C overnight.

7.10 Transfer the dried sand to a nest of sieves that has a top-to-bottom order of 1.0, 0.5, 0.25, 0.1, and 0.047 mm. Shake the sand for 3 min on a shaker that has 1.3-cm vertical and lateral movements and oscillates at 500 strokes min^{-1}. Record the weight of each separate sand fraction (SW$_i$) to the nearest mg. If optical analysis is requested, place the very fine sand and fine sand fractions in gelatin capsules and the remaining sand fractions in a labelled vial. Store capsules in the labelled vial. Wash sand dishes after every use.

7.11 Determine the percentage of fine silt and clay gravimetrically by removing an aliquot from the suspension in the 1-L cylinder with a Lowy, 25-mL pipet. Periodically, gravimetrically calibrate the delivery volume of the pipet by weighing the amount of distilled water dispensed from the pipet. Record the delivery volume (DV) and use the value to calculate the results. Regulate the vacuum such that the pipet fills in ≈ 12 s. Record temperature (T$_1$) of blank. Mount the pipet on an adjustable pipet rack (Shaw, 1932). Stir the silt and clay suspension with mechanical stirrer for 6 min or for 8 min, if the suspension has stood for >24 h (Kilmer and Mullins, 1954). Place pipe insulation around sample and blank cylinders to prevent rapid changes in temperatures. Place the cylinder on a stable, vibrationless table and stir with a hand stirrer in an up-and-down motion for 30 s. Timing is started upon completion of the stirring. Record the time that stirring is stopped. For the <20-μm fraction, slowly lower the closed pipet to a 10-cm depth in the suspension, turn on the vacuum, open the pipet, and withdraw an aliquot at the calculated time (Table 1). Dispense the aliquot into a tared and numbered, 90-mL weighing bottle. Rinse the pipet twice with distilled water and dispense into the tared, weighing bottle with the aliquot. For the <2-μm fraction, pipet after a time of 4.5, 5, 5.5, or 6.5 h. Record temperature (T$_2$) of blank. Use the average of T$_1$ and T$_2$ and adjust the pipet depth in the suspension as indicated in Table 2. Repeat the procedure described for the <20-μm fraction. If determination of carbonate is required, use weighing bottle with screw threads. Dry the aliquots at 105°C overnight and cool in a desiccator that contains P$_2$O$_5$ or an equivalent desiccant. Record the weight of the residue (RW) to the nearest 0.1 mg.

7.12 Use the 90-mL, round-bottomed, weighing bottles for the <20-μm aliquots. Wash and tare after every fourth use. Use the 90-mL, square-bottomed, weighing bottles for the <2-μm aliquots. Wash and tare after every use.

7.13 If fine clay analyses are requested, use the remaining suspension and follow procedure 3A1b. If necessary, save the sediment for optical mineralogy.

7.14 If optical mineralogy is requested, decant the suspension and transfer the sediment to a 400-mL beaker. Fill the beaker to a 5.5-cm height. Stir the sediment and allow to settle for 5 min. Discard the supernatant. Refill the beaker to 5.5-cm height. Stir again, allow to settle for 3 min, and then decant. Repeat the filling and the stirring; allow to settle for 2 min; and then decant until top half of suspension is clear. Transfer the sediment, which is dominantly 20 to 50 μm, to a labelled drying dish. Wash with ethanol, air-dry, and save in the drying dish for optical mineralogy.

8. CALCULATIONS

8.1 Clay % = 100 x ((RW_2 - DW) x (CF/TW))

where:
RW_2 = residue weight (g), <2-μm fraction
DW = dispersing agent weight (g) = (0.4408/CF)
CF = 1000 mL/DV
DV = dispensed pipet volume
TW = total weight (g), H_2O_2-treated, oven-dry sample

8.2 Fine Silt % = 100 x ((RW_{20}-DW) x (CF/TW)) - Clay %

where:
RW_{20} = residue weight (g) of <20-μm fraction

8.3 Sand % = $\sum$ (SW/TW) x 100

where:
i = 1.0, 0.5, 0.25, 0.1, and 0.047-mm sand fractions

8.4 Coarse silt % = 100 - (Clay + Fine Silt + Sand %)

9. REPORT
Report percentages of each particle size.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is included in every batch of 24 samples for PSA determinations. The C.V for the sand, silt, and clay fractions of the quality control check sample are 13, 3, and 3% respectively.

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PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)

Kilmer, V.J., and J.F. Mullins. 1954. Improved stirring and pipetting apparatus for mechanical analysis of soils. Soil Sci. 77:437-441.

Shaw, T.M. 1932. New aliquot and filter devices for analytical laboratories. Ind. Eng. Chem. Anal. Ed. 4:409.

Table 1. Sampling times at 10-cm sampling depth, 0.4408 g L^{-1} NaHMP solution, and 2.65 g cc^{-1} particle density.[1]

Temp (°C)	20 μm		5 μm	
	min	s	min	s
18.00	4	53	78	10
19.00	4	45	76	7
20.00	4	38	74	13
20.25	4	36	73	46
20.50	4	34	73	19
20.75	4	33	72	52
21.00	4	31	72	26
21.25	4	30	72	0
21.50	4	28	71	34
21.75	4	26	71	8
22.00	4	25	70	43
22.25	4	23	70	18
22.50	4	22	69	53
22.75	4	20	69	28
23.00	4	19	69	4
23.25	4	17	68	39
23.50	4	15	68	15
23.75	4	14	67	52
24.00	4	13	67	28
24.25	4	11	67	5
24.50	4	10	66	41
24.75	4	8	66	18
25.00	4	7	65	56
25.25	4	5	65	33
25.50	4	4	65	11
25.75	4	3	64	49
26.00	4	1	64	27
26.25	4	0	64	5
26.50	3	59	63	43
26.75	3	57	63	22
27.00	3	56	63	1
27.25	3	55	62	40
27.50	3	53	62	19
27.75	3	52	61	59
28.00	3	51	61	38
28.25	3	49	61	18
28.50	3	48	60	58
28.75	3	47	60	38
29.00	3	46	60	18
29.25	3	44	59	59
29.50	3	43	59	39
29.75	3	42	59	20
30.00	3	41	59	1

[1]Use this table with procedures 3A1, 3A2, 3A1h, and 3A2h.

Table 2. Sampling depths (cm) for 2-µm clay, 0.4408 g L^{-1}
NaHMP solution, and 2.65 g cc^{-1} particle density.[1]

Temp (°C)	Time (h)				
	4.5	5.0	5.5	6.0	6.5
18.00	5.53	6.14	6.75	7.37	7.98
19.00	5.67	6.31	6.94	7.57	8.20
20.00	5.82	6.47	7.11	7.76	8.41
20.25	5.86	6.51	7.16	7.81	8.46
20.50	5.89	6.55	7.20	7.86	8.51
20.75	5.93	6.59	7.24	7.90	8.56
21.00	5.96	6.63	7.29	7.95	8.61
21.25	6.00	6.67	7.33	8.00	8.67
21.50	6.04	6.71	7.38	8.05	8.72
21.75	6.07	6.75	7.42	8.10	8.77
22.00	6.11	6.79	7.47	8.14	8.82
22.25	6.14	6.83	7.51	8.19	8.88
22.50	6.18	6.87	7.55	8.24	8.93
22.75	6.22	6.91	7.60	8.29	8.98
23.00	6.25	6.95	7.64	8.34	9.03
23.25	6.29	6.99	7.69	8.39	9.09
23.50	6.33	7.03	7.73	8.44	9.14
23.75	6.37	7.07	7.78	8.49	9.19
24.00	6.40	7.11	7.83	8.54	9.25
24.25	6.44	7.16	7.87	8.59	9.30
24.50	6.48	7.20	7.92	8.64	9.36
24.75	6.51	7.24	7.96	8.69	9.41
25.00	6.55	7.28	8.01	8.74	9.46
25.25	6.59	7.32	8.05	8.79	9.52
25.50	6.63	7.36	8.10	8.84	9.57
25.75	6.66	7.41	8.15	8.89	9.63
26.00	6.70	7.45	8.19	8.94	9.68
26.25	6.74	7.49	8.24	8.99	9.74
26.50	6.78	7.53	8.28	9.04	9.79
26.75	6.82	7.57	8.33	9.09	9.85
27.00	6.85	7.62	8.38	9.14	9.90
27.25	6.89	7.66	8.42	9.19	9.96
27.50	6.93	7.70	8.47	9.24	10.01
27.75	6.97	7.74	8.52	9.29	10.07
28.00	7.01	7.79	8.57	9.34	10.12
28.25	7.05	7.83	8.61	9.40	10.18
28.50	7.09	7.87	8.66	9.45	10.23
28.75	7.12	7.92	8.71	9.50	10.29
29.00	7.16	7.96	8.75	9.55	10.35
29.25	7.20	8.00	8.80	9.60	10.40
29.50	7.24	8.05	8.85	9.65	10.46
29.75	7.28	8.09	8.90	9.71	10.52
30.00	7.32	8.13	8.95	9.76	10.57

[1]Use this table with procedures 3A1, 3A2, 3A1h, and 3A2h.

PARTICLE-SIZE ANALYSIS
PARTICLES <2mm (pipet method) (3A)
MOIST SAMPLES (3A2)
FINE CLAY (<0.2 μm) (3A2b)

1. APPLICATION

The fine clay fraction is mineral soil particles with an effective diameter of <0.2 μm. The percentage fine clay is determined for soils that are suspected of having illuviated clay. Fine clay data can be used to determine the presence of argillic horizons or as a tool to help explain soil genesis.

2. SUMMARY OF METHOD

A soil suspension from the moist PSA procedure (3A2) is stirred, poured into a centrifuge bottle, and centrifuged at 1500 rpm. A 25-mL aliquot is withdrawn with a pipet. The aliquot is dried in the oven, weighed, and the percentage of fine clay is calculated based on the total sample weight. The time of centrifugation is determined from the following equation modified from Stokes' law (Jackson, 1969).

$$t_m = (63.0 \times 10^8 \eta \ \log \ (rs^{-1})) \ (N_m^2 \ D\mu^2 \ \Delta\rho)^{-1}$$

where:
t_m = time in minutes
η = viscosity in poises
r = radius in cm from center of rotation to sampling depth (3 cm + s)
s = radius in cm from center of rotation to surface of suspension
N_m = rpm (1500)
$D\mu$ = particle diameter in microns (0.2 μm)
$\Delta\rho$ = difference in specific gravity between solvated particles and suspension liquid

3. INTERFERENCES

Assumptions used in applying Stokes' law to soil sedimentation measurements are as follows:

1. Terminal velocity is attained as soon as settling begins.

2. Settling and resistance are entirely due to the viscosity of the fluid.

3. Particles are smooth and spherical.

4. There is no interaction between individual particles in the solution (Gee and Bauder, 1986).

The distance from the center of rotation to the surface of the suspension must be constant for each centrifuge bottle. The particle density of the fine clay is assumed to be 2.5 g cc^{-1}. The suspension temperature must be used to enter the correct liquid viscosity in the equation. Position the bottle under pipet without sudden movement of the centrifuge rotor which causes disturbance of solution. The withdrawal rate with pipet should be constant.

4. SAFETY

Users should be familiar with centrifuge operation. Opposite centrifuge bottles need to be balanced. Centrifuge should not be opened until centrifuge rotor has completely stopped.

5. EQUIPMENT
5.1 Motor driven stirrer, (Kilmer and Mullins, 1954)
5.2 Hand stirrer, perforated disk fastened to a rod
5.3 Centrifuge, International No. 11, with No. 949 rotor head, International Equip. Co., Boston, MA

5.4 Centrifuge bottle, 500 mL
5.5 Lowy pipet, 25 mL, with overflow bulb
5.6 Adjustable pipet rack (Shaw, 1932)
5.7 Weighing bottles, 90 mL, tared to 0.1 mg
5.8 Electronic balance, ±0.1-mg sensitivity
5.9 Torsion balance
5.10 Timer or clock with second hand
5.11 Thermometer, 0 to 100°C
5.12 Oven, 105°C

6. REAGENTS
     None

7. PROCEDURE

7.1 After the completion of procedure 3A2, stir the silt and clay suspension with mechanical stirrer for 5 min. Remove sample from mechanical stirrer and place on table. Stir with the hand stirrer in an up-and-down motion for 30 s and allow the suspension to settle for 15 min.

7.2 Pour the suspension into a centrifuge bottle and fill to the line marked on the bottle. The line on each bottle is 13 cm which is the distance from the center of rotation to the surface of the suspension. Stopper and shake well to mix the suspension.

7.3 Balance opposite centrifuge loads, which consist of centrifuge bottle, trunnion carrier and bucket. Place loads on a torsion balance and add water to the lighter bucket until both loads weigh the same.

7.4 Read the temperature of the suspension.

7.5 Centrifuge at 1500 rpm. Vary the centrifuge time according to the temperature as follows:

Temp (°C)	Viscosity η	Density $\Delta\rho$	Time Min
19	0.01047	1.499	38.7
20	0.01021	1.499	37.7
21	0.00997	1.499	36.8
22	0.00973	1.499	36.0
23	0.00950	1.500	35.1
24	0.00928	1.500	34.3
25	0.00907	1.500	33.5
26	0.00887	1.500	32.8
27	0.00868	1.501	32.0
28	0.00848	1.501	31.3
29	0.00830	1.501	30.7
30	0.00812	1.502	30.0

PARTICLE-SIZE ANALYSIS
PARTICLES <2mm (pipet method) (3A)
MOIST SAMPLES (3A2)
FINE CLAY (<0.2 μm) (3A2b)

where:

s   = 15 cm

r   = 18 cm

N_m = 1500 rpm

7.6 After centrifuging, lower the pipet to a 3-cm depth in the suspension. Withdraw a 25-mL aliquot at a rate of $\approx$ 12 s. Avoid turbulence. Transfer the aliquot to a weighing bottle.

7.7 Place weighing bottle with aliquot in oven. Dry overnight at 105°C. Remove sample from oven, place in desiccator with P_2O_5 or equivalent desiccant, and cool to ambient temperature.

7.8 Weigh residue weight (RW) to nearest 0.1 mg.

7.9 Use the 90-mL, round-bottomed, weighing bottles for the <0.2μm aliquots. Wash and tare after every fourth use.

8. CALCULATIONS

Fine Clay (%) = 100 x ((RW-DW) x (CF/TW))

where:

RW   = residue weight (g) of <0.2 μm fraction

DW   = dispersing agent weight (g) = (0.4364/CF)

CF   = 1000 mL/DV

DV   = dispensed pipet volume

TW   = total weight of H_2O_2-treated, oven-dry sample (procedure 3A2)

9. REPORT
Report the percentage of fine clay.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is included in every batch of 24 samples for PSA determination. The fine clay of the quality control check sample is determined only when fine clay analysis is requested. The C.V. for the fine clay fraction is 21%.

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PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)
WATER DISPERSIBLE CLAY (3A2c)

1. APPLICATION

Water dispersible clay provides a means of evaluating the susceptibility of a soil to water erosion. The degree to which a soil disperses without the oxidation of organic matter or the removal of soluble salts, or the addition of a chemical dispersant may be compared with results from chemical dispersion (Bouyoucos, 1929).

2. SUMMARY OF METHOD

A 10-g sample of <2-mm, moist soil is mechanically shaken overnight in distilled water. The sand fraction is removed from the suspension by wet sieving and then fractionated by dry sieving. The clay and fine silt fractions are determined using the solution remaining from the wet sieving process. This solution is diluted to 1 L in a sedimentation cylinder, stirred, and 25-mL aliquots removed with a pipet at calculated, predetermined intervals based on Stokes' law (Kilmer and Alexander, 1949). The aliquots are dried at 105°C and weighed. Coarse silt is the difference between 100% and the sum of the sand, clay, and fine silt percentages.

3. INTERFERENCES

Assumptions used in applying Stokes' law to soil sedimentation measurements are as follows:

1. Terminal velocity is attained as soon as settling begins.

2. Settling and resistance are entirely due to the viscosity of the fluid.

3. Particles are smooth and spherical.

4. There is no interaction between individual particles in the solution (Gee and Bauder, 1986).

Since soil particles are not smooth and spherical, the radius of the particle is considered an equivalent rather than an actual radius. In this method, particle density is assumed to be 2.65 g cc^{-1}.

Hydrophobic soils may not completely saturate when water is added to the soil. When the soils are hydrophobic, a few mL of ethyl alcohol are added to wet the sample, and the procedure is continued. The addition of ethyl alcohol to reduce surface tension is assumed to have no effect on mineral structure.

4. SAFETY

No special precautions are specified.

5. EQUIPMENT

5.1 Fleakers, 300 mL, tared to 1 mg
5.2 Mechanical shaker, horizontal, 120 oscillations min^{-1}
5.3 Cylinders, 1 L, white line fused onto glass at 1-L mark
5.4 Oven, 105°C
5.5 Desiccator
5.6 Thermometer, 0 to 100°C
5.7 Motor driven stirrer, (Kilmer and Mullins, 1954)
5.8 Hand stirrer, perforated disk fastened to a rod
5.9 Adjustable pipet rack (Shaw, 1932)
5.10 Lowy pipets, 25 mL, with overflow bulb
5.11 Polyurethane foam, pipe insulation that fits snugly around cylinder.
5.12 Sieve shaker with 12.7-mm (1/2 in) vertical and lateral movement at 500 oscillations min^{-1}.
    Accommodates a nest of 76-mm (3 in) sieves.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)
WATER DISPERSIBLE CLAY (3A2c)

5.13 Weighing bottles, 90 mL, with screw caps, tared to 1 mg
5.14 Weighing bottles, 90 mL, tared to 1 mg
5.15 Timer or clock with second hand
5.16 Electronic balance, ±0.1-mg sensitivity
5.17 Electronic balance, ±1-mg sensitivity
5.18 Watch glass, 50- and 65-mm diameters
5.19 Evaporating dish, porcelain, 160-mm diameter, 31-mm height, with lip
5.20 Set of 76-mm (3 in) sieves, square weave phosphor bronze wire cloth except 300 mesh which is
    twilled weave. U.S. series and Tyler Screen Scale equivalent designations are as follows:

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Sand      Opening     U.S.     Tyler
Size       (mm)       No.      Mesh
                               Size


VCS        1.0         18        16
CS         0.5         35        32
MS         0.25        60        60
FS         0.105      140       150
VFS        0.047      300       300
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6. REAGENTS
6.1 Distilled water
6.2 Ethyl alcohol

7. PROCEDURE

7.1 Weigh two 10-g samples of <2-mm, moist soil to nearest mg on an electronic balance and place into numbered, tared, 300-mL, tared fleakers. Wash and tare these fleakers once every two months.

7.2 Dry one sample in an oven at 105°C overnight. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.3 Record the total weight (TW) of the sample to the nearest mg. The oven-dry sample is not used in the remaining PSA procedural steps. Use the sample that was not dried in the oven for all the following PSA procedural steps.

7.4 Add ≈ 175 mL of distilled water to sample that was not dried in the oven. Place sample in an horizontal shaker set at 120 oscillations min^{-1} and shake for 15 h (overnight).

7.5 Remove the sample from the shaker and pour through a 300-mesh (0.047-mm) sieve mounted on a ring stand. Place a funnel below the sieve and a 1-L cylinder below the funnel. Collect the silt and clay in the 1-L cylinder. Avoid using jets of water in washing the sample. Wash and rub all particles from the fleaker into the sieve. Continue to wash until the suspension volume in the cylinder is ≈ 800 mL. Sand and some of the coarse silt remain on the sieve. Rinseall <20-μm particles into the cylinder. Fill the cylinder to 1 L and cover with a 65-mm watch glass. Prepare a distilled water blank to measure temperature fluctuations. Allow the cylinder to stand overnight to equilibrate the suspension with the room temperature. Wash the sand into an evaporation dish and dry the sand at 105°C overnight.

7.6 Transfer the dried sand to a nest of sieves that has a top-to-bottom order of 1.0, 0.5, 0.25, 0.1, and 0.047 mm. Shake the sand for 3 min on a shaker that has 1.3-cm vertical and lateral movements and

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
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oscillates at 500 strokes min^{-1}. Record the weight of each separate sand fraction (SW$_i$) to the nearest mg. If optical analysis is requested, place the very fine sand and fine sand fractions in gelatin capsules and the remaining sand fractions in a labelled vial. Store capsules in the labelled vial. Wash sand dishes after every use.

7.7 Determine the percentage of fine silt and clay gravimetricallyby removing an aliquot from the suspension in the 1-L cylinder with a Lowy, 25-mL pipet. Periodically, gravimetrically calibrate the delivery volume of the pipet by weighing the amount of distilled water dispensed from the pipet. Record the delivery volume (DV) and use the value to calculate the results. Regulate the vacuum such that the pipet fills in ≈ 12 s. Record temperature (T$_1$) of blank. Mount the pipet on an adjustable pipet rack (Shaw, 1932). Stir the silt and clay suspension with mechanical stirrer for 6 min or for 8 min, if the suspension has stood for >24 h (Kilmer and Mullins, 1954). Place pipe insulation around sample and blank cylinders to prevent rapid changes in temperatures. Place the cylinder on a stable, vibrationless table and stir with a hand stirrer in an up-and-down motion for 30 s. Timing is started upon completion of the stirring. Record the time that stirring is stopped. For the <20-μm fraction, slowly lower the closed pipet to a 10-cm depth in the suspension, turn on the vacuum, open the pipet, and withdraw an aliquot at the calculated time (Table 1). Place the aliquot into a tared and numbered, 90-mL weighing bottle. Rinse the pipet with distilled water into the tared, weighing bottle. For the <2-μm fraction, pipet after a time of 4.5, 5, 5.5, or 6.5 h. Record the temperature (T$_2$) of blank. Use the average of T$_1$ and T$_2$ and adjust the pipet depth in the suspension as indicated in Table 2. Repeat the procedure described for the <20-μm fraction.

7.8 Dry the aliquots at 105°C overnight and cool in a desiccator that contains phosphorous pentoxide (P$_2$O$_5$) or an equivalent desiccant.

7.9 Record the residue weight (RW) to the nearest 0.1 mg.

7.10 Use the 90-mL, round-bottomed, weighing bottles for the <20-μm aliquots. Wash and tare after every fourth use. Use the 90-mL, square-bottomed, weighing bottles for the <2-μm aliquots. Wash and tare after every use.

7.11 In fine clay analyses are requested, use the remaining suspension and follow procedure 3A2b. If necessary, save the sediment for optical mineralogy.

7.12 If optical mineralogy is requested, decant the suspension and transfer the sediment to a 400-mL beaker. Fill the beaker to a 5.5-cm height. Stir the sediment and allow to settle for 5 min. Discard the supernatant. Refill the beaker to 5.5-cm height. Stir again, allow to settle for 3 min, and then decant. Repeat the filling and the stirring; allow to settle for 2 min; and then decant until top half of suspension is clear. Transfer the sediment, which is dominantly 20 to 50 μm, to a labelled drying dish. Wash with ethanol, air-dry, and save in the drying dish for optical mineralogy.

8. CALCULATIONS

8.1 Clay % = 100 x ((RW$_2$ x CF)/TW)

where:
RW$_2$ = residue weight (g), <2-μm fraction
CF   = 1000 mL/DV
DV   = dispensed pipet volume
TW   = total weight (g), H$_2$O$_2$-treated, oven-dry sample

8.2 Fine Silt % = (100 x (RW$_{20}$ x CF)/TW)) - Clay %

where:
RW$_{20}$ = residue weight (g) of <20-μm fraction

8.3 Sand % = $\sum$ (SW$_i$/TW) x 100

where:
i = 1.0, 0.5, 0.25, 0.1, and 0.047-mm sand fractions

8.4 Coarse silt % = 100 - (Clay + Fine Silt + Sand %)

9. REPORT

Report percentages of each particle size and specify procedure 3A2c..

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

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Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:383-411.
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analysis of soils. Soil Sci. 77:437-441.
Shaw, T. M. 1932. New aliquot and filter devices for analytical laboratories. Ind. Eng. Chem. Anal.
Ed. 4:409.

Table 1. Sampling times at 10-cm sampling depths and 2.65 g cc^{-1} particle density.[1]

Temp (°C)	20 µm		5 µm	
	min	s	min	s
18.00	4	52	78	0
19.00	4	45	76	7
20.00	4	38	74	13
20.25	4	36	73	46
20.50	4	34	73	19
20.75	4	33	72	52
21.00	4	31	72	26
21.25	4	30	72	0
21.50	4	28	71	34
21.75	4	26	71	8
22.00	4	25	70	43
22.25	4	23	70	18
22.50	4	22	69	53
22.75	4	20	69	28
23.00	4	19	69	4
23.25	4	17	68	39
23.50	4	15	68	15
23.75	4	14	67	52
24.00	4	13	67	28
24.25	4	11	67	5
24.50	4	10	66	41
24.75	4	8	66	18
25.00	4	7	65	56
25.25	4	5	65	33
25.50	4	4	65	11
25.75	4	3	64	49
26.00	4	1	64	27
26.25	4	0	64	5
26.50	3	59	63	43
26.75	3	57	63	22
27.00	3	56	63	1
27.25	3	55	62	40
27.50	3	53	62	19
27.75	3	52	61	59
28.00	3	51	61	38
28.25	3	49	61	18
28.50	3	48	60	58
28.75	3	47	60	38
29.00	3	46	60	18
29.25	3	44	59	59
29.50	3	43	59	39
29.75	3	42	59	20
30.00	3	41	59	1

[1]Use this table with procedures 3A1c and 3A2c.

Table 2. Sampling depths (cm) for 2-µm clay and 2.65 g cc^{-1} particle density.[1]

Temp (°C)	Time (h)				
	4.5	5.0	5.5	6.0	6.5
18.00	5.54	6.15	6.77	7.38	8.00
19.00	5.67	6.31	6.94	7.57	8.20
20.00	5.82	6.47	7.11	7.76	8.41
20.25	5.86	6.51	7.16	7.81	8.46
20.50	5.89	6.55	7.20	7.86	8.51
20.75	5.93	6.59	7.24	7.90	8.56
21.00	5.96	6.63	7.29	7.95	8.61
21.25	6.00	6.67	7.33	8.00	8.67
21.50	6.04	6.71	7.38	8.05	8.72
21.75	6.07	6.75	7.42	8.10	8.77
22.00	6.11	6.79	7.47	8.14	8.82
22.25	6.14	6.83	7.51	8.19	8.88
22.50	6.18	6.87	7.55	8.24	8.93
22.75	6.22	6.91	7.60	8.29	8.98
23.00	6.25	6.95	7.64	8.34	9.03
23.25	6.29	6.99	7.69	8.39	9.09
23.50	6.33	7.03	7.73	8.44	9.14
23.75	6.37	7.07	7.78	8.49	9.19
24.00	6.40	7.11	7.83	8.54	9.25
24.25	6.44	7.16	7.87	8.59	9.30
24.50	6.48	7.20	7.92	8.64	9.36
24.75	6.51	7.24	7.96	8.69	9.41
25.00	6.55	7.28	8.01	8.74	9.46
25.25	6.59	7.32	8.05	8.79	9.52
25.50	6.63	7.36	8.10	8.84	9.57
25.75	6.66	7.41	8.15	8.89	9.63
26.00	6.70	7.45	8.19	8.94	9.68
26.25	6.74	7.49	8.24	8.99	9.74
26.50	6.78	7.53	8.28	9.04	9.79
26.75	6.82	7.57	8.33	9.09	9.85
27.00	6.85	7.62	8.38	9.14	9.90
27.25	6.89	7.66	8.42	9.19	9.96
27.50	6.93	7.70	8.47	9.24	10.01
27.75	6.97	7.74	8.52	9.29	10.07
28.00	7.01	7.79	8.57	9.34	10.12
28.25	7.05	7.83	8.61	9.40	10.18
28.50	7.09	7.87	8.66	9.45	10.23
28.75	7.12	7.92	8.71	9.50	10.29
29.00	7.16	7.96	8.75	9.55	10.35
29.25	7.20	8.00	8.80	9.60	10.40
29.50	7.24	8.05	8.85	9.65	10.46
29.75	7.28	8.09	8.90	9.71	10.52
30.00	7.32	8.13	8.95	9.76	10.57

[1]Use this table with procedures 3A1c and 3A2c.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)
CARBONATE AND NONCARBONATE CLAY II (3A2d)
(II = electronic manometer with pressure sensor)

1. APPLICATION

Carbonate clay is considered important in PSA because clay-size carbonate particles have properties that are different from noncarbonate clay. The cation exchange capacity of carbonate clay is very low compared to noncarbonate clay. Water holding capacity of carbonate clay is $\approx$ two thirds that of noncarbonate clay. Since carbonate clay is a diluent, it is often subtracted from the total clay in order to make inferences about soil genesis and clay activities.

2. SUMMARY OF METHOD

Clay residue from moist PSA (procedure 3A2) is treated with acid in a closed system. The pressure of the evolved gas is measured. The pressure is related linearly to the CO_2 content in the carbonates. A manometer is used to measure the pressure.

3. INTERFERENCES

The method is semi-quantitative. It is assumed that all of the carbonates are converted to CO_2. This method measures all forms of carbonates. In addition to Ca, the carbonates of Mg, Na, and K also react with the acid. Analytical interferences may be caused by temperature changes within the reaction vessel. The analyst should not touch the glass of the vessel when reading the pressure. When sealing the vessel, the analyst should not hold onto the vessel any longer than necessary to tighten the cap. The internal pressure must be equalized with the atmosphere. Approximately 3 to 5 s are required to equalize the internal pressure of the bottle when piercing the septa with a needle. The analyst should replace septa at regular intervals. The septa develop leaks after extensive use.

4. SAFETY

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PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)
CARBONATE AND NONCARBONATE CLAY II (3A2d)
(II = electronic manometer with pressure sensor)

7. PROCEDURE

Manometer Calibration

7.1 Calibrate the manometer quarterly or whenever equipment changes. Calibrate by placing 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 mL of the Na_2CO_3 reagent into tared, 90-mL weighing bottles. Dry the standard samples in the oven overnight at 105°C. Remove samples from oven, place in desiccator and cool to ambient temperature. Record the weight of the standard samples to nearest 0.1 mg.

7.2 Lubricate the lip of the 90-mL, weighing bottle that contains the Na_2CO_3 with a thin film of glycerine. Dispense 3 mL of 6 *N* HCl into a gelatin capsule and place the top on the capsule. If HCl leaks from the capsule, discard the capsule. Place the capsule into the glass bottle and immediately cap the bottle. Release pressure in the bottle by piercing the septa with a hypodermic needle which is not connected to the manometer. Allow 3 to 5 s for internal pressure in bottle to equalize.

7.3 After the gelatin capsule has dissolved (several minutes), slowly tip the bottle and rotate it to saturate the standard sample adhering to the sides of the bottle. Avoid changing the temperature of the container by only handling the cap. Allow sample to stand for at least 30 min.

7.4 Adjust the manometer to zero before taking measurements. Insert the hypodermic needle in the septa stopper which is connected to the transducer. Measure the pressure inside the weighing bottle. Record the manometer readings using the rounding-up procedure.

7.5 Calculate the linear regression equation, i.e., the dependent variable is the Na_2CO_3 weights (regressed or predicted values) and the independent variable is the corresponding manometer readings.

Carbonate Determination

7.6 Determine the presence of carbonates in <2-mm soil by placing soil on a spot plate and adding two or three drops of 1 *N* HCl. The rate of CO_2 evolution indicates the relative amount of carbonates (procedure 1B).

7.7 If the soil contains more than a trace amount of carbonates, determine the amount of carbonate clay in the <2-μm dry residue (procedure 3A2).

7.8 With a thin film of glycerine, lubricate the lip of the 90-mL, weighing bottle that contains the <2-μm residue. In each analysis batch, include an empty weighing bottle as a blank. Dispense 3 mL of 6 *N* HCl into a gelatin capsule and place the top on the capsule. If HCl leaks from the capsule, discard the capsule. Place the capsule into the glass bottle and immediately cap the bottle. Release any pressure in the bottle by piercing the septa with a hypodermic needle that is not connected to the manometer. Approximately 3 to 5 s are required to equalize the internal pressure of the bottle.

7.9 After the gelatin capsule has dissolved (several minutes), slowly tip the bottle and rotate it to saturate the clay adhering to the sides of the bottle. Handle only the cap to avoid changing the temperature of the container. Allow sample to stand for at least 30 min.

7.10 Turn on the manometer at least 30 min before use. Adjust the manometer to zero before taking measurements. Insert the hypodermic needle in septa stopper which is connected to the transducer. Measure the pressure inside the weighing bottle and record the manometer readings (MR). Begin readings with the blank (BR).

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)
CARBONATE AND NONCARBONATE CLAY II (3A2d)
(II = electronic manometer with pressure sensor)

7.11 Compare the sample readings with those of a standard curve prepared by measuring CO_2 evolved from a series of Na_2CO_3 aliquots with a range 0 to 35 mg.

7.12 Use the 90-mL, square-bottomed, weighing bottles for the <2-μm aliquots and carbonate determination. Wash and tare after every use.

8. CALCULATIONS

8.1 Calculate the linear regression equation, i.e., the dependent variable is the Na_2CO_3 weights (regressed or predicted values) and the independent variable is the corresponding manometer readings.

8.2 Correct the manometer reading as follows:

$$CR = (MR - BR)$$

where:
CR = corrected reading
MR = manometer reading
BR = blank reading

8.3 Use the calculated linear regression equation and the CR for the standard samples to estimate the g of $CaCO_3$ in sample.

8.4 Carbonate Clay Equivalent (<2 μm) (%) = ((g $CaCO_3$) x 100 x CF)/TW

where:
CF = 1000 mL/dispensed pipet volume (mL)
TW = total weight of H_2O_2-treated oven-dry sample (procedure 3A2)

8.5 Noncarbonate Clay (<2 µm) (%) = Total Clay (%) - Carbonate Clay Equivalent (%)

9. REPORT
Report percentages of carbonate and noncarbonate clay.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Shields, L.G., and M.W. Meyer. 1964. Carbonate clay: measurement and relationship to clay distribution and cation exchange capacity. Soil Sci. Soc. Am. Proc. 28:416-419.
Williams, D.E. 1948. A rapid manometric method for the determination of carbonate in soils. Soil Sci. Soc. Am. Proc. 13:127-129.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)
PRETREATMENT TO REMOVE CARBONATES (with pH 5 NaOAc) (3A2e)

1. APPLICATION

Soils high in carbonate content do not readily disperse. Pretreatment of these soils with acid destroys the carbonates (Grossman and Millet, 1961; Jackson, 1969; Gee and Bauder, 1986). This method may be requested by project coordinators to determine the particle-size distribution after pretreatment to remove carbonates. This determination is used primarily for studies of soil genesis and parent material.

2. SUMMARY OF METHOD

Carbonates are destroyed with NaOAc solution buffered to pH 5. The NaOAc solution is added to sample until carbonate bubbles no longer evolve. The NaOAc solution is then washed from the sample. After destruction of carbonates, the moist PSA (procedure 3A2) is followed.

3. INTERFERENCES

Acidification can destroy primary mineral structure of clay (Gee and Bauder, 1986).

4. SAFETY

Use rubber gloves and a face shield when handling acids. Mix acids in ventilated fume hoods. Never add water to acid.

5. EQUIPMENT

5.1 Fleaker, 300 mL, tared to 1 mg
5.2 Rubber policeman
5.3 Stirring rod
5.4 Ceramic filter candles, .3μm absolute retention
5.5 Watch glass, 50-mm diameter
5.6 Hot plate, 100°C.
5.7 Vacuum, 0.8 bars (80 kPa)

6. REAGENTS

6.1 Distilled water
6.2 1 *N* sodium acetate (NaOAc) solution, buffered to pH 5. Dissolve 680 g of NaOAc in 4 L of distilled water. Add ≈ 250 mL of acetic acid. Make to 5-L volume with distilled water.
6.3 Ethyl alcohol
6.4 Hydrogen peroxide (H_2O_2), 30 to 35%

7. PROCEDURE

7.1 Weigh two 10-g samples of <2-mm, moist soil to nearest mg on an electronic balance and place into 300-mL, tared fleakers. Weigh sufficient samples to yield 10 g of <2-mm, moist, carbonate-free soil sample, e.g., if the sample contains 50% carbonates, weigh 20 g of soil.

7.2 Add ≈ 200 mL of the 1 *N* NaOAc solution to both samples, mix with a stirring rod, and cover with a watch glass. Allow the samples to stand overnight.

7.3 Place the samples on the hot plate and heat to ~ 90°C until bubbles are no longer evident. Do not boil. Heating accelerates reaction. Decant the solution and add more 1 *N* NaOAc solution. If a reaction occurs, repeat the heating procedure. Continue to decant, add NaOAc solution, and heat until all the carbonates are removed. The speed of dissolution can be increased by lowering the pH of the 1 *N* NaOAc solution (Rabenhorst and Wilding, 1984).

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)
PRETREATMENT TO REMOVE CARBONATES (with pH 5 NaOAc) (3A2e)

7.4 When no more carbonate bubbles are observed, insert the ceramic filter candle into the solution. Apply vacuum and candle the samples to dryness. Rinse once with 200 mL of distilled water.

7.5 Add ≈ 50 mL of distilled water and 5 mL of H_2O_2 to both soil samples at ambient temperature. Cover the soil samples with 50-mm watch glass. Allow initial oxidation of organic matter to complete and then place samples on hot plate. If the froth from the reaction exceeds the capacity of the fleakers, transfer the samples to larger beakers.

7.6 Place the samples on the hot plate and heat to ~ 90°C. Add 5-mL increments of H_2O_2 at 45-min intervals until oxidation has completed or until 30 mL of H_2O_2 have been added. Heat the sampled for an additional 45 min to decompose excess H_2O_2. If the reaction is violent, add small increments of ethyl alcohol to the samples or remove the samples from the hot plate to slow the reaction.

7.7 Place the samples on the filter rack. Add 150 mL of distilled water. Insert filter candle, connect to the vacuum trap assembly with tubing, and turn on vacuum. Wash the samples four additional times with ≈ 150 mL of distilled water. If the samples contain gypsum and flocculates, then the following additional washings may be used. If the samples contain 1 to 5% gypsum, stir the samples with a magnetic stirrer for 5 min and wash 5 times with ≈ 250 mL of distilled water each time. If the samples contain >5% gypsum, stir the samples with a magnetic stirrer for 5 min then wash 5 times with ≈ 750 mL of distilled water each time to remove soluble gypsum.

7.8 Place one of the samples in the oven and dry overnight at 105°C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.9 Record the total weight (TW) of the H_2O_2-treated, oven-dry sample to the nearest mg. The H_2O_2-treated, oven-dry sample is not used in the remaining PSA procedural steps. Use the H_2O_2-treated sample that was not dried in the oven for the remaining procedural steps.

7.10 Proceed with moist PSA (procedure 3A2).

8. CALCULATIONS
Calculations are reported in procedure 3A2.

9. REPORT
Report as carbonate-free PSA data and specify procedure 3A2e.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES

Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:383-411.

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PARTICLE-SIZE ANALYSIS
PARTICLES <2-mm (pipet method) (3A)
MOIST SAMPLES (3A2)
PRETREATMENT TO REMOVE IRON (3A2f)
(with sodium dithionite-citrate)

1. APPLICATION

Iron and other oxides coat and bind clay, silt and sand particles to form aggregates. Soils with iron cementation do not readily disperse. The iron oxides are removed using bicarbonate-buffered, sodium dithionite-citrate solution (Mehra and Jackson, 1960; Gee and Bauder, 1986). This chemical pretreatment is used when requested by the project coordinator.

2. SUMMARY OF METHOD

Soil samples are pretreated with H_2O_2 to remove organic matter. Iron oxides are removed with bicarbonate-buffered, sodium dithionite-citrate solution and heated until the sample color changes to a grayish color. The suspension is flocculated with saturated NaCl solution and filtered to remove soluble salts. After iron oxide removal, standard PSA (3A2) is followed.

3. INTERFERENCES

If the temperature of the water bath exceeds 80°C, elemental sulfur will precipitate (Mehra and Jackson, 1960). This pretreatment destroys primary mineral grains in the clay fraction (El-Swaify, 1980).

4. SAFETY

Use rubber gloves and a face shield when handling acid and H_2O_2. Mix acids in ventilated fume hoods. Heat samples for removal of organic matter or cementing agents in ventilation hoods. Handle heated samples with leather gloves.

5. EQUIPMENT

5.1 Ceramic filter candles, .3μm absolute retention
5.2 Electronic balance, ±1-mg sensitivity
5.3 Fleaker, 300 mL, tared to 1 mg
5.4 Rubber policeman
5.5 Calibrated scoop, 1 g
5.6 Glass stirring rod
5.7 Thermometer, 0 to 100°C
5.8 Timer or clock with second hand
5.9 Water bath, 80°C
5.10 Centrifuge
5.11 Vacuum, 0.8 bars (80 kPa)

6. REAGENTS

6.1 Sodium citrate solution, 0.3 M $Na_3C_6H_5O_7 \cdot 2H_2O$ (88.4 g L^{-1})
6.2 Sodium bicarbonate buffer solution, 1 M $NaHCO_3$ (84 g L^{-1})
6.3 Sodium dithionite ($Na_2S_2O_4$ - hydrosulphite)
6.4 Saturated NaCl solution (solubility at 20°C; 360 g L^{-1})
6.5 Ethyl alcohol
6.6 Hydrogen peroxide (H_2O_2), 30 to 35%

7. PROCEDURE

7.1 Weigh two 10-g samples of <2-mm, moist soil to nearest mg on an electronic balance and place into 2O

PARTICLE-SIZE ANALYSIS
PARTICLES <2-mm (pipet method) (3A)
MOIST SAMPLES (3A2)
PRETREATMENT TO REMOVE IRON (3A2f)
(with sodium dithionite-citrate)

7.2 Add $\approx$ 50 mL of distilled water and 5 mL of H_2O_2 to both soil samples at ambient temperature. Cover the soil samples with 50-mm watch glass. Allow initial oxidation of organic matter to complete, and then place samples on hot plate. If the froth from the reaction exceeds the capacity of the fleaker, transfer the samples to larger beakers.

7.3 Place the samples on a hot plate and heat to 90°C. Add 5-mL increments of H_2O_2 at 45-min intervals until oxidation has complete or until 30 mL of H_2O_2 have been added. Heat the samples for an additional 45 min to decompose excess H_2O_2. If the reaction is violent, add small increments of ethyl alcohol to the samples or remove the samples from the hot plate to slow the reaction.

7.4 Add 40 mL of the citrate solution and 5 mL of the sodium bicarbonate. Heat to 80°C in a water bath, but do not exceed 80°C. Add 1 g of sodium dithionite powder with a calibrated scoop. Stir constantly with a glass rod for 1 min and then occasionally for 15 min. Add 10 mL of saturated NaCl solution and mix.

7.5 Centrifuge or candle the samples to remove the dissolved Fe_2O_3. Combine the split samples into fewer fleakers.

7.6 If the samples contain less than 0.5 g of Fe_2O_3, repeat the dissolution treatment. For samples with more than 0.5 g of Fe_2O_3, repeat the dissolution treatment two more times.

7.7 Place the samples on the filter rack. Add 150 mL of distilled water. Insert a filter candle, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Wash the samples four additional times with $\approx$ 150 mL of distilled water. If the samples contain gypsum and flocculates, then the following additional washings may be used. If the sample contains 1 to 5% gypsum, stir the sample with a magnetic stirrer for 5 min and wash 5 times with $\sim$ 250 mL of distilled water each time. If the sample contains >5% gypsum, stir the sample with a magnetic stirrer for 5 min then wash 5 times with $\approx$ 750 mL of distilled water each time to remove soluble gypsum.

7.8 Place one sample in the oven and dry overnight at 105°C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.9 Record the total weight (TW) of the sample to the nearest mg. The H_2O_2 oven-dry sample is not used in the remaining PSA procedural steps. Use the H_2O_2-treated sample that was not dried in the oven for the remaining PSA procedural steps.

7.10 Proceed with moist PSA (procedure 3A2).

8. CALCULATIONS
Calculations are reported in procedure 3A2.

9. REPORT
Report as iron-free PSA data and specify procedure 3A2f.

10. PRECISION
Precision data are not available for this procedure.

**PARTICLE-SIZE ANALYSIS
PARTICLES <2-mm (pipet method) (3A)
MOIST SAMPLES (3A2)
PRETREATMENT TO REMOVE IRON (3A2f)
(with sodium dithionite-citrate)**

11. REFERENCES

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PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)
PRETREATMENT TO REMOVE SILICA (with NaOH) (3A2g)

1. APPLICATION

Soils that are cemented by Si do not completely disperse with hydrogen peroxide pretreatment and sodium hexametaphosphate. A pretreatment with a weak base dissolves the Si bridges and coats and increases the soil dispersion. This method is experimental and can be used when requested by project coordinators. The determination is used for soil parent material and genesis studies.

2. SUMMARY OF METHOD

Soils are pretreated with H_2O_2 to remove organic matter. Soils with Si cementation or coatings are pretreated with a weak NaOH solution overnight. After removal of siliceous cementing agents, moist PSA (procedure 3A2) is followed.

3. INTERFERENCES

The effects of this pretreatment on clay minerals and particle size distribution are unknown.

4. SAFETY

Use rubber gloves and a face shield when handling bases. Mix bases in ventilated fume hoods.

5. EQUIPMENT
5.1 Fleakers, 300 mL, tared to 1 mg
5.2 Ceramic filter candles, .3μm absolute retention
5.3 Vacuum, 0.8 bars (80 kPa)
5.4 Electronic balance, ±1-mg sensitivity
5.5 Watch glass, 50-mm diameter

6. REAGENTS
6.1 Distilled water
6.2 Hydrogen peroxide (H_2O_2), 30 to 35%
6.3 Sodium hydroxide solution (NaOH), 0.1 N. Dissolve 4 g NaOH pellets in 1 L of distilled water.
6.4 Ethyl alcohol

7. PROCEDURE

7.1 Weigh two 10-g of <2-mm, moist soil to nearest mg on an electronic balance and place in 300-mL, tared fleakers.

7.2 Add ≈ 50 mL of distilled water and 5 mL of H_2O_2 to both soil samples at ambient temperature. Cover the soil samples with 50-mm watch glass. Allow initial oxidation of organic matter to complete, and then place samples on hot plate. If the froth from the reaction exceeds the capacity of the fleaker, transfer the sample to larger beakers.

7.3 Place the samples on a hot plate and heat to 90°C. Add 5-mL increments of H_2O_2 at 45-min intervals until oxidation has completed or until 30 mL of H_2O_2 have been added. Heat the samples for an additional 45 min to decompose excess H_2O_2. If the reaction is violent, add small increments of ethyl alcohol to the samples or remove the samples from the hot plate to slow the reaction.

7.4 Soak the samples overnight in 100 mL of 0.1 N NaOH.

7.5 Place the samples on the filter rack. Add 150 mL of distilled water. Insert filter candle, connect to the vacuum trap assembly with tubing, and turn on the vacuum. Wash the samples four additional times with ≈ 150 mL of distilled water. If the sample contains gypsum and flocculates, then the following

additional washings may be used. If the samples contain 1 to 5% gypsum, stir the samples with a magnetic stirrer for 5 min and wash 5 times with $\approx$ 250 mL of distilled water each time. If the samples contain >5% gypsum, stir the sample with a magnetic stirrer for 5 min then wash 5 times with $\approx$ 750 mL of distilled water each time to remove soluble gypsum.

7.6 Place one sample in the oven and dry overnight at 105°C. Remove the sample from the oven, place in a desiccator, and cool to ambient temperature.

7.7 Record the total weight (TW) of the sample to the nearest mg. The H_2O_2-treated, oven-dry sample is only used for calculation of results and is not used in the remaining PSA procedural steps. Use the sample that was not dried in the oven for the remaining PSA procedural steps.

7.8 Proceed with moist PSA (procedure 3A2).

8. CALCULATIONS
Calculations are reported in procedure 3A2.

9. REPORT
Report as Si-free PSA data and specify procedure 3A2g.

10. PRECISION
Precision data are not available for this procedure.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)
DISPERSION USING ULTRASONIC PROBE (3A2h)

1. APPLICATION

Soils that do not completely disperse with standard PSA can be dispersed using ultrasonic dispersion (Gee and Bauder, 1986). Pretreatments coupled with ultrasonic dispersion yield maximum clay concentrations (Mikhail and Briner, 1978). This is a developmental procedure as no standard method has been adopted using ultrasonic dispersion. This method is used when requested by project coordinators.

2. SUMMARY OF METHOD

A 10-g sample of <2-mm, moist soil is pretreated to remove organic matter and soluble salts. The sample is dried in the oven and weighed to obtain the initial weight. Sodium hexametaphosphate solution is added to the sample and then made to 100-mL volume with distilled water. The sample is subjected to ultrasonic vibration for 5 min. The sand fraction is removed by wet sieving and then fractionated by dry sieving. The clay and fine silt fractions are determined using the suspension remaining from the wet sieving process. This suspension is diluted to 1 L in a sedimentation cylinder, stirred, and 25-mL aliquots removed with a pipette at calculated, predetermined intervals based on Stokes' law (Kilmer and Alexander, 1949). The aliquots are dried at 105°C and weighed. Coarse silt is the difference between 100% and the sum of the sand, clay, and fine silt percentages.

3. INTERFERENCES

Ultrasonic dispersion has been reported to destroy primary soil particles. Watson (1971) summarized studies that reported the destruction of biotite and breakdown of microaggregates by ultrasonic dispersion. However, Saly (1967) reported that ultrasonic vibration did not cause the destruction of the clay crystalline lattice or the breakdown of primary grains. The samples ranged from sandy to clayey soils. The cementing agents represented humus, carbonates, and hydroxides of Fe and Al. No standard procedures have been adopted using ultrasonic dispersion.

4. SAFETY

Use rubber gloves and a face shield when handling acid and H_2O_2. Mix acids in ventilated fume hoods. Heat samples for removal of organic matter or cementing agents in ventilation hoods. Handle heated samples with leather gloves. Never add water to dry phosphorous pentoxide. Use ear protection when using the ultrasonic probe.

5. EQUIPMENT

5.1 Ultrasonic probe, 19-mm (3/4 in) horn, 20 kHz, 300 watts
5.2 Fleakers, 300 mL, tared to 1 mg
5.3 Ceramic filter candles, .3μm absolute retention
5.4 Mechanical shaker, horizontal, 120 oscillations min^{-1}
5.5 Cylinders, 1 L, white line fused onto glass at 1 L
5.6 Oven, 105°C
5.7 Hot plate, 100°C
5.8 Ring stand to support 300-mesh sieve
5.9 Vacuum, 0.8 bars (80 kPa)
5.10 Thermometer, 0 to 100°C
5.11 Desiccator
5.12 Motor driven stirrer, (Kilmer and Mullins, 1954)
5.13 Hand stirrer, perforated disk fastened to a rod
5.14 Adjustable pipet rack (Shaw, 1932)
5.15 Lowy pipets, 25 mL, with overflow bulb
5.16 Polyurethane foam, pipe insulation that fits snugly around cylinder.

5.17 Sieve shaker with 12.7-mm (1/2 in) vertical and lateral movement at 500 oscillations min^{-1}

7.6 Record the total weight (TW) of the H_2O_2-treated, ovendry sample to the nearest mg. The H_2O_2-treated, ovendry sample is only used for the calculations of results and is not used in the remaining PSA procedural steps. Use the H_2O_2-treated sample that was not dried in oven for all of the following PSA procedural steps.

7.7 Add ~ 100 mL of distilled water and 10 mL of sodium hexametaphosphate solution, equivalent to 0.4408 g of sodium hexametaphosphate, to sample. Subtract the weight of the sodium hexametaphosphate (D) contained in the extracted aliquot from the silt and clay weights in the calculation of silt and clay percentages. Determine the exact volume of sodium hexametaphosphate to add to each sample by regressing the volume of sodium hexametaphosphate against the dry residue weight of sodium hexametaphosphate and then by predicting the volume needed to dispense 0.4408 g of sodium hexametaphosphate into each sample.

7.8 Disperse the suspension with ultrasonic vibrations. Ensure the power supply is properly tuned. Consult the instruction manual. Immerse the probe in the suspension to a 3-cm depth. Set timer to 5 min. Press start button. Adjust output control as required. Between samples, clean the probe by placing it in water or alcohol and energizing it for a few seconds.

7.9 After ultrasonic dispersion, pour the suspension through a 300-mesh (0.047-mm) sieve mounted on a ring stand. Place a funnel below the sieve and a 1-L cylinder below the funnel. Collect the silt and clay in the 1-L cylinder. Avoid using jets of water in washing the sample. Wash and rub all particles from the fleaker into the sieve. Continue to wash until the suspension volume in the cylinder is ~ 800 mL. Sand and some of the coarse silt remain on the sieve. Rinse all <20-μm particles into the cylinder. Fill the cylinder to 1 L and cover with a 65-mm watch glass. Prepare a distilled water blank to measure temperature fluctuations. Allow the cylinder to stand overnight to equilibrate the suspension with the room temperature. Wash the sand into an evaporation dish and dry the sand at 105°C overnight.

7.10 Transfer the dried sand to a nest of sieves that has a top-to-bottom order of 1.0, 0.5, 0.25, 0.1, and 0.047 mm. Shake the sand for 3 min on a shaker that has 1.3-cm vertical and lateral movements and oscillates at 500 strokes min^{-1}. Record the weight of each separate sand fraction (SW_i) to the nearest mg. If optical analysis is requested, place the very fine sand and fine sand fractions in gelatin capsules and the remaining sand fractions in a labeled vial. Store capsules in the labeled vial. Wash sand dishes after every use.

7.11 Determine the percentage of fine silt and clay gravimetrically by removing an aliquot from the suspension in the 1-l cylinder with a Lowy, 25-mL pipette. Periodically, gravimetrically calibrate the delivery volume of the pipette by weighing the amount of distilled water dispensed from the pipette. Record the delivery volume (DV) and use the value to calculate the results. Regulate the vacuum so that the pipette fills in $\approx$ 12 s. Record temperature (T_1) of blank. Mount the pipette on an adjustable pipette rack (Shaw, 1932). Stir the silt and clay suspension with mechanical stirrer for 6 min or for 8 min, if suspension has stood more than 24 h. (Kilmer and Mullins, 1954). Place pipe insulation around sample and blank cylinders to prevent rapid changes in temperatures. Place the cylinder on a stable, vibrationless table and stir with a hand stirrer in an up-and-down motion for 30 s. Timing is started upon completion of the stirring. Record the time that stirring is stopped. For the <20-μm fraction, slowly lower the closed pipet to a 10-cm depth in suspension, turn on the vacuum, open the pipet, and withdraw an aliquot at the calculated time (Table 1). Place the aliquot into a tared and numbered, 90-mL weighing bottle. Rinse the pipet twice with distilled water and dispense into the tared, weighing bottle with aliquot. For the <2-μm fraction, pipet after a time of 4.5, 5, 5.5, or 6.5 h. Record the temperature (T_2) of blank. Use the average of T_1 and T_2 and adjust the depth of the pipet in the suspension as indicated in Table 2.

PARTICLE-SIZE ANALYSIS
PARTICLES <2 mm (pipet method) (3A)
MOIST SAMPLES (3A2)
DISPERSION USING ULTRASONIC PROBE (3A2h)

Repeat the procedure described for the <20-μm fraction. If determination of carbonate clay is required, use weighing bottle with screw threads.

7.12 Place the aliquots and weighing bottles in an oven. Dry the aliquots at 105°C overnight and cool to ambient temperature in a desiccator that contains P_2O_5 or an equivalent desiccant.

7.13 Record the weight of the residue (RW) to the nearest 0.1 mg.

7.14 Use the 90-mL, round-bottomed, weighing bottles for the <20-μm aliquots. Wash and tare after every fourth use. Use the 90-mL, square-bottomed, weighing bottles for the <2-μm aliquots. Wash and tare after every use.

7.15 If fine clay analyses are requested, use the remaining suspension and follow procedure 3A2b. If necessary, save the sediment for optical mineralogy.

7.16 If optical mineralogy is requested, decant the suspension and transfer the sediment to a 400-mL beaker. Fill the beaker to a 5.5-cm height. Stir the sediment and allow to settle for 5 min. Discard the supernatant. Refill the beaker to 5.5-cm height. Stir again, allow to settle for 3 min, and then decant. Repeat the filling and the stirring; allow to settle for 2 min; and then decant until top half of suspension is clear. Transfer the sediment, which is dominantly 20 to 50 μm, to a labeled, drying dish. Wash with ethanol, air-dry, and save in the drying dish for optical mineralogy.

8. CALCULATIONS

8.1 Clay % = 100 x ((RW_2 - DW) x (CF/TW))

where:
RW_2 = residue weight (g), <2-μm fraction
DW   = dispersing agent weight (g) = (0.4408/CF)
CF   = 1000 mL/DV
DV   = dispensed pipet volume
TW   = total weight (g), H_2O_2-treated, oven-dry sample

8.2 Fine Silt % = 100 x ((RW_{20}-DW) x (CF/TW)) - Clay %

where:
RW_{20} = residue weight (g) of <20-μm fraction

8.3 Sand % = $\sum$ (SW/TW) x 100

where:
i = 1.0, 0.5, 0.25, 0.1, and 0.047-mm sand fractions

8.4 Coarse silt % = 100 - (Clay + Fine Silt + Sand %)

9. REPORT
Report percentages of each particle size and specify procedure 3A2h.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES

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PARTICLE-SIZE ANALYSES
PARTICLES >2 mm (3B)

INTRODUCTION

The SSL determines weight percentages of the >2-mm fractions by field and laboratory weighings by procedure 3B1a. In the field or in the laboratory, the sieving and weighing of the >2-mm fraction are limited to the <75-mm fractions. In the field, fraction weights are usually recorded in pounds, whereas in the laboratory, fraction weights are recorded in grams. The 20- to 75-mm fraction is generally sieved, weighed, and discarded in the field. This is the preferred and usually the most accurate method. Less accurately, the 20- to 75-mm fraction is estimated as a volume percentage of the whole soil. If it is sieved and weighed in the laboratory, the results are usually not reliable because of small sample size.

The SSL estimates weight percentages of the >2-mm fractions from volume estimates of the >20-mm fractions and weight determinations of the <20-mm fractions by procedure 3B1b. The volume estimates are visual field estimates. Weight percentages of the >20-mm fractions are calculated from field volume estimates of the 20- to 75-mm, 75- to 250-mm, and >250-mm fractions. The >250-mm fraction includes stones and boulders that have horizontal dimensions that are smaller than the size of the pedon. Weight measurements for the 2- to 20-mm fraction are laboratory measurements. Weight measurements of the 20- to 75-mm fractions in the field are more accurate than visual volume estimates. Weight measurements of this fraction in the laboratory are not reliable. The volume estimates that are determined in the field are converted to dry weight percentages. For any >2-mm fractions estimated by volume in the field, the SSL calculates weight percentages by procedure 3B2. The visual volume estimates of the >20-mm fraction are subjective. The conversion of a volume estimate to a weight estimate assumes a particle density of 2.65 g cc^{-1} and a bulk density for the fine-earth fraction of 1.45 g cc^{-1}.

Soil variability and sample size are interferences to weight determinations of the >2-mm particles. Enough soil material needs to be sieved and weighed to obtain statistically accurate rock fragment content. In order to accurately measure rock fragments with maximum particle diameters of 20 and 75 mm, the minimum specimen sizes ("dry" weights) that need to be sieved and weighed are 1.0 and 60.0 kg, respectively. Refer to ASTM method D 2487 (American Society for Testing and Materials, 1993). Whenever possible, the field samples or "moist" material should have weights two to four times larger (American Society for Testing and Materials, 1993). Therefore, sieving and weighing the 20- to 75-mm fraction should be done in the field. The <20-mm fractions are sieved and weighed in the laboratory.

Procedures for reporting data for a size fraction base are outlined in Section 2A. Unless otherwise specified, the particle-size fractions 2 to 5, 5 to 20, 20 to 75, and 0.1 to 75 mm are reported on a <75-mm oven-dry weight percentage basis. The total >2-mm fraction is reported on a whole soil oven-dry weight percentage base.

REFERENCES

American Society for Testing and Materials. 1993. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

PARTICLE-SIZE ANALYSIS
PARTICLES >2 mm (3B)
WEIGHT ESTIMATES (3B1)
BY FIELD AND LABORATORY WEIGHING (3B1a)

1. APPLICATION

Procedure 3B1a is used to determine weight percentages of the >2 mm fractions by field and laboratory weighings. The 20- to 75-mm fraction is generally sieved, weighed, and discarded in the field or is obtained from a field volume percentage estimate. However, the 20- to 75-mm fraction can be sieved and weighed in the laboratory. The <20-mm fractions are sieved and weighed in the laboratory.

2. SUMMARY OF METHOD

Field weights are determined for the 20- to 75-mm fraction. This is the preferred method. When field determinations are not possible, weight measurements for the 20- to 75-mm fraction can be determined in the laboratory. The <20-mm fractions are sieved and weighed in the laboratory. The percentage of any 2- to 75-mm fraction on a <75-mm oven-dry weight basis is calculated.

3. INTERFERENCES

Soil variability and sample size are interferences to weight determinations of the >2-mm particles. Enough soil material needs to be sieved and weighed to obtain statistically accurate rock fragment content. In order to accurately measure rock fragments with maximum particle diameters of 20 and 75 mm, the minimum specimen sizes ("dry" weights) that need to be sieved and weighed are 1.0 and 60.0 kg, respectively. Refer to ASTM method D 2487 (American Society for Testing and Materials, 1993). Samples received in the laboratory generally have a maximum weight of 4 kg. Therefore, sieving and weighing the 20- to 75-mm fraction should be done in the field. The <20-mm fractions are sieved and weighed in the laboratory.

4. SAFETY

The main hazards are in the field during sample collection. Some hazards are sharp-edged excavation tools, snake bites, and falls.

5. EQUIPMENT

5.1 Electronic balance, ±1-g sensitivity and 15-kg capacity
5.2 Trays, plastic, tared
5.3 Sieves, square-hole
5.3.1 9 mesh, 2 mm
5.3.2 4 mesh, 4.76 mm
5.3.3 20 mm, 3/4 in
5.3.4 76 mm, 3 in
5.4 Mechanical shaker with 9-mesh and 4-mesh sieves
5.5 Rubber roller
5.6 Metal plate, 76 x 76 x 0.5 cm
5.7 Scale, 45-kg (100-lb) capacity
5.8 Brown kraft paper

6. REAGENTS

6.1 Distilled water
6.2 1 *N* HCl. Refer to procedure 1B.
6.3 Sodium hexametaphosphate solution (NaHMP). Dissolve 35.7 g of sodium hexametaphosphate $(NaPO_3)_6$ and 7.94 g of sodium carbonate (Na_2CO_3) in L of distilled water.

PARTICLE-SIZE ANALYSIS
PARTICLES >2 mm (3B)
WEIGHT ESTIMATES (3B1)
BY FIELD AND LABORATORY WEIGHING (3B1a)

7. PROCEDURE

Field

7.1 Sieve a representative horizon sample with a 76-mm sieve. Sieve about 60 kg of material to accurately measure rock fragments that have a maximum particle diameter of 75 mm. As a 60-kg sample may not be possible because of limitations of time and/or soil material, actual sample size may be 30 or 40 kg. Discard the >75-mm material. Weigh and record weight (lbs) of <75-mm fraction. Sieve this material with a 20-mm sieve. Discard the 20- to 75-mm fraction. Weigh and record weight (lbs) of <20-mm fraction. Place a subsample of the <20-mm material in an 8-mil, plastic bag. Label and send to laboratory for analyses.

Laboratory

7.2 Distribute the field sample on a plastic tray, weigh, and record moist weight. Air-dry, weigh, and record weight.

7.3 Process air-dry material on a flat, metal plate that is covered with brown kraft paper. Thoroughly mix material by moving the soil from the corners to the middle of the processing area and then by redistributing the material. Repeat process four times. Roll material with wooden rolling pin to crush clods to pass a 2-mm sieve. For samples with easily crushed coarse fragments, substitute rubber roller for wooden rolling pin. Sieve clayey soils that contain many coarse fragments in the mechanical shaker. Roll and sieve until only the coarse fragments that do not slake in NaHMP remain on the sieve.

7.4 If more sample is received than is needed for processing, select a subsample for preparation. Weigh subsample and record weight.

7.5 Weigh soil material with diameters of 2 to 5 mm. Soak in NaHMP for 12 h. Air-dry, weigh the material that does not slake, and discard. Weigh, record weight, and discard coarse fragments with diameters of 20 to 75 mm and 5 to 20 mm. Most laboratory samples do not contain 20- to 75-mm fragments, as this fraction is generally sieved, weighed, and discarded in the field.

8. CALCULATIONS

8.1 If field weight measurements are determined for the <75-mm and the 20- to 75-mm fraction, convert these weights in pounds to grams. If laboratory measurements are determined for the <75 mm and the 20- to 75-mm fractions, these weights are already in grams.

8.2 Determine field moist weight of the subsample as received in the laboratory. Determine air-dry weight of subsample. Air-dry weight is defined in procedure 1B.

8.3 Determine ratio of slaked, air-dried weight (g) to unslaked, air-dried weight (g) for the 2- to 5-mm fraction. Using this ratio, adjust weight of coarse fragments with <5-mm diameters.

8.4 Base coarse fragment calculation on oven-dry weight-basis. Use the AD/OD (air-dry/oven-dry ratio) (procedure 4B5) to calculate the oven-dry weight of <2-mm fraction. Use the following equation to determine the percentage of any 2- to 75-mm fraction on a <75-mm oven-dry weight-basis.

```
Percentage >2 mm fraction =
      (<75-mm basis)
                       Weight 2- to 5-mm fraction (g) x 100
                       Weight of < 75-mm fraction (g)
```

PARTICLE-SIZE ANALYSIS
PARTICLES >2 mm (3B)
WEIGHT ESTIMATES (3B1)
BY FIELD AND LABORATORY WEIGHING (3B1a)

8.5 Determine oven-dry weight by weighing the sample after oven-drying at 105°c for 24 h or by calculating as follows:

$$\text{Oven-dry weight (g)} = \frac{\text{Air-dry weight (g)}}{\text{AD/OD}}$$

8.6 Similarly, determine oven-dry weight from the field-moist weight of a sample by calculating as follows:

$$\text{Oven-dry weight (g)} = \frac{\text{Field-moist weight (g)}}{\text{Field-moist weight/Oven-dry weight (g)}}$$

8.7 In calculations of the oven-dry weight percentages of the >2-mm fraction, make corrections for the field moisture content of the <75-mm sample at sampling and for the moisture content of the air-dry bulk laboratory sample. Base the corrections for the field moisture content on the difference between the field moist weight and air-dry weight of the bulk sample.

9. REPORT

Field
9.1 Weight (lbs) of field moist, <75-mm fraction
9.2 Weight (lbs) of field moist, 20- to 75-mm fraction

Laboratory
9.3 Weight (g) of field moist soil sample
9.4 Weight (g) of air-dry soil sample
9.5 Weight (g) of air-dry processed soil sample
9.6 Weight (g) 20-to 75-mm fraction
9.7 Weight (g) 5- to 20-mm fraction
9.8 Weight (g) 2- to 5-mm fraction
9.9 Weight (g) of subsample 2- to 5-mm fraction before slaking
9.10 Weight (g) of subsample 2- to 5-mm fraction after slaking

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
American Society for Testing and Materials. 1993. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

PARTICLE-SIZE ANALYSIS
PARTICLES >2mm
WEIGHT ESTIMATES (3B1)
FROM VOLUME AND WEIGHT ESTIMATES (3B1b)
VOLUME ESTIMATES (3B2)

1. APPLICATION

Procedure 3B1b is used to determine weight percentages of the the >2 mm fractions from volume estimates and weight determinations. The volume estimates are visual field estimates for any fractions that are >20 mm. The weight estimates are laboratory measurements for the 2-to 20-mm or 2-to 75-mm fractions. The volume estimates for any fractions that are >20 mm are converted to weight percentages. The total >2-mm fraction is reported on an oven-dry weight basis for whole soil. Method 3B2 is the calculations used to derive weight percentages from volume percentages of all the >2-mm material.

2. SUMMARY OF METHOD

Visual field volume estimates are determined for any fractions that are >20 mm. These volume

PARTICLE-SIZE ANALYSIS
PARTICLES >2mm
WEIGHT ESTIMATES (3B1)
FROM VOLUME AND WEIGHT ESTIMATES (3B1b)
VOLUME ESTIMATES (3B2)

6. REAGENTS
6.1 Distilled water

6.2 1 *N* HCl. Refer to procedure 1B.

6.3 Sodium hexametaphosphate solution (NaHMP). Dissolve 35.7 g of sodium hexametaphosphate $(NaPO_3)_6$ and 7.94 g of sodium carbonate (Na_2CO_3) in L of distilled water.

7. PROCEDURE

Field
7.1 Determine volume estimates as percentages of soil mass for the 75- to 250-mm and for the >250-mm fractions. The >250-mm fraction includes stones and boulders with horizontal dimensions less than those of the pedon.

7.2 Determine either weight measurements in pounds or visual field volume estimates in percentages for the 20- to 75-mm fragments. Weight measurements for the 20- to 75-mm fraction are the preferred method. However, volume estimates are more accurate than laboratory weights using small samples.

7.3 If field weight measurements are determined for the 20- to 75-mm fraction, sieve an entire horizon sample with a 76-mm sieve. Sieve ≈ 60 kg of material to accurately measure rock fragments that have a maximum particle diameter of 75 mm. A 60-kg sample may not be possible because of limitations of time and/or soil material. Actual sample size may be 30 or 40 kg. Discard the >75-mm material. Weigh and record weight of <75-mm fraction. Sieve this material with a 20-mm sieve. Discard the 20- to 75-mm fraction. Weigh and record weight of <20-mm fraction. Place a subsample of the <20-mm material in an 8-mL, plastic bag. Label and send to laboratory for analyses.

Laboratory
7.4 Distribute the field sample on a plastic tray, weigh, and record moist weight. Air-dry, weigh, and record weight.

7.5 Process air-dry material on a flat, metal plate that is covered with brown kraft paper. Thoroughly mix material by moving the soil from the corners to the middle of the processing area and then by redistributing the material. Repeat process four times. Roll material with wooden rolling pin to crush clods to pass a 2-mm sieve. For samples with easily crushed coarse fragments, substitute rubber roller for wooden rolling pin. Sieve clayey soils that contain many coarse fragments in the mechanical shaker. Roll and sieve until only the coarse fragments that do not slake in NaHMP remain on the sieve.

7.6 If more sample is received than is needed for processing, select subsample for preparation. Weigh subsample and record weight.

7.7 Weigh soil material with diameters of 2 to 5 mm. Soak in NaHMP for 12 h. Air-dry, weigh the material that does not slake, and discard. Weigh, record weight, and discard coarse fragments with diameters of 20 to 75 mm and 5 to 20 mm. Most laboratory samples do not contain 20- to 75-mm fragments as this fraction is generally weighed, sieved, and discarded in the field.

8. CALCULATIONS

From Volume and Weight Estimates 3B1b
8.1 Calculate weight percentages from volume percentages using measured bulk density (Db_m) and particle density (Dp). If measurements are unavailable, assume a Db_m of 1.45 g cc^{-1} and a D_p of 2.65 g cc^{-1}.

PARTICLE-SIZE ANALYSIS
PARTICLES >2mm
WEIGHT ESTIMATES (3B1)
FROM VOLUME AND WEIGHT ESTIMATES (3B1b)
VOLUME ESTIMATES (3B2)

8.2 Use the following equation to convert all volume estimates to weight percentages for specified fractions.

$$\text{Percentage} > 2 \text{ mm (wt basis)} = \frac{100 \; D_p \; (x)}{D_p \; (x) + Db_m \; (1-x)}$$

where:
D_p = Particle density (2.65 g cc^{-1}, unless measured)
Db_m = Bulk density (1.45 g cc^{-1} for <2-mm fraction, unless measured)

$$x = \frac{\text{volume fragments} > i \text{ mm}}{\text{volume whole soil}}$$

where:
i = size fraction above which volume estimates are made and below which weight percentages are determined, usually 20 or 75 mm in diameter

8.3 Use the preceeding equation to calculate any individual fraction >j mm (j = any size fraction) by substituting an appropriate value of Db_m representing the fabric <j mm.

Volume Estimates 3B2
8.4 Use the following equation to determine the volume of the <2-mm fraction per unit volume of whole soil.

$$Cm = \frac{\text{Volume moist} < 2\text{-mm fabric}}{\text{Volume moist whole soil}} = \frac{D_p \; (1-y) \; (1-x)}{D_p \; (1-y) + Db_m \; (y)}$$

where:
Cm = Rock fragment conversion factor
Volume moist whole soil = volume of fine earth plus rock fragments on moist whole soil basis

$$y = \frac{\text{weight material between 2 mm and i mm}}{\text{weight material} < i \text{ mm}}$$

8.5 Use the following formula to convert laboratory data on a <2-mm weight basis to moist whole soil volume basis.

$$Cm \; x \; Db_m \; x \; \text{lab datum}$$

8.6 Use the following formula to determine the volume percentage of <2-mm fabric in whole soil.

$$Cm \; x \; 100$$

8.7 Use the following formula to determine the volume percentage of >2-mm fabric in whole soil.

$$100 \; (1-Cm)$$

8.8 Use the following formula to report weight of <2-mm fabric per unit volume of whole soil for some soils.

$$(Cm \ x \ Db_m)$$

9. REPORT

Field

9.1 Volume (%) >250-mm fraction (includes stones and boulders with horizontal dimensions smaller than size of a pedon)

9.2 Volume (%) 75- to 250-mm fraction

9.3 Volume (%) 20- to 75-mm fraction (not needed if weighed in field)

9.4 Weight (lbs) <75-mm fraction

9.5 Weight (lbs) 20-to 75-mm fraction

Laboratory

9.6 Weight (g) of field moist soil sample

9.7 Weight (g) of air-dry soil sample

9.8 Weight (g) of air-dry processed soil sample

9.9 Weight (g) 20-to 75-mm fraction

9.10 Weight (g) 5- to 20-mm fraction

9.11 Weight (g) 2- to 5-mm fraction

9.12 Weight (g) of subsample 2- to 5-mm fraction before slaking

9.13 Weight (g) of subsample 2- to 5-mm fraction after slaking

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

American Society for Testing and Materials. 1993. Annual book of ASTM standards. Construction. Section 4. Soil and rock; dimension stone; geosynthesis. Vol. 04.08. ASTM, Philadelphia, PA.

FABRIC-RELATED ANALYSES
BULK DENSITY (4A)

INTRODUCTION

Density is defined as mass per unit volume. Soil bulk density of a sample is the ratio of the mass of solids to the total or bulk volume. This total volume includes the volume of both solids and pore space. Bulk Density (Db) is distinguished from particle density which is mass per unit volume of only the solid phase. Particle density excludes pore spaces between particles. As bulk density is usually reported for the <2-mm soil fabric, the mass and volume of rock fragments are subtracted from the total mass and volume.

Bulk density is highly dependent on soil conditions at the time of sampling. Changes in soil swelling due to changes in water content will alter bulk density. Soil mass remains fixed, but the volume of soil may change as water content changes (Blake and Hartge, 1986). Bulk density, as a soil characteristic, is actually a function rather than a single value. Therefore, subscripts are added to the bulk density notation, Db, to designate the water state of the sample when the volume was measured. The SSL uses the bulk density notations of Db_f, $Db_{1/3}$, Db_d, and Db_r for field state, 1/3-bar equilibration, oven-dry, and rewet, respectively. Field state (Db_f) is the bulk density of a soil sample at field soil water content at time of sampling. The 1/3-bar equilibration ($Db_{1/3}$) is the bulk density of a soil sample that has been desorbed to 1/3 bar (33kPa). The oven-dry (Db_d) is the bulk density of a soil sample that has been dried in an oven at 105°C. The rewet (Db_r) is the bulk density of soil sample that has been equilibrated, air-dried, and reequilibrated. The Db_r is used to determine the irreversible shrinkage of soils and subsidence of organic soils. The determinations of these bulk density values, Db_f, $Db_{1/3}$, Db_d, and Db_r, are described in procedures 4A1a, 4A1d, 4A1h, and 4A1i, respectively. Bulk density also may be determined for moist soil cores of known volume (procedure 4A3a). The bulk density of a weak or loose soil material for which the clod or core method is unsuitable may be determined by the compliant cavity method (procedure 4A5).

REFERENCES

Blake, G.R. and K.H. Hartge. 1986. Bulk density. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:363-382.

5.4 Wire. The SSL uses a 28-awg coated copper wire.

5.5 Hairnets

5.6 Stock tags, 25.4-mm (1-in) diameter paper tag, with metal rim

5.7 Hook assembly for weighing below balance

5.8 Plexiglass water tank mounted on a fulcrum and lever to elevate tank

5.9 Oven, 105°C

5.10 Sieve, No. 10 (2-mm openings)

5.11 Rope, 3 m

5.12 Clothespins

5.13 Silt loam soil

5.14 Hot plate

5.15 Spray bottle

5.16 Liquid vapor trap. The SSL constructs a tin enclosure over hot plate with a chimney and duct to transfer vapor to water stream.

6. REAGENTS

6.1 Methyl ethyl ketone (MEK), practical (2-butanone)

6.2 Water

6.3 Alcohol

6.4 Liquid detergent. The SSL uses Liqui-Nox.

6.5 Dow Saran F-310 Resin. Available from Dow Chemical Company.

6.6 Plastic lacquer. Prepare plastic lacquer with resin to solvent ratios of 1:4 and 1:7 on a weight basis. Fill a 3.8-L (1-gal) metal paint can with 2700 ± 200 mL of solvent. Fill to the bottom of handle rivet. Add 540 g or 305 g of resin to make 1:4 or 1:7 plastic lacquer, respectively. For the initial field and laboratory coatings, use the 1:4 plastic lacquer. Use 1:7 plastic lacquer for the last two laboratory coats. The 1:7 plastic lacquer is used to conserve the resin and to reduce cost. In the field, mix solvent with a wooden stick. In the laboratory, stir solvent with a non-sparking, high speed stirrer while slowly adding resin. Stir plastic lacquer for 30 min at 25°C. Store plastic lacquer in covered plastic or steel containers. Acetone may be substituted for MEK.

7. PROCEDURE

Field

7.1 Collect natural clods, ≈ 100 to 200 cm^3 in volume (fist-sized), from the face of the excavation. Three clods per horizon are recommended. Remove a piece of soil larger than clod from the face of sampling pit. From this piece, prepare a clod by gently cutting or breaking protruded peaks and compacted material from clod. If roots are present, trim roots with shears. No procedure for sampling clods is applicable to all soils. Adjust field sampling techniques to meet field conditions at time of sampling.

7.2 Make a clothesline by stretching a rope between two fixed points. Tie clod with fine copper wire or place clod in a hairnet. If clod is dry, moisten surface with a fine mist of water. Quickly dip entire clod into plastic lacquer. Suspend clod from clothesline to dry. Dry clod for 30 min or until odor of solvent dissipates. If the value of Db$_f$ is required, store clods in waterproof plastic bags as soon as coating dries because coating is permeable to water vapor.

7.3 Pack clods in rigid containers to protect them during transport.

Laboratory

7.4 Prepare a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record weight (TAG) of tag and wire. Loop fine copper wire around clod, leaving a tail to which round stock tag is attached. Record weight of clod (CC1).

7.5 Dip clod in 1:4 plastic lacquer. Wait 7 min and then dip clod in 1:7 plastic lacquer. Wait 12 min and then dip clod in 1:7 plastic lacquer. Wait 55 min and then reweigh clod. If clod has adsorbed >3% plastic by clod weight or smells excessively of solvent, allow longer drying time, then reweigh clod and record weight (CC2).

7.6 The clod should be waterproof and ready for volume measurement by water displacement. Suspend the clod below the balance, submerge in water, and record weight (WMCW).

7.7 Dry clod in an oven at 105°C until weight is constant. Weigh oven-dry clod in air (WODC) and in water (WODCW) and record weights.

7.8 If clod contains >5% rock fragments by weight, remove them from clod. Place clod in a beaker and place on hot plate. Cover hot plate with a liquid vapor trap. Use a fume hood. Heat clod on hot plate in excess of 200°C for 3 to 4 h. The plastic coating disintegrates at temperatures above 200°C. After heating, clod should appear black and charred. Remove clod from hot plate, lightly coat with liquid detergent, and add hot water.

7.9 Wet sieve the cool soil through a 2-mm, square- hole sieve. Dry and record weight (RF) of rock fragments that are retained on the sieve. Determine rock fragment density by weighing them in air to obtain their mass and in water to obtain their volume. If rock fragments are porous and have a density similar to soil sample, do not correct clod mass and volume measurement for rock fragments.

7.10 Correct bulk density for weight and volume of plastic coating. The coating has an air-dry density of ≈ 1.3 g cc^{-1}. The coating loses 10 to 20% of its air-dry weight when dried in oven at 105°C.

8. CALCULATIONS

$$Db_f = \frac{WODC - RF - ODPC - TAG}{[(CC2 - WMCW)/WD] - (RF/PD) - (MPC/1.3)} \quad [1]$$

where:
Db$_f$ = bulk density in g cc^{-1} of <2-mm fabric at field sampled water state
WODC = weight of oven-dry coated clod
RF = weight of rock fragments
ODPC = MPC x 0.85, weight of oven-dry plastic coat
TAG = weight of tag and wire
CC2 = weight of clod after three laboratory plastic coats
WMCW= weight of coated clod in water before oven drying
WD = water density
PD = density of rock fragments

FABRIC-RELATED ANALYSES
BULK DENSITY (4A)
SARAN-COATED CLODS (4A1)
FIELD STATE (Db$_f$) (4A1a)

MPC = [(CC2 - CC1) + FCE] x RV   [2]

where:
MPC   = weight of plastic coat before oven-drying
CC1   = weight of clod before three laboratory plastic coats
RV   = percent estimate of remaining clod volume after cutting to obtain flat surface (~ 80%)
FCE   = 1.5 x [(CC2 - CC1)/3]   [3]

where:
FCE = estimate of field-applied plastic coat

$$Db_{od} = \frac{WODC - RF - ODPC - TAG}{[(WODC - WODCW)/WD] - (RF/PD) - (MPC/1.3)} \qquad [4]$$

where:
Db$_{od}$ = bulk density in g cc^{-1} of <2-mm fabric at oven dryness
WODCW   = weight of oven-dry coated clod in water

$$W_f = \frac{(CC2 - MPC) - (WODC - ODPC) \times 100}{WODC - RF - ODPC - TAG} \qquad [5]$$

where:
W$_f$ = percent water weight in sampled clod

9. REPORT

Bulk density is reported to the nearest 0.01 g cc^{-1} of <2-mm soil fabric. Report procedure code 4A1a.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Blake, G.R. and K.H. Hartge. 1986. Bulk density. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:363-382.

Brasher, B.R., D.P. Franzmeier, V.T. Volassis, and S.E. Davidson. 1966. Use of Saran resin to coat natural soil clods for bulk density and water retention measurements. Soil Sci. 101:108.

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FABRIC-RELATED ANALYSES
BULK DENSITY (4A)
SARAN-COATED CLODS (4A1)
1/3-BAR DESORPTION I ($Db_{1/3}$) (4A1d)

1. APPLICATION

Bulk density is used to convert data from a weight to a volume basis; to determine the coefficient of linear extensibility; to estimate saturated hydraulic conductivity; and to identify compacted horizons. The procedure 4A1d determines the bulk density value ($Db_{1/3}$) of a soil sample equilibrated at 1/3-bar (33 kPa).

2. SUMMARY OF METHOD

Natural clods are collected from the face of an excavation. One coat of plastic lacquer is applied in the field. Additional coats of plastic lacquer are applied in the laboratory. The clod is desorbed to 1/3 bar (33 kPa). After equilibration, the clod is weighed in air to measure its mass and in water to measure its volume. After the clod is dried in the oven at 105°C, its mass and volume are determined again. A correction is made for the mass and volume of rock fragments and for plastic coatings (Brasher et al., 1966; Blake and Hartge, 1986).

3. INTERFERENCES

Errors are caused by nonrepresentative samples. Only naturally occurring clods should be sampled. The whole soil bulk density may be overestimated because sampled clods frequently exclude the crack space between clods (Tisdale, 1951).

The penetration of plastic lacquer into the voids of sandy soils interferes with the corrections for mass and volume of the plastic coat and with the accuracy of water content determinations. Penetration can be reduced by spraying water on the clod and by immediately dipping the clod in the plastic lacquer. Dipping should be done as quickly as possible to reduce penetration of plastic.

Loss of soil during the procedure will void the analyses because all calculations are based on the oven-dry soil mass. Holes in the plastic coating, which are detected by escaping air bubbles from submerged clod, introduce errors in volume measurement. An inadequate evaporation of plastic solvent results in overestimation of the soil mass. A drying time of 1 h is usually sufficient time for evaporation of solvent. However, clods with high organic matter content may need to dry longer.

Clods placed in an unsealed plastic bag can lose moisture during storage prior to analysis. If clods irreversibly dry below 1/3-bar moisture content, then $Db_{1/3}$ values for 1/3 bar will be erroneous. Completely seal the plastic storage bag to prevent drying.

Bulk density is reported for <2-mm soil fabric. Correction for rock fragments with >2-mm diameters requires either knowledge or assumption of the rock fragment density. Estimate or measurement errors of rock fragment density will affect the accuracy of the value for soil bulk density. The porosity of the rock fragments is also a factor that must be considered when correcting the values for soil bulk density and water holding capacity.

4. SAFETY

Methyl ethyl ketone (MEK) is extremely flammable. A type B fire extinguisher should be in close proximity in the laboratory. No open flames are permitted while using MEK. The MEK vapor is classified as a sensory irritant. The 8 h time weighted average (TWA) exposure limit is 200 ppm, and the short term exposure limit (STEL) is 300 ppm (Occupational Safety and Health Administration, 1989). Avoid physical contact. Use with adequate ventilation. In closed buildings, use a fume hood. Keep in tightly closed containers. Use safety glasses, proper gloves, and a lab coat. Wash hands immediately after handling MEK. Additional information on the safe handling of MEK is available in Chemical Safety Data Sheet SD-83, Manufacturing Chemists' Association, Inc., 1825 Connecticut Avenue, NW, Washington, D.C.

Saran F-310 resin will decompose rapidly at temperatures >200°C releasing hydrogen chloride gas. Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

FABRIC-RELATED ANALYSES
BULK DENSITY (4A)
SARAN-COATED CLODS (4A1)
1/3-BAR DESORPTION I ($Db_{1/3}$) (4A1d)

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity

5.2 Pressure plate extractor with porous ceramic plate.

5.3 Air pressure, 1/3-Bar (33-kPa)

5.4 Rigid shipping containers. The SSL uses a compartmented, corrugated box.

5.5 Plastic bags, 1 mil, 127 x 89 x 330 mm

5.6 Wire. The SSL uses a 28-awg coated copper wire.

5.7 Hairnets

5.8 Stock tags, 25.4-mm (1-in) diameter paper tag, with metal rim

5.9 Hook assembly for weighing below balance

5.10 Plexiglass water tank mounted on a fulcrum and lever to elevate tank

5.11 Oven, 105°C

5.12 Sieve, No. 10 (2-mm openings)

5.13 Rope, 3 m

5.14 Clothespins

5.15 Knife

5.16 Tile cut-off saw with diamond blade

5.17 Silt loam soil

5.18 Hot plate

5.19 Desiccator with ceramic plate

5.20 Vacuum, 0.8 bars (80 kPa)

5.21 Metal probe

5.22 Spray bottle

5.23 Liquid vapor trap. The SSL constructs a tin enclosure over hot plate with a chimney and duct to transfer vapor to water stream.

5.24 Reinforced paper towels or cheesecloth

5.25 Tension table. The SSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.

6. REAGENTS

6.1 Methyl ethyl ketone (MEK), practical (2-butanone)

6.2 Water

6.3 Alcohol

6.4 Liquid detergent. The SSL uses Liqui-Nox.

6.5 Dow Saran F-310 Resin. Available from Dow Chemical Company.

6.6 Plastic lacquer. Prepare plastic lacquer with resin to solvent ratios of 1:4 and 1:7 on a weight basis. Fill a 3.8-L (1-gal) metal paint can with 2700 ±200 mL of solvent. Fill to the bottom of handle rivet. Add 540 g or 305 g of resin to make 1:4 or 1:7 plastic lacquer, respectively. For the initial field and laboratory coatings, use the 1:4 plastic lacquer. Use 1:7 plastic lacquer for the last two laboratory coats. The 1:7 plastic lacquer is used to conserve the resin and to reduce cost. In the field, mix solvent with a wooden stick. In the laboratory, stir solvent with a non-sparking, high speed stirrer while slowly adding resin. Stir plastic lacquer for 30 min at 25°C. Store plastic lacquer in covered plastic or steel containers. Acetone may be substituted for MEK.

7. PROCEDURE

Field

7.1 Collect natural clods, ≈ 100 to 200 cm^3 in volume (fist-sized), from the face of the excavation. Three clods per horizon are recommended. Remove a piece of soil larger than clod from the face of sampling pit. From this piece, prepare a clod by gently cutting or breaking protruded peaks and compacted

material from clod. If roots are present, trim roots with shears. No procedure for sampling clods is applicable to all soils. Adjust field sampling techniques to meet field conditions at time of sampling.

7.2 Make a clothesline by stretching a rope between two fixed points. Tie clod with fine copper wire or place clod in a hairnet. If the clod is dry, moisten surface with a fine mist of water. Quickly dip entire clod into plastic lacquer. Suspend clod from clothesline to dry. Dry clod for 30 min or until odor of solvent dissipates. If the value of Db$_f$ is required, store clods in waterproof plastic bags as soon as coating dries because coating is permeable to water vapor.

7.3 Pack clods in rigid containers to protect them during transport.

Laboratory

7.4 Prepare a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record weight (TAG) of tag and wire. Loop fine copper wire around clod, leaving a tail to which round stock tag is attached. Record weight of clod (CC1).

7.5 Dip clod in 1:4 plastic lacquer. Wait 7 min and then dip clod in 1:7 plastic lacquer. Wait 12 min and then dip clod in 1:7 plastic lacquer. Wait 55 min and then reweigh clod. If clod has adsorbed >3% plastic by clod weight or smells excessively of solvent, allow longer drying time, then reweigh clod and record weight (CC2).

7.6 With a diamond saw, cut a flat surface on the clod. Place cut clod surface on a tension table, maintained at 5-cm tension. Periodically check clod to determine if it has reached equilibrium by inserting metal probe, touching, or by weight comparison. When clod has reached equilibrium, remove clod and record weight (WSC).

7.7 If cut clod does not adsorb water, place clod in a desiccator on a water-covered plate with a 0-cm tension. Submerge only the surface of clod in the water. Add a few mL of alcohol. Use in-house vacuum and apply suction until clod has equilibrated at saturation. Remove clod and record weight (WSC).

7.8 Place clod in a pressure plate extractor. To provide good contact between clod and ceramic plate, cover ceramic plate with a 5-mm layer of silt loam soil and saturate with water. Place a sheet of reinforced paper towel or cheesecloth over the silt loam soil. Place surface of cut clod on paper towel. Close container and secure lid. Apply gauged air pressure of 1/3 bar (33 kPa). When water ceases to discharge from outflow tube, clod is at equilibrium. Extraction usually takes 3 to 4 weeks. Remove clod and record weight (WMC). Compare WMC to WSC. If WMC $\geq$ WSC, equilibrate clod on tension table and repeat desorption process.

7.9 Dip clod in the 1:4 plastic lacquer. Wait 7 min and then dip clod in 1:7 plastic lacquer. Wait 12 min and then dip clod in 1:7 plastic lacquer. Wait 12 min and dip clod in 1:7 plastic lacquer. After 55 min, reweigh clod and record weight (CC3). If clod has adsorbed >3% plastic by weight or smells excessively of solvent, allow longer drying time, then reweigh clod.

7.10 The clod should be waterproof and ready for volume measurement by water displacement. Suspend clod below the balance, submerge in water, and record weight (WMCW).

7.11 Dry clod in an oven at 105°C until weight is constant. Weigh oven-dry clod in air (WODC) and in water (WODCW) and record weights.

7.12 If clod contains >5% rock fragments by weight, remove them from clod. Place clod in a beaker and place on hot plate. Cover hot plate with a liquid vapor trap. Use a fume hood. Heat clod on hot plate in excess of 200°C for 3 to 4 h. The plastic coating disintegrates at temperatures above 200°C. After heating, clod should appear black and charred. Remove clod from hot plate, lightly coat with liquid detergent, and add hot water.

7.13 Wet sieve the cool soil through a 2-mm, square- hole sieve. Dry and record weight (RF) of rock fragments that are retained on the sieve. Determine rock fragment density by weighing them in air to obtain their mass and in water to obtain their volume. If rock fragments are porous and have a density similar to soil sample, do not correct clod mass and volume measurement for rock fragments.

7.14 Correct bulk density for weight and volume of plastic coating. The coating has an air-dry density of ≈ 1.3 g cc^{-1}. The coating loses 10 to 20% of its air-dry weight when dried in oven at 105°C.

8. CALCULATIONS

$$Db_{1/3} = \frac{WODC - RF - ODPC - TAG}{[(CC3 - WMCW)/WD] - (RF/PD) - (MPC/1.3)} \qquad [1]$$

where:
$Db_{1/3}$ = bulk density in g cc^{-1} of <2-mm fabric at 1/3-bar (33-kPa) tension
WODC = oven-dry coated clod weight
RF = weight of rock fragments
ODPC = MPC x 0.85, oven-dry plastic coat weight
TAG = tag and wire weight
CC3 = weight of equilibrated clod after four additional plastic coats
WMCW = weight of coated clod equilibrated at 1/3-bar (33-kPa) tension in water
PD = density of rock fragments
WD = water density

$$MPC = \{[(CC2 - CC1) + FCE] \times RV\} + (CC3 - WMC) \qquad [2]$$

where:
MPC = weight of plastic coat before oven-drying
CC2 = weight of clod after three laboratory plastic coats
CC1 = weight of clod before three laboratory plastic coats
RV = percent estimate of remaining clod volume after cutting to obtain flat surface (~ 80%)
WMC = weight of coated clod equilibrated at 1/3-bar (33 kPa) tension

$$FCE = 1.5 \times [(CC2 - CC1)/3] \qquad [3]$$

where:
FCE = field-applied plastic coat estimate

FABRIC-RELATED ANALYSES
BULK DENSITY (4A)
SARAN-COATED CLODS (4A1)
1/3-BAR DESORPTION I ($Db_{1/3}$) (4A1d)

$$Db_{od} = \frac{WODC - RF - ODPC - TAG}{[(WODC - WODCW)/WD] - (RF/PD) - (MPC/1.3)} \quad [4]$$

where:
Db_{od} = bulk density in g cc^{-1} of <2-mm, oven-dry fabric
WODCW = weight of oven-dry coated clod in water

$$W_{1/3} = \frac{(CC3 - MPC) - (WODC - ODPC) \times 100}{WODC - RF - ODPC - TAG} \quad [5]$$

where:
$W_{1/3}$ = percent water weight retained at 1/3-bar (33-kPa) tension

9. REPORT
Bulk density is reported to the nearest 0.01 g cc^{-1} of <2-mm soil fabric. Report procedure code 4A1d.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES

Blake, G.R., and K.H. Hartge. 1986. Bulk density. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:363-382.

Brasher, B.R., D.P. Franzmeier, V.T. Volassis, and S.E. Davidson. 1966. Use of Saran resin to coat natural soil clods for bulk density and water retention measurements. Soil Sci. 101:108.

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Tisdale, A.L. 1951. Comparison of methods of determining apparent density of soils. Aust. J. Agric. Res. 2:349-354.

FABRIC-RELATED ANALYSES
BULK DENSITY (4A)
SARAN-COATED CLODS (4A1)
OVENDRY (Db$_d$) (4A1h)

1. APPLICATION

Bulk density is used to convert data from a weight to a volume basis; to determine the coefficient of linear extensibility; to estimate saturated hydraulic conductivity; and to identify compacted horizons. The procedure 4A1h determines the bulk density value (Db$_d$) of an oven-dry soil sample.

2. SUMMARY OF METHOD

Natural clods are collected from the face of an excavation. One coat of plastic lacquer is applied in the field. Additional coats of plastic lacquer are applied in the laboratory. The clod is dried in an oven at 105°C and then weighed in air to measure its mass and in water to measure its volume. A correction is made for the mass and volume of rock fragments and for plastic coatings (Brasher et al., 1966; Blake and Hartge, 1986).

3. INTERFERENCES

Errors are caused by nonrepresentative samples. Only naturally occurring clods should be sampled. The whole soil bulk density may be overestimated because sampled clods frequently exclude the crack space between clods (Tisdale, 1951).

The penetration of plastic lacquer into the voids of sandy soils interferes with the corrections for mass and volume of the plastic coat and with the accuracy of water content determinations. Penetration can be reduced by spraying water on the clod and by immediately dipping the clod in the plastic lacquer. Dipping should be done as quickly as possible to reduce penetration of plastic.

Loss of soil during the procedure will void the analyses because all calculations are based on the oven-dry soil mass. Holes in the plastic coating, which are detected by escaping air bubbles from submerged clod, introduce errors in volume measurement. An inadequate evaporation of plastic solvent results in overestimation of the soil mass. A drying time of 1 h is usually sufficient time for evaporation of solvent. However, clods with high organic matter content may need to dry longer.

Bulk density is reported for <2-mm soil fabric. Correction for rock fragments with >2-mm diameters requires either knowledge or assumption of the rock fragment density. Estimate or measurement errors of rock fragment density will affect the accuracy of the value for soil bulk density. The porosity of the rock fragments is also a factor that must be considered when correcting the values for soil bulk density and water holding capacity.

4. SAFETY

Methyl ethyl ketone (MEK) is extremely flammable. A type B fire extinguisher should be in close proximity in the laboratory. No open flames are permitted while using MEK. The MEK vapor is classified as a sensory irritant. The 8 h time weighted average (TWA) exposure limit is 200 ppm, and the short term exposure limit (STEL) is 300 ppm (Occupational Safety and Health Administration, 1989). Avoid physical contact. Use with adequate ventilation. In closed buildings, use a fume hood. Keep in tightly closed containers. Avoid physical contact. Use safety glasses, proper gloves, and a lab coat. Wash hands immediately after handling MEK. Additional information on the safe handling of MEK is available in Chemical Safety Data Sheet SD-83, Manufacturing Chemists' Association, Inc., 1825 Connecticut Avenue, NW, Washington, D.C.

Saran F-310 resin will decompose rapidly at temperatures >200°C releasing hydrogen chloride gas. Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity
5.2 Rigid shipping containers. The SSL uses a compartmented, corrugated box.
5.3 Plastic bags, 1 mil, 127 x 89 x 330 mm
5.4 Wire. The SSL uses a 28-awg coated copper wire.
5.5 Hairnets

FABRIC-RELATED ANALYSES
BULK DENSITY (4A)
SARAN-COATED CLODS (4A1)
OVENDRY (Db$_d$) (4A1h)

5.6 Stock tags, 25.4-mm (1-in) diameter paper tag with metal rim

5.7 Hook assembly for weighing below balance

5.8 Plexiglass water tank mounted on a fulcrum and lever

5.9 Oven, 105°C

5.10 Sieve, no. 10 (2-mm openings)

5.11 Rope, 3 m

5.12 Clothespins

5.13 Hot plate

5.14 Spray bottle

5.15 Liquid vapor trap. The SSL constructs a tin enclosure over hot plate with a chimney and duct to transfer vapor to water stream.

5.16 Tension table. The SSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.

6. REAGENTS

6.1 Methyl ethyl ketone (MEK), practical (2-butanone).

6.2 Water.

6.3 Liquid detergent. The SSL uses Liqui-Nox.

6.4 Dow Saran F-310 Resin. Available from Dow Chemical Company.

6.5 Plastic lacquer. Prepare plastic lacquer with resin to solvent ratios of 1:4 and 1:7 on a weight basis. Fill a 3.8-L (1-gal) metal paint can with 2700 ±200 mL of solvent. Fill to the bottom of handle rivet. Add 540 g or 305 g of resin to make 1:4 or 1:7 plastic lacquer, respectively. For the initial field and laboratory coatings, use the 1:4 plastic lacquer. Use 1:7 plastic lacquer for the last two laboratory coats. The 1:7 plastic lacquer is used to conserve the resin and to reduce cost. In the field, mix solvent with a wooden stick. In the laboratory, stir solvent with a non-sparking, high speed stirrer while slowly adding resin. Stir plastic lacquer for 30 min at 25°C. Store plastic lacquer in covered plastic or steel containers. Acetone may be substituted for MEK.

7. PROCEDURE

Field

7.1 Collect natural clods, ≈ 100 to 200 cm^3 in volume (fist-sized), from the face of the excavation. Three clods per horizon are recommended. Remove a piece of soil larger than clod from the face of sampling pit. From this piece, prepare a clod by gently cutting or breaking protruded peaks and compacted material from clod. If roots are present, trim roots with shears. No procedure for sampling clods is applicable to all soils. Adjust field sampling techniques to meet field conditions at time of sampling.

7.2 Make a clothesline by stretching a rope between two fixed points. Tie clod with fine copper wire or place clod in a hairnet. If the clod is dry, moisten surface with a fine mist of water. Quickly dip entire clod into plastic lacquer. Suspend clod from clothesline to dry. Dry clod for 30 min or until odor of solvent dissipates. If the value of Db$_f$ is required, store clods in waterproof plastic bags as soon as coating dries because coating is permeable to water vapor.

7.3 Pack clods in rigid containers to protect them during transport.

Laboratory

7.4 Prepare a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record weight (TAG) of tag and wire. Loop fine copper wire around clod, leaving a tail to which round stock tag is attached. Record weight of clod (CC1).

7.5 Dip clod in 1:4 plastic lacquer. Wait 7 min and then dip clod in 1:7 plastic lacquer. Wait 12 min and then dip clod in 1:7 plastic lacquer. Wait 55 min and then reweigh clod. If clod has adsorbed >3% plastic by clod weight or smells excessively of solvent, allow longer drying time, then reweigh clod and record weight (CC2).

7.6 Dry clod in an oven at 105°C until weight is constant. Weigh oven-dry clod in air (WODC) and in water (WODCW) and record weights.

7.7 If clod contains >5% rock fragments by weight, remove them from clod. Place clod in a beaker and place on hot plate. Cover hot plate with a liquid vapor trap. Use a fume hood. Heat clod on hot plate in excess of 200°C for 3 to 4 h. The plastic coating disintegrates at temperatures above 200°C. After heating, clod should appear black and charred. Remove clod from hot plate, lightly coat with liquid detergent, and add hot water.

7.8 Wet sieve the cool soil through a 2-mm, square- hole sieve. Dry and record weight (RF) of rock fragments. that are retained on the sieve. Determine rock fragment density by weighing them in air to obtain their mass and in water to obtain their volume. If rock fragments are porous and have a density similar to soil sample, do not correct clod mass and volume measurement for rock fragments.

7.9 Correct bulk density for weight and volume of plastic coating. The coating has an air-dry density of ≈ 1.3 g cc^{-1}. The coating loses 10 to 20% of its air-dry weight when dried in oven at 105°C.

8. CALCULATIONS

$$Db_{od} = \frac{WODC - RF - ODPC - TAG}{[(WODC - WODCW)/WD] - (RF/PD) - (MPC/1.3)} \qquad [1]$$

where:
Db$_{od}$ = bulk density in g cc^{-1} of <2-mm, oven-dry fabric
WODC = weight of oven-dry coated clod
RF = weight of rock fragments
ODPC = MPC x 0.85, weight of oven-dry plastic coat
TAG = weight of tag and wire
PD = density of rock fragments
WODCW = weight of oven-dry coated clod in water
WD = water density

MPC = [(CC2 - CC1) + FCE] x RV   [2]

where:
MPC = weight of plastic coat before oven drying
CC2 = weight of clod after three laboratory plastic coats
CC1 = weight of clod before three laboratory plastic coats
RV = percent estimate of remaining clod volume after cutting to obtain flat surface (~ 80%)

FCE = 1.5 x [(CC2 - CC1)/3]   [3]

where:
FCE   = field-applied plastic coat estimate

9. REPORT

Bulk density is reported to the nearest 0.01 g cc^{-1} of <2-mm soil fabric. Report procedure code 4A1h.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Blake, G.R., and K.H. Hartge. 1986. Bulk density. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:363-382.

Brasher, B.R., D.P. Franzmeier, V.T. Volassis, and S.E. Davidson. 1966. Use of Saran resin to coat natural soil clods for bulk density and water retention measurements. Soil Sci. 101:108.

Occupational Safety and Health Administration. 1989. Federal Register. Air contaminants; final rule. 29 CFR Part 1910. Vol. 54. No. 12. p. 2452-2453. U.S. Govt. Print. Office, Washington, DC.

Tisdale, A.L. 1951. Comparison of methods of determining apparent density of soils. Aust. J. Agric. Res. 2:349-354.

FABRIC-RELATED ANALYSES
BULK DENSITY (4A)
SARAN-COATED CLODS (4A1)
REWET BULK DENSITY (Db_r) (4A1i)

1. APPLICATION

Bulk density is used to convert data from a weight to a volume basis; to determine the coefficient of linear extensibility; to estimate saturated hydraulic conductivity; and to identify compacted horizons. The rewet bulk density (Db_r) is used to determine irreversible shrinkage of soils and subsidence of organic soils. The procedure 4A1i determines the bulk density value (Db_r) of a rewetted soil sample.

2. SUMMARY OF METHOD

Natural clods are collected from the face of an excavation. One coat of plastic lacquer is applied in the field. Additional coats of plastic lacquer are applied at the laboratory. After equilibration, the clod is weighed in air to measure its mass and in water to measure its volume. The clod is air-dried, reequilibrated, and its mass and volume remeasured. After the clod is dried in the oven at 105°C, its mass and volume are determined again. A correction is made for the mass and volume of rock fragments and for plastic coatings (Brasher et al., 1966; Blake and Hartge, 1986).

3. INTERFERENCES

Errors are caused by nonrepresentative samples. Only naturally occurring clods should be sampled. The whole soil bulk density may be overestimated because sampled clods frequently exclude the crack space between clods (Tisdale, 1951).

The penetration of plastic lacquer into the voids of sandy soils interferes with the corrections for mass and volume of the plastic coat and with the accuracy of water content determinations. Penetration can be reduced by spraying water on the clod and by immediately dipping the clod in the plastic lacquer. Dipping should be done as quickly as possible to reduce penetration of plastic.

Loss of soil during the procedure will void the analyses because all calculations are based on the oven-dry soil mass. Holes in the plastic coating, which are detected by escaping air bubbles from submerged clod, introduce errors in volume measurement. Inadequate drying results in overestimation of the soil mass. An inadequate evaporation of plastic solvent results in overestimation of the soil mass. A drying time of 1 h is usually sufficient time for evaporation of solvent. However, clods with high organic matter content may need to dry longer.

Bulk density is reported for <2-mm soil fabric. Correction for rock fragments with >2-mm diameters requires either knowledge or assumption of the rock fragment density. Estimate or measurement errors of rock fragment density will affect the accuracy of the value for soil bulk density. The porosity of the rock fragments is also a factor that must be considered when correcting the values for soil bulk density and water holding capacity.

4. SAFETY

Methyl ethyl ketone (MEK) is extremely flammable. A type B fire extinguisher should be in close proximity in the laboratory. No open flames are permitted while using MEK. The MEK vapor is classified as a sensory irritant. The 8 h time weighted average (TWA) exposure limit is 200 ppm, and the short term exposure limit (STEL) is 300 ppm (Occupational Safety and Health Administration, 1989). Avoid physical contact. Use with adequate ventilation. In closed buildings, use a fume hood. Keep in tightly closed containers. Avoid physical contact. Use safety glasses, proper gloves, and a lab coat. Wash hands immediately after handling MEK. Additional information on the safe handling of MEK is available in Chemical Safety Data Sheet SD-83, Manufacturing Chemists' Association, Inc., 1825 Connecticut Avenue, NW, Washington, D.C.

Saran F-310 resin will decompose rapidly at temperatures >200°C releasing hydrogen chloride gas. Avoid contact with Fe, Zn, Cu, and Al in solution. Avoid all contact with strong bases.

5. EQUIPMENT
5.1 Electronic balance, ±0.01-g sensitivity
5.2 Pressure plate extractor with porous ceramic plate.

5.3 Air pressure, 1/3 Bar (33 kPa)

5.4 Rigid shipping containers. The SSL uses a compartmented, corrugated box.

5.5 Plastic bags, 1 mil, 127 x 89 x 330 mm

5.6 Wire. The SSL uses a 28-awg coated copper wire.

5.7 Hairnets

5.8 Stock tags, 25.4-mm (1-in) diameter paper tag, with metal rim

5.9 Hook assembly for weighing below balance

5.10 Plexiglass water tank mounted on a fulcrum and lever to elevate tank

5.11 Oven, 105°C

5.12 Sieve, No. 10 sieve (2-mm openings)

5.13 Rope, 3 m

5.14 Clothespins

5.15 Knife

5.16 Tile cut-off saw with diamond blade

5.17 Silt loam soil

5.18 Hot plate

5.19 Desiccator with ceramic plate

5.20 Vacuum, 0.8 bars (80 kPa)

5.21 Metal probe

5.22 Spray bottle

5.23 Liquid vapor trap. The SSL constructs a tin enclosure over hot plate with a chimney and duct to transfer vapor to water stream.

5.24 Reinforced paper towels or cheesecloth

5.25 Tension table. The SSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.

6. REAGENTS

6.1 Methyl ethyl ketone (MEK), practical (2-butanone).

6.2 Water.

6.3 Alcohol.

6.4 Liquid detergent. The SSL uses Liqui-Nox.

6.5 Dow Saran F-310 Resin. Available from Dow Chemical Company.

6.6 Plastic lacquer. Prepare plastic lacquer with resin to solvent ratios of 1:4 and 1:7 on a weight basis. Fill a 3.8-L (1-gal) metal paint can with 2700 ±200 mL of solvent. Fill to the bottom of handle rivet. Add 540 g or 305 g of resin to make 1:4 or 1:7 plastic lacquer, respectively. For the initial field and laboratory coatings, use the 1:4 plastic lacquer. Use 1:7 plastic lacquer for the last two laboratory coats. The 1:7 plastic lacquer is used to conserve the resin and to reduce cost. In the field, mix solvent with a wooden stick. In the laboratory, stir solvent with a non-sparking, high speed stirrer while slowly adding resin. Stir plastic lacquer for 30 min at 25°C. Store plastic lacquer in covered plastic or steel containers. Acetone may be substituted for MEK.

7. PROCEDURE

Field

7.1 Collect natural clods, ≈ 100 to 200 cm^3 in volume (fist-sized), from the face of the excavation. Three clods per horizon are recommended. Remove a piece of soil larger than clod from the face of sampling pit. From this piece, prepare a clod by gently cutting or breaking protruded peaks and compacted material from clod. If roots are present, trim roots with shears. No procedure for sampling clods is applicable to all soils. Adjust field sampling techniques to meet field conditions at time of sampling.

7.2 Make a clothesline by stretching a rope between two fixed points. Tie clod with fine copper wire or place clod in a hairnet. If the clod is dry, moisten surface with a fine mist of water. Quickly dip entire clod into plastic lacquer. Suspend clod from clothesline to dry. Dry clod for 30 min or until odor of solvent dissipates. If the value of Db$_f$ is required, store clods in waterproof plastic bags as soon as coating dries because coating is permeable to water vapor.

7.3 Pack clods in rigid containers to protect them during transport.

Laboratory

7.4 Prepare a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record weight (TAG) of tag and wire. Loop fine copper wire around clod, leaving a tail to which round stock tag is attached. Record weight of clod (CC1).

7.5 Dip clod in 1:4 plastic lacquer. Wait 7 min and then dip clod in 1:7 plastic lacquer. Wait 12 min and then dip clod in 1:7 plastic lacquer. Wait 55 min and then reweigh clod. If clod has adsorbed >3% plastic by clod weight or smells excessively of solvent, allow longer drying time, then reweigh clod and record weight (CC2).

7.6 With a diamond saw, cut a flat surface on the clod.

7.7 Place cut clod surface on a tension table, maintained at 5-cm tension. Periodically check clod to determine if it has reached equilibrium by inserting metal probe, touching, or by weight comparison. When clod has reached equilibrium, remove clod and record weight (WSC).

7.8 If cut clod does not adsorb water, place clod in a desiccator on a water-covered plate with a 0-cm tension. Submerge only the surface of clod in the water. Add a few mL of alcohol. Use in-house vacuum and apply suction until clod has equilibrated at saturation. Remove clod and record weight (WSC).

7.9 Place clod in a pressure plate extractor. To provide good contact between clod and ceramic plate, cover ceramic plate with a 5-mm layer of silt loam soil and saturate with water. Place a sheet of reinforced paper towel or cheesecloth over the silt loam soil. Place surface of cut clod on paper towel. Close container and secure lid. Apply gauged air pressure of 1/3 bar (33 kPa). When water ceases to discharge from outflow tube, clod is at equilibrium. Extraction usually takes 3 to 4 weeks. Remove clod and record weight (WMC). Compare WMC to WSC. If WMC $\geq$ WSC, equilibrate clod on tension table and repeat desorption process.

7.10 Dip clod in the 1:4 plastic lacquer. Wait 7 min and then dip clod in 1:7 plastic lacquer. Wait 12 min and then dip clod in 1:7 plastic lacquer. Wait 12 min and dip clod in 1:7 plastic lacquer. After 55 min, reweigh clod and record weight (CC3). If clod has adsorbed >3% plastic by weight or smells excessively of solvent, allow longer drying time, then reweigh clod.

7.11 The clod should be waterproof and ready for volume measurement by water displacement. Suspend clod below the balance, submerge in water, and record weight (WMCW).

7.12 Remove layer of plastic from flat surface of clod. Air-dry clod at room temperature ($\sim$ 20 to 25°C) for 4 to 6 days. Dry clod at 40 to 50°C for 2 to 3 days or until weight is constant.

7.13 Repeat steps 7.7, 7.8, and 7.9. After equilibrium is obtained, remove clod and record weight (WAR).

7.14 Dip clod in the 1:4 plastic lacquer. Wait 7 min and then dip clod in 1:7 plastic lacquer. Wait 12 min and then dip clod in 1:7 plastic lacquer. Wait 12 min and dip clod in 1:7 plastic lacquer. After 55 min, reweigh clod and record weight (CC3). If clod has adsorbed >3% plastic by weight or smells excessively of solvent, allow longer drying time, then reweigh clod.

7.15 After coating, record weight of clod suspended in air (CC4) and in water (WARW).

7.16 Dry clod in an oven at 105°C until weight is constant. Weigh oven-dry clod in air (WODC) and in water (WODCW) and record weights.

7.17 If clod contains >5% rock fragments by weight, remove them from clod. Place clod in a beaker and place on hot plate. Cover hot plate with a liquid vapor trap. Use a fume hood. Heat clod on hot plate in excess of 200°C for 3 to 4 h. The plastic coating disintegrates at temperatures above 200°C. After heating, clod should appear black and charred. Remove clod from hot plate, lightly coat with liquid detergent, and add hot water.

7.18 Wet sieve the cool soil through a 2-mm, square-hole sieve. Dry and record weight (RF) of rock fragments that are retained on the sieve. Determine rock fragment density by weighing them in air to obtain their mass and in water to obtain their volume. If rock fragments are porous and have a density similar to soil sample, do not correct clod mass and volume measurement for rock fragments.

7.19 Correct bulk density for weight and volume of plastic coating. The coating has an air-dry density of $\approx$ 1.3 g cc^{-1}. The coating loses 10 to 20% of its air-dry weight when dried in oven at 105°C.

8. CALCULATIONS

$$Db_{1/3} = \frac{WODC - RF - ODPC - TAG}{[(CC3 - WMCW)/WD] - (RF/PD) - (MPC1/1.3)} \qquad [1]$$

where:
$Db_{1/3}$ = bulk density in g cc^{-1} of <2-mm fabric at 1/3-bar (33-kPa) tension
WODC = weight of oven-dry coated clod
RF = weight of rock fragments
ODPC = MPC1 x 0.85, weight of oven-dry plastic coat
CC3 = weight of equilibrated clod after four additional plastic coats
WMCW = weight in water of coated clod equilibrated at 1/3-bar (33-kPa) tension
WD = water density
PD = density of rock fragments

MPC1 = {[(CC2 - CC1) + FCE] x RV} + (CC3-WMC)   [2]

where:
MPC1 = weight of plastic coat before air-drying and rewet
CC2 = weight of clod after three laboratory plastic coats
CC1 = weight of clod before three laboratory plastic coats
RV = percent estimate of remaining clod volume after cutting to obtain flat surface (~ 80%)
WMC = weight of coated clod equilibrated at 1/3-bar (33-kPa) tension

FABRIC-RELATED ANALYSES
BULK DENSITY (4A)
SARAN-COATED CLODS (4A1)
REWET BULK DENSITY (Db$_r$) (4A1i)

FCE = 1.5 x [(CC2 -CC1)/3]   [3]

where:
FCE   = field-applied estimate of applied plastic coat

$$Db_r = \frac{WODC - RF - ODPC - TAG}{[(CC4 - WARW)/WD] - (RF/PD) - (MPC2/1.3)}$$ [4]

where:
Db$_r$ = bulk density in g cc^{-1} <2-mm fabric at 1/3-bar (33-kPa) tension after rewetting
CC4   = weight of clod after twelve plastic coats
WARW   = weight in water of coated clod equilibrated at 1/3-bar (33-kPa) tension after rewet

MPC2 = {[(CC2-CC1) + FCE] x RV} + (CC3-WMC) + (CC4-WAR)   [5]

where:
MPC2   = weight of plastic coat after rewet and before oven drying
WAR   = weight of clod after rewet equilibration

$$Db_{od} = \frac{WODC - RF - ODPC - TAG}{(WODC - WODCW)WD - (RF/PD) - (MPC2/1.3)}$$ [6]

where:
Db$_{od}$ = bulk density in g cc^{-1} of <2-mm fabric at oven dryness
WODCW = weight in water of oven-dry coated clod

$$W_{1/3} = \frac{(CC3 - MPC1) - (WODC - ODPC) \times 100}{WODC - RF - ODPC - TAG}$$ [7]

where:
W$_{1/3}$ = percent water weight retained at 1/3-bar (33-kPa) tension

$$W_r = \frac{(CC4 - MPC2) - (WODC - ODPC) \times 100}{WODC - RF - ODPC - TAG}$$ [8]

where:
W$_r$ = percent water weight retained at 1/3-bar (33-kPa) tension after rewet

9. REPORT

Bulk density is reported to the nearest 0.01 g cc^{-1} of <2-mm soil fabric. Report water content percent using procedure code 4B1e.

10. PRECISION

Precision data are not available for this method.

11. REFERENCES

Blake, G.R., and K.H. Hartge. 1986. Bulk density. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:363-382.

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Tisdale, A.L. 1951. Comparison of methods of determining apparent density of soils. Aust. J. Agric. Res. 2:349-354.

BULK DENSITY
CORES (4A3)
FIELD MOIST (4A3a)

1. APPLICATION

Bulk density is used to convert data from a weight to a volume basis; to determine the coefficient of linear extensibility; to estimate saturated hydraulic conductivity; and to identify compacted horizons. Procedure 4A3a determines the bulk density value of a moist soil core of known volume.

2. SUMMARY OF METHOD

A metal cylinder is pressed or driven into the soil. The cylinder is removed extracting a sample of known volume. The moist sample weight is recorded. The sample is then dried in a oven and weighed.

3. INTERFERENCES

During coring process, compaction of the sample is a common problem. Compression can be estimated by comparing the soil elevation inside the cylinder with the original soil surface outside the cylinder. Rock fragments in the soil interfere with core collection. Dry or hard soils often shatter when hammering the cylinder into the soil. Pressing the cylinder into the soil reduces the risk of shattering the sample.

4. SAFETY

No known hazard exists with this procedure.

5. EQUIPMENT

5.1 Containers, air-tight, tared, with lids
5.2 Electronic balance, ±0.01-g sensitivity
5.3 Oven 105°C
5.4 Sieve, No. 10 (2 mm-openings)
5.5 Coring equipment. Sources described in Blake and Hartge (1986).

6. REAGENTS

None

7. PROCEDURE

7.1 Record the empty core weights (CW).

7.2 Prepare a flat surface, either horizontal or vertical, at the required depth in sampling pit.

7.3 Press or drive core sampler into soil. Use caution to prevent compaction. Remove core from the inner liner, trim protruding soil flush with ends of cylinder, and place in air-tight container for transport to laboratory. If soil is too loose to remain in the liner, use core sampler without the inner liner and deposit only the soil sample in air-tight container. Moisture cans can also be pushed directly into a prepared face. For fibrous organic materials, trim sample to fit snugly into a moisture can.

7.4 Dry core in an oven at 105°C until weight is constant. Record oven-dry weight (ODW).

7.5 Measure and record cylinder volume (CV).

7.6 If sample contains rock fragments, wet sieve sample through a 2-mm sieve. Dry and weigh the rock fragments that are retained on sieve. Record weight of rock fragments (RF). Determine density of rock fragments (PD).

8. CALCULATIONS

$$Db = \frac{ODW - RF - CW}{CV - (RF/PD)}$$

where:
Db   = bulk density of < 2-mm fabric at sampled, field water state (g cc^{-1})
ODW = oven-dry weight
RF   = weight of rock fragments
CW   = empty core weight
CV   = core volume
PD   = density of rock fragments

9. REPORT
Bulk density is reported as g cc^{-1} to the nearest 0.01 g cc^{-1}.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Blake, G.R., and K.H. Hartge. 1986. Bulk density. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:363-382.

FABRIC-RELATED ANALYSES
BULK DENSITY (4A)
COMPLIANT CAVITY (4A5)

1. APPLICATION

Bulk density is used to convert data from a weight to a volume basis; to estimate saturated hydraulic conductivity; and to identify compacted horizons. The compliant cavity procedure is designed to measure bulk density of weak or loose soil material for which the core or clod method is unsuitable. The compliant cavity procedure is particularly applicable to fragile, near-surface soil zones. This method also may be applicable to deeper zones. Zones as thin as 2 cm may be measured. The immediate soil surface is undisturbed in the procedure.

2. SUMMARY OF METHOD

The cavity volume on the zone surface is lined with thin plastic and water is added to a datum level. Soil is quantitatively excavated in a cylindrical form to the required depth. The difference between the initial volume and that after excavation is the sample volume. The excavated soil is dried in an oven and then weighed. A correction is made for the weight and volume of rock fragments.

3. INTERFERENCES

If soil cracks are present, select the sampling area so that crack space is representative of sample, if possible. If this is not possible, make measurements between the cracks and determine the areal percentage of total cracks or of cracks in specimen.

4. SAFETY

Follow standard field and laboratory safety precautions.

5. EQUIPMENT

5.1 Fabricated Plexiglass rings, 9-mm thick, 130-mm inside diameter, and $\geq$200-mm outside diameter. Make three 16-mm diameter holes that are 10 mm from the outer edge of ring. Position holes equidistant apart. Use three, 25 x 50 mm, Plexiglass pieces as guides. Attach two pieces on one side to form an "L". Allow a 15-mm gap to permit removal of soil material. On the other side, position the single piece in line with the longer leg of the "L" so that an adjacent, parallel line forms a diameter.

5.2 Make 50-mm thick foam rings from flexible polyurethane with an "Initial Load Displacement" of 15 to 18 kg. The foam rings have the same inside diameter as the Plexiglass rings.

5.3 Fabricate a 240-mm crossbar from 5 x 18 mm metal stock to which legs (25-mm high and 180 x 180 mm in cross section) are welded. Drill a hole 100 mm from one end of the crossbar and 7 mm from the edge and through which a no. 6 machine bolt is placed.

5.4 Mount hook gauge on crossbar. Make hook gauge from No. 6, round-headed, 100-mm long machine bolts and from hexagonal nuts. Obtain the machine bolts from toggle bolt assemblies. Sharpen the machine bolt to a sharp point. Drill a hole in the center of the crossbar. Insert the machine bolt in the hole. Place nuts above and below the crossbar. The two nuts adjust the hook length below the crossbar and provide rigidity. Hold the machine bolt by the tightened nuts and heat the bolt. After softening, sharply bend the bolt upward to form a U-shape.

5.5 Use wing nuts and three, 250- to 400-mm long, 10- to 13-mm diameter, threaded rods to mount and position the compliant cavity. Sharpen the rods. Place two regular nuts at the end of threaded rod to increase the area of surface struck.

5.6 Syringe, 60 mL

5.7 Plastic film, 1/2 mil, 380-mm wide or wider; 460-mm wide for larger ring.

5.8 Plastic bags, 105°C-capability, with ties

5.9 Sharpie pen

5.10 Graduate cylinders, plastic, 250 to 2000 mL

5.11 Level, small

5.12 Kitchen knife, small

5.13 Scissors, small, to cut fine roots

FABRIC-RELATED ANALYSES
BULK DENSITY (4A)
COMPLIANT CAVITY (4A5)

5.14 Hack saw blade to cut large roots
5.15 Weights for plastic film
5.16 Clothespins. If wind, use clothespins for corners of plastic film.
5.17 Hard rubber or plastic mallet
5.18 Sieve, square-hole, 10 mesh, 2 mm

6. REAGENTS
6.1 Water

7. PROCEDURE

7.1 Place a ring of plastic foam on ground and cover with rigid ring (130-mm inside diameter). Mount the assembly on the soil surface by securely driving threaded rods into the ground through holes in ring and by tightening ring with wing nuts.

7.2 Line cavity with 1/2-mL plastic. Fill cavity to tip of hook gauge with a known quantity of water from graduate cylinder.

7.3 Remove plastic film and water. Measure the volume of water to tip of hook gauge. This volume (Vd) is the measurement of cavity volume prior to excavation (dead space).

7.4 Excavate soil quantitatively and in a cylindrical form to the required depth. Fill the excavation cavity to tip of hook gauge with water from graduated cylinder. Measure the volume of water. This volume (Vf) is the measurement of excavated soil and dead space. The difference between the two water volumes (Vf - Vd) is the volume of excavated soil (Ve).

7.5 The excavated soil is dried in oven. If necessary, make a correction for weight and volume of >2-mm material (Vg) in sample and compute bulk density. The weight of macroscopic vegetal material (g cc^{-1}) also may be reported.

8. CALCULATIONS

8.1 Excavation volume (Ve)

$$Ve = Vf - Vd - Vg$$

where:
Ve   = Excavation volume of <2-mm fraction (cc)
Vf   = Water volume measurement of excavated soil and dead space (cc)
Vd   = Water volume measurement of dead space (cc)
Vg   = Gravel volume (>2mm- fraction) (cc). Calculate Vg by dividing the weight of >2-mm fraction by particle density of the >2-mm fraction. Default value of 2.65 g cc^{-1}.

8.2

$$Wf = Wo - Wc$$

where:
Wf   = oven-dry weight of <2-mm soil (g)
Wo = oven-dry weight of excavated soil (g)
Wc = oven-dry weight of rock fragments (g)

8.3 Bulk Density

$D_b = W_f/V_e$

where:
D_b = bulk density (g cc^{-1})
W_f = oven-dry weight of <2-mm soil (g)
V_e = excavation volume of <2-mm material (cc)

9. REPORT
Report bulk density (D_b) in g cc^{-1} and specify compliant cavity, procedure 4A5.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Grossman, R.B. 1983. Bulk density by excavation procedure using compliant cavity. Unpublished.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)

INTRODUCTION

Water retention is defined as the soil water content at a given soil suction. By varying the soil suction and recording the changes in soil water content, a water retention function is determined. The water retention function is dependent on particle-size distribution, clay mineralogy, organic matter, and structure or physical arrangement of the particles. The water retention function is also dependent upon hysteresis, i.e., whether the water is adsorbing or desorbing from the soil. The data collected in these procedures are from water desorption.

Two desorption procedures are commonly used to measure water retention, a suction method or a pressure method. The SSL uses the pressure method (U.S. Salinity Laboratory, 1954) with either a pressure-plate or pressure-membrane extractor. Procedure 4B1a (pressure-plate extraction) is used to determine moisture retention at 0.06, 0.1, or 1/3 bar (6, 10, 33 kPa) for nonswelling soils, loamy sand or coarser soil and for some sandy loams. In procedure 4B1a, <2-mm (sieved), air-dry soil samples are used. Procedures 4B1c and 4B1d (pressure-plate extractions) are used to measure moisture retention of natural clods and cores, respectively, that have been equilibrated at 0.06, 0.1, 1/3, or 1 bar (6, 10, 33, or 100 kPa). Procedures 4B1c and 4B1d are usually used in conjunction with the bulk density procedure 4A1d.

Procedure 4B1e (pressure-plate extraction) is used to determine the moisture retention of a clod equilibrated at 1/3 bar (33 kPa), air-dried, and reequilibrated. The resulting data are called rewet water retention data and are usually used in conjunction with the rewet bulk density data in procedure 4A1i to estimate changes in physical properties of a soil as it undergoes wetting and drying cycles. Procedure 4B2a (pressure-membrane extraction) is used to determine moisture retention at 15 bar (1500 kPa) for <2-mm (sieved), air-dry soil samples. Procedure 4B2b is used to measure moisture retention at 15 bar (1500 kPa) for <2-mm (sieved), field moist soil samples. Procedure 4B4 is used to determine field water content at the time of sampling for cores, clods, or bulk samples.

REFERENCES

U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
PRESSURE-PLATE EXTRACTION (4B1)
AIR-DRY, <2-mm (sieved) SAMPLES (4B1a)
(0.06, 0.1, 1/3, 1, or 2 Bar)

1. APPLICATION

The data collected from this pressure desorption procedure can be used to determine the water retention function, water-holding capacity, pore-size distribution, and porosity of a soil sample at a specific water content. The data are also used to calculate unsaturated hydraulic conductivity. Procedure 4B1a is used to determine the moisture retention at 0.06, 0.1, or 1/3 bar (6, 10, or 33 kPa) for nonswelling soils, loamy sand or coarser soils, and for some sandy loams.

2. SUMMARY OF METHOD

The pressure desorption method (U.S. Salinity Laboratory Staff, 1954) is used. A sample of <2-mm (sieved), air-dry soil is placed in a retainer ring sitting on a porous ceramic plate in a pressure-plate extractor. The plate is covered with water to wet the samples by capillarity. The sample is equilibrated at the specified pressures of 0.06, 0.1, 1/3, 1, or 2 bar (6, 10, 33, 100, or 200 kPa). The pressure is kept constant until equilibrium is obtained (Klute, 1986). The gravimetric moisture content is determined.

3. INTERFERENCES

A leaking pressure extractor prevents equilibration of samples. A quality control sample is included in each pressure-plate extractor to verify that the extractor is functioning properly and does not leak. The pressure should be monitored for stability. Equilibration must be done at constant temperature and humidity.

With extended use, the porous ceramic plate becomes clogged and water outflow is restricted. The plate is cleaned by flushing sequentially with 500 mL of 10% H_2O_2, 1000 mL of 0.045 N HCl, and 500 mL of distilled water. The solutions are pulled through the plate with a vacuum, and the waste is captured in a trap.

The rubber membrane on the bottom of the plate is checked for leaks. The membrane is inflated and then submerged in water. If air bubbles escape from the membrane, the plate is removed from service.

Laboratory-determined, water retention data are usually higher than field-determined, water retention data because the confining soil pressure is not present in the laboratory. Water retention data for soils with expansive clay is overestimated when sieved samples are used in place of natural soil fabric for tensions of 0.06, 0.1, and 1/3 bar (6, 10, and 33 kPa) (Young and Dixon, 1966).

4. SAFETY

High pressure plumbing must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure extractor lid. Ensure that the bolts are tightened before applying pressure. Do not drop the heavy lid.

5. EQUIPMENT

5.1 Pressure plate extractor

5.2 Electronic balance, ±0.01-g sensitivity

5.3 Oven, 105°C

5.4 Pressure source, regulator, and gauge.

5.5 Retainer rings. Use 10-mm height and 50-mm diameter rings for organic soils and 10-mm height and 40-mm diameter rings for all other soils.

5.6 Metal weighing cans with lids

6. REAGENTS

6.1 Distilled water

6.2 Hydrogen peroxide (H_2O_2), 10% solution. Dilute 333 mL of 30% H_2O_2, technical grade, in l L of distilled water.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
PRESSURE-PLATE EXTRACTION (4B1)
AIR-DRY, <2-mm (sieved) SAMPLES (4B1a)
(0.06, 0.1, 1/3, 1, or 2 Bar)

6.3 Hydrochloric acid (HCl), 0.05 *N*. Dilute 8 mL of concentrated HCl in 1 L of distilled water.
6.4 Ethyl alcohol, 95%, technical grade

7. PROCEDURE

7.1 Place the ceramic plate in a pressure plate extractor. Place retainer rings on the ceramic plate. Use 50-mm diameter rings for soils that are >12% in organic matter. Use 40-mm diameter rings for all other soils.

7.2 Fill retaining ring with 10 to 15 g of <2-mm (sieved), air-dry soil. Include a quality control sample with each plate.

7.3 Add water to cover the ceramic plate but not to cover the rings. Continue to add water until all samples have moistened by capillarity. If samples do not moisten, apply ethyl alcohol to the surface of the samples. Close the apparatus and let stand overnight.

7.4 Apply the specified pressure. Monitor the outflow tube for water discharge. Samples are equilibrated when water ceases to emit from the outflow tube.

7.5 When samples have equilibrated, quickly transfer the samples to tared moisture cans (M_c), cover with lids, and record the weights (M_{s+w}).

7.6 Remove lids, place samples in oven, and dry at 105°C until sample weights are constant. Record weights (M_s).

8. CALCULATIONS

$$H_2O\ \% \ = \ 100 \ x \ \frac{(M_{s+w} \ - \ M_s)}{(M_s \ - \ M_c)}$$

where:
$H_2O\ \%$ = Percent gravimetric water content
M_{s+w} = Weight of solids + H_2O + container
M_s = Weight of solids + container
M_c = Weight of container

9. REPORT
Report moisture content as a percentage of <2-mm, oven-dry soil weight. Report procedure code 4B1a and the equilibrium tension.

10. PRECISION
Precision data are available for this procedure. Quality control check samples are analyzed with the respective procedure. The number of observations, mean, standard deviation, and C.V. are reported in the following table for the respective procedure.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
PRESSURE-PLATE EXTRACTION (4B1)
AIR-DRY, <2-mm (sieved) SAMPLES (4B1a)
(0.06, 0.1, 1/3, 1, or 2 Bar)

Water Retention (bars)	N	Mean	Std.	C.V. Dev. (%)
0.06	4	40.05	1.21	2.95
0.1	13	37.34	1.44	3.86
0.33	150	33.01	0.97	2.95
1	2	19.93	1.32	6.60
2	60	17.81	1.00	5.60
16	147	11.80	0.46	3.88

11. REFERENCES

Klute, A. 1986. Water retention: Laboratory methods. *In* Klute, A.(ed.) Methods of soil analysis. Part 1. Physical and mineralogical Methods. Agronomy 9:635-662.

U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

Young, K.K., and J.D. Dixon. 1966. Overestimation of water content at field capacity from sieved-sample data. Soil Sci. 101:104-107.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
PRESSURE-PLATE EXTRACTION (4B1)
NATURAL CLODS (4B1c)
(0.06, 0.1, 1/3, or 1 Bar)

1. APPLICATION

The data collected in this pressure desorption procedure are used to determine the water retention function, water-holding capacity, pore-size distribution, and porosity of a natural clod at a specific water content. The data are also used to calculate unsaturated hydraulic conductivity. Procedure 4B1c is used to determine the moisture retention of natural clods at 0.06, 0.1, 1/3, or 1 bar (6, 10, 33, or 100 kPa).

2. SUMMARY OF METHOD

The pressure desorption method (U.S. Salinity Laboratory Staff, 1954) is used. Natural clods are placed on a tension table and equilibrated at a 5-cm tension. The clods are placed on a porous ceramic plate which is in a pressure-plate extractor. The sample is equilibrated at the specified pressures of 0.06, 0.1, 1/3, or 1 bar (6, 10, 33, or 100 kPa). The pressure is kept constant until equilibrium is obtained (Klute, 1986). The gravimetric moisture content is determined.

3. INTERFERENCES

A leaking pressure extractor prevents equilibration of samples. A quality control sample is included in each pressure-plate extractor to verify that the extractor is functioning properly and does not leak. The pressure should be monitored for stability. Equilibration must be done at constant temperature and humidity.

With extended use, the porous ceramic plate becomes clogged and water outflow is restricted. The plate is cleaned by flushing sequentially with 500 mL of 10% H_2O_2, 1000 mL of 0.045 N HCl, and 500 mL of distilled water. The solutions are pulled through the plate with a vacuum, and the waste is captured in a trap.

The rubber membrane on the bottom of the plate is checked for leaks in the gasket. The membrane is inflated and then submerged in water. If air bubbles escape from the membrane, the plate is removed from service.

Laboratory-determined, water retention data are usually higher than field-determined, water retention data because the confining soil pressure is not present in the laboratory.

4. SAFETY

High pressure plumbing must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure-apparatus lid. Ensure that the bolts are tightened before applying pressure. Do not drop the heavy lid.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity
5.2 Pressure plate extractor with porous ceramic plate.
5.3 Pressure source, regulator, and gauge.
5.4 Oven, 105°C
5.5 Retainer rings, 10-mm height and 40-mm diameter
5.6 Metal weighing cans with lids
5.7 Clothespins
5.8 Knife
5.9 Tile cut-off saw with diamond blade
5.10 Silt loam soil
5.11 Desiccator with ceramic plate
5.12 Vacuum, 0.8 bar (80 kPa)
5.13 Metal probe
5.14 Sieve, No. 10 (2-mm openings)

5.15 Hot plate

5.16 Fume hood

5.17 Reinforced paper towel or cheesecloth

5.18 Liquid vapor trap. The SSL constructs a tin enclosure over hot plate with a chimney and duct to transfer vapor to water stream.

5.19 Tension table. The SSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.

5.20 Stock tags, 25.4-mm (1-in) diameter paper tag, with metal rim

5.21 Wire. The SSL uses a 28-awg coated copper wire.

6. REAGENTS

6.1 Distilled water

6.2 Hydrogen peroxide (H_2O_2), 10% solution. Dilute 333 mL of 30% H_2O_2, technical grade, in l L of distilled water.

6.3 Hydrochloric acid (HCl), 0.05 *N*. Dilute 8 mL of concentrated HCl in 1 L of distilled water.

6.4 Ethyl alcohol, 95%, technical grade

6.5 Liquid detergent. The SSL uses Liqui-Nox.

6.6 Methyl ethyl ketone (MEK), practical (2-butanone).

6.7 Dow Saran F-310 Resin. Available from Dow Chemical Company.

6.8 Plastic lacquer. Prepare plastic lacquer with resin to solvent ratios of 1:4 and 1:7 on a weight basis. Fill a 3.8-L (1-gal) metal paint can with 2700 ± 200 mL of solvent. Fill to the bottom of handle rivet. Add 540 g or 305 g of resin to make 1:4 or 1:7 plastic lacquer, respectively. For the initial field and laboratory coatings, use the 1:4 plastic lacquer. Use 1:7 plastic lacquer for the last two laboratory coats. The 1:7 plastic lacquer is used to conserve the resin and to reduce cost. In the field, mix solvent with a wooden stick. In the laboratory, stir solvent with a non-sparking, high speed stirrer while slowly adding resin. Stir plastic lacquer for 30 min at 25°C. Store plastic lacquer in covered plastic or steel containers. Acetone may be substituted for MEK.

7. PROCEDURE

7.1 This procedure is usually combined with the bulk density procedure (4A1d).

7.2 Prepare a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record the weight of the tag and wire (TAG). Loop fine copper wire around the clod, leaving a tail to which the round stock tag is attached. Record the weight of the clod (CC1).

7.3 Dip the clod in the 1:4 plastic lacquer. Wait 7 min and then dip the clod in the 1:7 plastic lacquer. Wait 12 min and then dip the clod in the 1:7 plastic lacquer. Wait 55 min and then reweigh the clod. If the clod has adsorbed >3% in plastic by clod weight or smells excessively of solvent, allow longer drying time, then reweigh the clod and record the weight (CC2).

7.4 Cut a flat surface on the clod with a tile saw. Place the cut clod surface on a tension table that is maintained at 5-cm tension. Periodically check the clod by inserting a metal probe, touching, or by weight comparison to determine if it has reached equilibrium. When the clod has reached equilibrium, remove the clod and record the weight (WSC).

7.5 If cut clod does not adsorb water, place clod in a desiccator on a water-covered plate with a 0-cm tension. Submerge only the surface of clod in the water. Add a few mL of alcohol. Use in-house

vacuum and apply suction until clod has equilibrated at saturation. Remove the clod and record the weight (WSC).

7.6 Place the clod in a pressure-plate extractor. To provide good contact between the clod and ceramic plate, cover the ceramic plate with a 5-mm layer of silt loam soil and saturate with water. Place a sheet of reinforced paper towel or cheesecloth over the silt loam soil. Place cut clod surface on the paper towel. Prepare a saturated, sieved soil standard. Place several retaining rings on the ceramic plate. Fill the retaining rings with the soil standard. Close the container and secure lid.

7.7 Apply gauged air pressure of 0.06, 0.1, 1/3, or 1 bar (6, 10, 33, or 100 kPa). If more than one water retention point is requested, begin with the lowest pressure. When water stops discharging from the outflow tube, the clod is at equilibrium. Determine the gravimetric water content of the standard. If the water content of the standard is higher than twice the standard deviation, apply pressure for additional time. Recheck the standard. If the water content of the standard is lower than twice the standard deviation, rewet the clods and desorb again. If the water content of the standard is within acceptable limits, then the apparatus has functioned properly.

7.8 Remove the clod and record the weight (WMC). Compare WMC to WSC. If WMC $\geq$ WSC, reequilibrate the clod on the tension table and repeat the desorption process. If additional water retention points are requested, then repeat the desorption process at the next higher pressure. When the clod is equilibrated at 1/3 bar (33 kPa) and bulk density is to be measured, continue with procedure 4A1d.

7.9 Dry the clod in an oven at 105°C until weight is constant and record oven-dry weight (WODC).

7.10 If the clod contains >5% in rock fragments by weight, remove the rock fragments from the clod. Place the clod in a beaker and place on a hot plate. Cover the hot plate with a liquid vapor trap. Use a fume hood. Heat on a hot plate in excess of 200°C for 3 to 4 h. The plastic coating disintegrates at temperatures above 200°C. After heating, the clod should appear black and charred. Remove clod from hot plate, lightly coat with liquid detergent, and add hot water.

7.11 Wet sieve the cool soil through a square-hole, 2-mm sieve. Dry and record the weight (RF) of the rock fragments that are retained on the sieve. If the rock fragments are porous and have a density similar to the soil sample, do not correct the clod mass for the rock fragments.

8. CALCULATIONS

$$H_2O \% = \frac{(WMC - MPC) - (WODC - ODPC)}{WODC - RF - ODPC - TAG} \times 100 \qquad [1]$$

where:
$H_2O \%$ = percent gravimetric water content
WMC   = weight of equilibrated, coated clod
WODC   = weight of oven-dry coated clod
RF   = weight of rock fragments
ODPC   = MPC x 0.85, weight of oven-dry plastic coat
TAG   = weight of tag and wire

MPC   = {[(CC2 - CC1) + FCE] x RV}   [2]

where:
MPC   = weight of plastic coat before oven drying
CC2   = weight of clod after three laboratory plastic coats
CC1   = weight of clod before three laboratory plastic coats
RV   = percent estimate of remaining clod volume after cutting to obtain flat surface ($\sim$ 80%)

FCE   = 1.5 x [(CC2 - CC1)/3]   [3]

where:
FCE   = estimate of field-applied plastic coat, if applied

9. REPORT

Report moisture content as a percentage of <2-mm, oven-dry soil weight. Report procedure code 4B1c and the equilibrium pressure.

10. PRECISION

Precision data are not available for this procedure. A quality control check sample is included in each pressure extractor. With 150 observations, the mean, standard deviation, and C.V. for 1/3 bar are 33.01, 0.97, and 2.95%, respectively. With 13 observations, the mean, standard deviation, and C.V. for 0.1 bar are 37.34, 1.44, and 3.86%, respectively.

11. REFERENCES

Klute, A. 1986. Water retention: laboratory methods. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:635-662.

U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
PRESSURE-PLATE EXTRACTION (4B1)
SOIL CORES (4B1d)
(0.06, 0.1, 1/3, or 1 Bar)

1. APPLICATION

The data collected from this pressure desorption procedure are used to determine the water retention function, water-holding capacity, pore-size distribution, and porosity of a soil core at a specific water content. The data are also used to calculate unsaturated hydraulic conductivity. Procedure 4B1d is used to determine the moisture retention of soil cores at 0.06, 0.1, 1/3, or 1 bar (6, 10, 33, or 100 kPa)

2. SUMMARY OF METHOD

The pressure desorption procedure (U.S. Salinity Laboratory Staff, 1954) is used. A metal cylinder is pressed or driven into the soil. Upon removal from the soil, the cylinder extracts a sample of known volume. The sample weight is recorded. The sample is dried in the oven and then weighed. Soil core is placed on a tension table and equilibrated at a 5-cm tension. The cores are placed on a porous ceramic plate which is placed in a pressure-plate apparatus. The sample is equilibrated at the specified pressures of 0.06, 0.1, 1/3, or 1 bar (6, 10, 33, or 100 kPa). The pressure is kept constant until equilibrium is obtained (Klute, 1986). The gravimetric moisture content is determined.

3. INTERFERENCES

A leaking pressure extractor prevents equilibration of samples. A quality control sample is included in each pressure-plate extractor to verify that the extractor is functioning properly and does not leak. The pressure should be monitored for stability. Equilibration must be done at constant temperature and humidity.

With extended use, the porous ceramic plate becomes clogged and water outflow is restricted. The plate is cleaned by flushing sequentially with 500 mL of 10% H_2O_2, 1000 mL of 0.045 N HCl, and 500 mL of distilled water. The solutions are pulled through the plate with a vacuum, and the waste is captured in a trap.

The rubber membrane on the bottom of the plate is checked for leaks in the gasket. The membrane is inflated and then submerged in water. If air bubbles escape from the membrane, the plate is removed from service.

Laboratory-determined, water retention data are usually higher than field-determined, water retention data because the confining soil pressure is not present in the laboratory.

Compaction of the sample during the coring process is a common problem. Compression can be estimated by comparing the soil elevation inside the cylinder with the original soil surface outside the cylinder. Rock fragments in the soil interfere with core collection. Dry or hard soils often shatter when hammering the cylinder into the soil. Pressing the cylinder into the soil reduces the risk of shattering the sample.

4. SAFETY

High pressure plumbing must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure-apparatus lid. Ensure that the bolts are tightened before applying pressure. Do not drop the heavy lid.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity
5.2 Pressure plate extractor with porous ceramic plate.
5.3 Pressure source, regulator, and gauge.
5.4 Oven, 105°C
5.5 Retainer rings, 10-mm height and 40-mm diameter
5.6 Metal weighing cans with lids
5.7 Silt loam soil
5.8 Desiccator with ceramic plate

5.9 Vacuum, 0.8 bar (80 kPa)

5.10 Metal probe

5.11 Sieve, No. 10 (2-mm openings)

5.12 Fume hood

5.13 Reinforced paper towel or cheesecloth

5.14 Coring equipment. Sources described in Blake and Hartge (1986).

5.15 Tension table. The SSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.

6. REAGENTS

6.1 Distilled water

6.2 Hydrogen peroxide (H_2O_2), 10% solution. Dilute 333 mL of 30% H_2O_2, technical grade, in l L of distilled water.

6.3 Hydrochloric acid (HCl), 0.05 *N*. Dilute 8 mL of concentrated HCl in 1 L of distilled water.

6.4 Alcohol.

6.5 Liquid detergent, The SSL uses Liqui-Nox.

7. PROCEDURE

7.1 This procedure can be combined with the bulk density procedure (4A1d).

7.2 Record the weight (CW) of the sampling cylinders.

7.3 Prepare a flat surface in the sampling pit, either horizontal or vertical, at the required depth. Press or drive the core sampler into the soil. Use caution to prevent compaction. Remove the core from the inner liner, trim the protruding soil flush with the cylinder ends, and place core in an air-tight container for transport to the laboratory.

7.4 Place the flat core surface on a tension table maintained at 5-cm tension. Periodically, check the core by inserting a metal probe, touching, or by weight comparison to determine if core has reached equilibrium. When the core has reached equilibrium, remove the core and record the weight (WSC).

7.5 If core does not adsorb water, place core in a desiccator on a water-covered plate with a 0-cm tension. Submerge only the surface of core in the water. Add a few mL of alcohol. Use in-house vacuum and apply suction until core has equilibrated at saturation. Remove the core and record the weight (WSC).

7.6 Place the core in a pressure plate extractor. To provide good contact between the core and ceramic plate, cover the ceramic plate with a 5-mm layer of silt loam soil and saturate with water. Place a sheet of reinforced paper towel or cheesecloth over the silt loam soil. Place the flat core surface on the paper towel. Prepare a saturated, sieved soil standard. Place several retaining rings on the ceramic plate. Fill the retaining rings with the soil standard. Close the container and secure lid.

7.7 Apply gauged air pressure of 0.06, 0.1, 1/3, or 1 bar (6, 10, 33, or 100 kPa). If more than one water retention point is requested, begin with the lowest pressure. When water stops discharging from the outflow tube, the core is at equilibrium. Determine the gravimetric water content of the standard. If the water content of the standard is higher than twice the standard deviation, apply pressure for additional time. Recheck the standard. If the water content of the standard is lower than twice the standard deviation, rewet the cores and desorb again. If the water content of the standard is within acceptable limits, then the apparatus has functioned properly.

7.8 Remove core and record the weight (WMC). Compare WMC to WSC. If WMC $\geq$ WSC, reequilibrate core on the tension table and repeat the desorption process. If additional water retention points are requested, then repeat the desorption process at the next higher pressure. When the core is equilibrated at 1/3 bar (33 kPa) and bulk density is to be measured, continue with method 4A1d.

7.9 Dry core in an oven at 105°C until weight is constant and record oven-dry weight (WODC).

7.10 If sample contains rock fragments, wet sieve the sample through a 2-mm sieve. Dry and weigh the rock fragments that are retained on the sieve. Record the weight of the rock fragments (RF).

8. CALCULATIONS

$$H_2O \ \% \ = \ 100 \ x \ \frac{(M_{s+w} - M_s)}{(M_s - M_c - RF)}$$

where:
$H_2O \ \%$ = percent gravimetric water content
M_{s+w} = weight of solids + H_2O + container
M_s = weight of solids + container
M_c = weight of container
RF = weight of rock fragments

9. REPORT

Report moisture content as a percentage of <2-mm, oven-dry soil weight. Report procedure code 4B1d and the equilibrium tension.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Klute, A. 1986. Water retention: laboratory methods *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:635-662.
U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
PRESSURE PLATE EXTRACTION (4B1)
REWET (4B1e)

1. APPLICATION

The data collected from this pressure desorption procedure are used to determine the water retention function, water-holding capacity, pore-size distribution, and porosity of a soil sample at a specific water content. The data are also used to calculate unsaturated hydraulic conductivity. The rewet water retention data are used in conjunction with the rewet bulk density data in procedure 4A1i to estimate the change in physical properties of a soil as it undergoes wetting and drying cycles.

2. SUMMARY OF METHOD

The pressure desorption method (U.S. Salinity Laboratory Staff, 1954) is used. Natural clods are placed on a tension table and equilibrated at a 5-cm tension. The clods are placed on a porous ceramic plate in a pressure-plate extractor. The sample is equilibrated at 1/3 bar (33kPa). The pressure is kept constant until equilibrium is obtained (Klute, 1986). The equilibrated clod weight is recorded. The clod is air dried and then placed on a tension table and desorbed again. After the second equilibration, the gravimetric moisture content is determined.

3. INTERFERENCES

A leaking pressure extractor prevents equilibration of samples. A quality control sample is included in each pressure-plate extractor to verify that the extractor is functioning properly and does not leak. The pressure should be monitored for stability. Equilibration must be done at constant temperature and humidity.

With extended use, the porous ceramic plate becomes clogged and water outflow is restricted. The plate is cleaned by flushing sequentially with 500 mL of 10% H_2O_2, 1000 mL of 0.045 N HCl, and 500 mL of distilled water. The solutions are pulled through the plate with a vacuum, and the waste is captured in a trap.

The rubber membrane on the bottom of the plate is checked for leaks in the gasket. The membrane is inflated and then submerged in water. If air bubbles escape from the membrane, the plate is removed from service.

Laboratory-determined, water retention data are usually higher than field-determined, water retention data because the confining soil pressure is not present in the laboratory.

4. SAFETY

High pressure plumbing must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure-plate lid. Ensure that the bolts are tightened before applying pressure. Do not drop the heavy lid.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity

5.2 Pressure plate extractor with porous ceramic plate.

5.3 Pressure source, regulator, and gauge.

5.4 Oven, 105°C-capability

5.5 Retainer rings, 10-mm height and 40-mm diameter

5.6 Metal weighing cans with lids

5.7 Clothespins

5.8 Knife

5.9 Tile cut-off saw with diamond blade

5.10 Silt loam soil

5.11 Desiccator with ceramic plate

5.12 Vacuum, 0.8 bar (80 kPa)

5.13 Metal probe

5.14 Sieve, No. 10 (2-mm openings)

5.15 Hot plate

5.16 Fume hood

5.17 Reinforced paper towel or cheesecloth

5.18 Liquid vapor trap. The SSL constructs a tin enclosure over hot plate with a chimney and duct to transfer vapor to water stream.

5.19 Tension table. The SSL constructs a tension table by placing porous firebricks, covered with reinforced paper towels, in a tub of water.

5.20 Stock tags, 25.4-mm (1-in) diameter paper tag, with metal rim

5.21 Wire. The SSL uses a 28-awg coated copper wire.

6. REAGENTS

6.1 Distilled water

6.2 Hydrogen peroxide (H_2O_2), 10% solution. Dilute 333 mL of 30% H_2O_2, technical grade, in l L of distilled water.

6.3 Hydrochloric acid (HCl), 0.05 *N*. Dilute 8 mL of concentrated HCl in 1 L of distilled water.

6.4 Ethyl alcohol, 95%, technical grade

6.5 Liquid detergent. The SSL uses Liqui-Nox.

6.6 Methyl ethyl ketone (MEK), practical (2-butanone).

6.7 Dow Saran F-310 Resin. Available from Dow Chemical Company.

6.8 Plastic lacquer. Prepare plastic lacquer with resin to solvent ratios of 1:4 and 1:7 on a weight basis. Fill a 3.8-L (1-gal) metal paint can with 2700 ±200 mL of solvent. Fill to the bottom of handle rivet. Add 540 g or 305 g of resin to make 1:4 or 1:7 plastic lacquer, respectively. For the initial field and laboratory coatings, use the 1:4 plastic lacquer. Use 1:7 plastic lacquer for the last two laboratory coats. The 1:7 plastic lacquer is used to conserve the resin and to reduce cost. In the field, mix solvent with a wooden stick. In the laboratory, stir solvent with a non-sparking, high speed stirrer while slowly adding resin. Stir plastic lacquer for 30 min at 25°C. Store plastic lacquer in covered plastic or steel containers. Acetone may be substituted for MEK.

7. PROCEDURE

7.1 This procedure is usually used in conjunction the bulk density procedure 4A1i.

7.2 Prepare a round stock tag with sample identification number. Cut the copper wire and loop around the clod. Record the weight of the tag and wire (TAG). Loop fine copper wire around the clod, leaving a tail to which the round stock tag is attached. Record the weight of the clod (CC1).

7.3 Dip the clod in the 1:4 plastic lacquer. Wait 7 min and then dip the clod in the 1:7 plastic lacquer. Wait 12 min and then dip the clod in the 1:7 plastic lacquer.i3yL017 9g 1.3855 -1.2If the clodı˝0.55412 min anhahe dsorbce

6.4

6.5 eriodilab lınd ck1:7 plastic lacquer.CC1).

6.6 PROCEDURE

7.7 Place the clod in a pressure plate extractor. To provide good contact between the clod and ceramic plate, cover the ceramic plate with a 5-mm layer of silt loam soil and saturate with water. Place a sheet of reinforced paper towel or cheesecloth over the silt loam soil. Place cut clod surface on the paper towel. Prepare a saturated, sieved soil quality control standard. Place several retaining rings on the ceramic plate. Fill the retaining rings with the soil standard. Close the container and secure lid.

7.8 Apply gauged air pressure of 0.06, 0.1, 1/3, or 1 bar (6, 10, 33, or 100 kPa). If more than one water retention point is requested, begin with the lowest pressure. When water stops discharging from the outflow tube, the clod is at equilibrium. Determine the gravimetric water content of the standard. If the water content of the standard is higher than twice the standard deviation, apply pressure for additional time. Recheck the standard. If the water content of the standard is lower than twice the standard deviation, rewet the clods and desorb again. If the water content of the standard is within acceptable limits, then the apparatus has functioned properly.

7.9 Remove the clod and record the weight (WMC). Compare WMC to WSC. If WMC $\geq$ WSC, reequilibrate the clod on the tension table and repeat the desorption process. If additional water retention points are requested, then repeat the desorption process at the next higher pressure. When the clod is equilibrated at 1/3 bar (33 kPa) and bulk density is to be measured, continue with procedure 4A1d.

7.10 Air-dry the clod at room temperature ($\approx$ 20 to 25°C) for 4 to 6 days. Dry the clods at 40 to 50°C for 2 to 3 days or until weights are constant.

7.11 Repeat steps 7.5, 7.6, 7.7, and 7.8. Record clod weight after equilibration (WMC2). Determine bulk density as described in method 4A1i.

7.12 Dry the clod in oven at 105°C until weight is constant and record oven-dry weight (WODC).

7.13 If the clod contains >5% in rock fragments by weight, remove the rock fragments from the clod. Place the clod in a beaker and place on a hot plate. Cover the hot plate with a liquid vapor trap. Use a fume hood. Heat on a hot plate in excess of 200°C for 3 to 4 h. The plastic coating disintegrates at temperatures above 200°C. After heating, the clod should appear black and charred. Remove clod from hot plate, lightly coat with liquid detergent, and add hot water.

7.14 Wet sieve the cool soil through a square-hole, 2-mm sieve. Dry and record the weight (RF) of the rock fragments that are retained on the sieve. If the rock fragments are porous and have a density similar to the soil sample, do not correct the clod mass for the rock fragments.

8. CALCULATIONS

$$(WMC - MPC) - (WODC - ODPC) \text{ x } 100$$

$$H_2$$

RF   = weight of rock fragments
ODPC   = MPC x 0.85, weight of oven-dry plastic coat

MPC = {[(CC2 - CC1) + FCE] x RV}   [2]

where:
MPC   = weight of plastic coat before oven drying
CC2   = weight of clod after three laboratory plastic coats
CC1   = weight of clod before three laboratory plastic coats
RV   = percent estimate of remaining clod volume after cutting to obtain flat surface ($\sim$ 80%)

FCE = 1.5 x [(CC2 - CC1)/3]   [3]

where:
FCE   = estimate of field applied plastic coat, if applied

$$H_2O_r \% = \frac{(WMC2 - MPC2) - (WODC - ODPC2) \times 100}{WODC - RF - ODPC}$$ [4]

where:
H_2O_r %   = percent water weight retained at 1/3-bar tension after rewetting
WMC2   = weight of equilibrated, coated clod after rewetting
MPC2   = weight of moist plastic coat after rewetting. Same as MPC unless additional plastic coats
            were added.
OPC2   = MPC2 x 0.85, weight of oven-dry plastic coat.

9. REPORT

Report moisture content as a percentage of <2-mm, oven-dry soil mass. Use procedure code 4B1e for rewet water content (H_2O_r %) and procedure code 4B1c for water contents before wetting (H_2O %).

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Klute, A. 1986. Water retention: laboratory methods. *In* A. Klute (ed.), Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:635-662.
U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
PRESSURE-MEMBRANE EXTRACTION (4B2)
AIR-DRY, <2 mm (sieved) SAMPLES (4B2a)
(15 Bar)

1. APPLICATION

The data collected in this procedure are from water desorption. The resulting data are used to determine the water retention function, water-holding capacity, pore-size distribution, and porosity of a soil sample at a specific water content. The data are also used to calculate unsaturated hydraulic conductivity. Procedure 4B2a is used to determine the moisture retention at 15 bar (1500 kPa) for <2-mm (sieved), air-dry soil samples.

2. SUMMARY OF METHOD

The pressure desorption procedure (U.S. Salinity Laboratory Staff, 1954) is used. A sample of <2-mm (sieved), air-dry soil is placed in a retainer ring sitting on a cellulose membrane in a pressure-membrane extractor. The membrane is covered with water to wet the samples by capillarity. The sample is equilibrated at 15 bar (1500 kPa). The pressure is kept constant until equilibrium is obtained (Klute, 1986). The gravimetric moisture content is determined.

3. INTERFERENCES

A leaking pressure extractor prevents equilibration of samples. A quality control sample is included in each pressure-membrane extractor to verify that the extractor is functioning properly and does not leak. The pressure should be monitored for stability. Equilibration must be done at constant temperature and humidity. Samples that do not wet by capillarity are moistened with ethyl alcohol.

Laboratory-determined, moisture retention data are usually higher than field-determined, water retention data because the confining soil pressure is not present in the laboratory.

4. SAFETY

High pressure plumbing must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure-appratus lid. Ensure that the bolts are tightened before applying pressure. Do not drop the heavy lid.

5. EQUIPMENT
5.1 Pressure membrane extractor
5.2 Cellulose membrane
5.3 Retainer rings. Use 10-mm height and 50-mm diameter rings for organic soils and 10-mm height and 40-mm diameter rings for all other soils.
5.4 Electronic balance, ±0.01-g sensitivity
5.5 Oven, 105°C
5.6 Pressure source, regulator, and gauge.
5.7 Metal weighing cans, tared, with lids
5.8 Vacuum trap assembly
5.9 Vacuum, 0.8 bar (80 kPa)

6. REAGENTS
6.1 Ethyl alcohol, 95%, technical grade

7. PROCEDURE

7.1 Submerge a cellulose membrane in distilled water for 12 h or more before use. Install the wet cellulose membrane in the pressure extractor.

7.2 Add water and retaining rings. Add enough water to keep membrane moist. Water level should be less than height of retaining rings. Use 5-cm diameter rings for soils that are >12% in organic matter. Use 4-cm diameter rings for all other soils.

7.3 Fill retaining rings with 10 to 15 g of <2-mm (sieved), air-dry soil sample. Include a quality control sample with each plate. Continue to add water until all samples have moistened by capillarity. If samples do not moisten, apply ethyl alcohol to the surface of the sample. Allow ethyl alcohol to evaporate. Cover samples with a sheet of plastic to reduce evaporation, close the extractor, and let stand overnight.

7.4 Remove excess water on the plate with a vacuum and trap assembly.

7.5 Assemble the extractor and uniformly tighten the bolts. Torque the bolts on both sides of the hinge to 200 psi (138.0 kPa). Torque the remaining bolts to 150 psi (103.5 kPa).

7.6 Increase air pressure ~ 1.5 bar (150 kPa) every 15 min until 15 bar (1500 kPa) is reached. After 4 h, apply the pressure differential by closing the valve that joins the mercury circuit and by opening the pressure release valve until air is forced through the mercury. Quickly close the pressure release valve. This forces the rubber diaphragm against the top of the samples. The samples are equilibrated when water ceases to emit from the outflow tube.

7.7 At equilibrium, open the extractor and quickly transfer the samples to moisture cans, cover with lids, and record the weights (M_{s+w}).

7.8 Remove the lids, place samples in the oven, and dry at 105°C until weights are constant. Remove samples from the oven, replace the lids, allow cans to cool to ambient temperature, and record the weights (M_s).

7.9 Record the weights of the empty cans (M_c).

8. CALCULATIONS

$$H_2O \text{ \%} = 100 \text{ x } \frac{(M_{s+w} - M_s)}{(M_s - M_c)}$$

where:
H_2O % = percent gravimetric water content
M_{s+w} = weight of solids + H_2O + container
M_s = weight of solids + can
M_c = weight of container

9. REPORT
Report moisture content as a percentage of <2-mm, oven-dry soil mass.

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FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
PRESSURE-PLATE EXTRACTION (4B2)
AIR-DRY, <2 mm (sieved) SAMPLES (4B2a)
(15 Bar)

10. PRECISION

Precision data are not available for this procedure. A quality control check sample is included in every batch of 36 samples. The mean, standard deviation, and C.V. are 11.8, 0.46, and 3.88%, respectively.

11. REFERENCES

Klute, A. 1986. Water retention: laboratory methods. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:635-662.

U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
PRESSURE-PLATE EXTRACTION (4B2)
FIELD MOIST, <2 mm (sieved) SAMPLES (4B2b)
(15 Bar)

1. APPLICATION

The data collected from this pressure desorption procedure are used to determine the water retention function, water-holding capacity, pore-size distribution, and porosity of a soil sample at a specific water content. The data are also used to calculate unsaturated hydraulic conductivity. Procedure 4B2b is used to determine the moisture retention at 15 bar (1500 kPa) for <2-mm (sieved), air-dry soil samples.

2. SUMMARY OF METHOD

The pressure desorption method (U.S. Salinity Laboratory Staff, 1954) is used. A sample of <2-mm (sieved) moist soil is placed in a retainer ring sitting on a cellulose membrane in a pressure-membrane extractor. The membrane is covered with water to wet the samples by capillarity. The sample is equilibrated at 15 bar (1500 kPa). The pressure is kept constant until equilibrium is obtained (Klute, 1986). The gravimetric moisture content is determined.

3. INTERFERENCES

A leaking pressure extractor prevents equilibration of samples. A quality control sample is included in each pressure-membrane extractor to verify that the extractor is functioning properly and does not leak. The pressure should be monitored for stability. Equilibration must be done at constant temperature and humidity. Samples that do not wet by capillarity are moistened with ethyl alcohol.

Laboratory-determined, water retention data are usually higher than field-determined, water retention data because the confining soil pressure is not present in the laboratory.

4. SAFETY

High pressure plumbing must be maintained in good working order. Ensure that the pressure is zero before removing bolts from the pressure-plate apparatus lid. Ensure that the bolts are tightened before applying pressure. Do not drop the heavy lid.

5. EQUIPMENT
5.1 Pressure membrane extractor
5.2 Cellulose membrane
5.3 Retainer rings. Use 10-mm height and 50-mm diameter rings for organic soils and 10-mm height and 40-mm diameter rings for all other soils.
5.4 Electronic balance, ±0.01-g sensitivity
5.5 Oven, 105°C
5.6 Pressure source, regulator, and gauge.
5.7 Metal weighing cans, tared, with lids
5.8 Vacuum trap assembly
5.9 Vacuum 0.8 bar (80 kPa)

6. REAGENTS
6.1 Ethyl alcohol, 95%, technical grade

7. PROCEDURE

7.1 Submerge a cellulose membrane in distilled water for 12 h or more before use. Install the wet cellulose membrane in the pressure apparatus.

7.2 Add water and retaining rings. Add enough water to keep membrane moist. Water level should be less than height of retaining rings. Use 5-cm diameter rings for soils that are >12% in organic matter. Use 4-cm diameter rings for all other soils.

7.3 Fill retaining rings with 10 to 15 g of <2-mm (sieved), field moist soil sample. Include a quality control sample with each plate. Continue to add water until all samples have moistened by capillarity. If samples do not moisten, apply ethyl alcohol to the surface of the sample. Cover samples with a sheet of plastic to reduce evaporation, close the extractor, and let stand overnight.

7.4 Remove excess water on the plate with a vacuum and trap assembly.

7.5 Assemble the extractor and uniformly tighten the bolts. Torque the bolts on both sides of the hinge to 200 psi (138.0 kPa). Torque the remaining bolts to 150 psi (103.5 kPa).

7.6 Increase air pressure $\approx$ 1.5 bar (150 kPa) every 15 min until 15 bar (1500 kPa) is reached. After 4 h, apply the pressure differential by closing the valve that joins the mercury circuit and by opening the pressure release valve until air is forced through the mercury. Quickly close the pressure release valve. This forces the rubber diaphragm against the top of the samples. The samples are equilibrated when water ceases to emit from the outflow tube.

7.7 At equilibrium, open the apparatus and quickly transfer the samples to moisture cans, cover with lids, and record the weights (M_{s+w}).

7.8 Remove the lids, place samples in the oven, and dry at 105°C until weights are constant. Remove samples from the oven, replace the lids, allow cans to cool to ambient temperature, and record the weights (M_s).

7.9 Record the weights of the empty cans (M_c).

8. CALCULATIONS

$$H_2O \text{ \%} = 100 \text{ x } \frac{(M_{s+w} - M_s)}{(M_s - M_c)}$$

where:
H_2O % = percent gravimetric water content
M_{s+w} = weight of solids + H_2O + container
M_s = weight of solids + container
M_c = weight of container

9. REPORT
Report moisture content as a percentage of <2-mm, oven-dry soil mass.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is included in every batch of 36 samples. The mean, standard deviation, and C.V. are 11.8, 0.46, and 3.88%, respectively.

11. REFERENCES

Klute, A. 1986. Water retention: laboratory methods. _In_ A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:635-662.

U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
FIELD STATE (4B4)

1. APPLICATION
Field water content can be obtained by weighing, drying, and reweighing a soil sample. The resulting data are used to estimate the water content at the time of sampling.

2. SUMMARY OF METHOD
Soil samples are collected in the field. The samples are stored in plastic or metal containers to prevent drying and then transported to the laboratory. Gravimetric moisture content is determined (Gardner, 1986).

3. INTERFERENCES
Leaks in the plastic or metal storage containers cause the samples to dry, resulting in an underestimation of the field water content.

4. SAFETY
Use insulated gloves to remove samples from the oven.

5. EQUIPMENT
5.1 Electronic balance, ±0.01-g sensitivity
5.2 Oven, 105°C
5.3 Moisture cans, tared

6. REAGENTS
None

7. PROCEDURE

7.1 Collect soil samples in the field. Place samples in air-tight, metal or plastic containers.

7.2 Record sample weight (M_{s+w}).

7.3 Dry sample in an oven at 105°C until weight is constant. Record oven-dry weight ($M_{s)}$.

7.4 Record tare weight of container (M_c).

8. CALCULATIONS

$$H_2O \% = 100 \text{ x } \frac{(M_{s+w} - M_s)}{(M_s - M_c)}$$

where:
$H_2O \%$ = percent gravimetric water content
M_{s+w} = weight of solids + H_2O + container
M_s = weight of solids + container
M_c = weight of container

9. REPORT
Report moisture content as a percentage of <2-mm, oven-dry soil mass.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES

Gardner, W.H. 1986. Water Content. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:493-544.

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
AIR-DRY (4B5)
CORRECTION FOR CRYSTAL WATER (6F3)

1. APPLICATION

Soil properties generally are expressed on an oven-dry weight basis. The calculation of the air-dry/oven-dry (AD/OD) ratio (procedure 4B5) is used to adjust all results to an oven-dry basis and, if required in a procedure, to calculate the sample weight that is equivalent to the required oven-dry soil weight.

Gypsiferous soils are a special case because gypsum ($CaSO_4 \cdot 2H_2O$) loses most of its two water molecules at 105°C. Properties of gypsiferous soils that are reported on an oven-dry weight basis should be converted to include the weight of crystal water in gypsum. In procedure 4B5, the AD/OD ratio is calculated. This ratio is used to convert soil properties to an oven-dry basis. In procedure 6F3, the AD/OD ratio is converted to a crystal water basis (Nelson et al., 1978). The inclusion of weight of crystal water in gypsum allows the properties of gypsiferous soils to be compared with those properties of nongypsiferous soils. This conversion also avoids the possible calculation error of obtaining >100% gypsum when the data are expressed on an oven-dry basis (Nelson, 1982).

2. SUMMARY OF METHOD

A sample is weighed, dried to a constant weight in an oven, and reweighed. The moisture content is expressed as a ratio of the air-dry to the oven-dry weight (AD/OD) in procedure 4B5. Soil properties of gypsiferous soils that are reported on an oven-dry weight basis are converted to include the weight of the crystal water in procedure 6F3. When reporting the water content of gypsiferous soils, the crystal water content must be subtracted from the total oven-dry water content. The AD/OD ratio is corrected to a crystal water basis when the gypsum content of the soil is $\geq 1\%$. Gypsum content of the soil is determined in procedure 6F1a.

3. INTERFERENCES

Traditionally, the most frequently used definition for a dry soil is the soil mass after it has come to a constant weight at a temperature of 100 to 110°C (American Society for Testing and Materials, 1993). Many laboratory ovens are not capable of maintaining this prescribed temperature range. Temperatures that are >50°C may promote oxidation or decomposition of some forms of organic matter.

Samples may not reach a constant weight with overnight drying. Do not add moist samples to an oven with drying samples unless the drying samples have been in the oven for at least 12 to 16 h. Soil samples may adsorb significant amounts of moisture from the atmosphere after cooling. Prompt weighing, i.e., <30 min after samples have cooled, helps to eliminate this problem. During the weighing or drying processes, the nonuniform weight of weighing vessels, sample contamination, or sample loss may lead to erroneous results.

The removal of structural water, most commonly in gypsum, can produce a positive error. When reporting the water content of gypsiferous soils, the crystal water content must be subtracted from the total oven-dry water content. Gypsum, hydrous oxides, and amorphous material may be affected.

4. SAFETY

Use heat resistant gloves to remove weighing containers from a hot oven. No other significant hazard is associated with this procedure. Follow standard laboratory procedures.

5. EQUIPMENT
5.1 Electronic balance, ±0.01-g sensitivity
5.2 Oven, thermostatically controlled, 105 ± 5°C
5.3 Thermometer, 0 to 200°C
5.4 Aluminum foil dish, 57-mm diameter x 15-mm deep, with lifting tab

FABRIC-RELATED ANALYSES
WATER RETENTION (4B)
AIR-DRY (4B5)
CORRECTION FOR CRYSTAL WATER (6F3)

6. REAGENTS

No reagents are required for this determination. The aluminum foil moisture dishes are not reused.

7. PROCEDURE

7.1 Tare the moisture dishes. Label each moisture dish with the appropriate sample number.

7.2 Add 10 to 20 g of air-dry soil to each moisture dish. Weigh the dish plus the sample and record the weight to the nearest 0.01 g. Place the sample dish in a drying oven set at 105 $\pm$ 5°C. Allow the sample to remain in the oven overnight (12 to 16 h).

7.3 Do not add moist samples to an oven with drying samples unless the drying samples have been in the oven for at least 12 to 16 h.

7.4 Remove the sample dish and allow to cool before reweighing. Record the oven-dry weight to the nearest 0.01 g.

7.5 Do not allow the sample dish to remain at room temperature for >30 min before reweighing.

7.6 Discard sample and dish. Do not use sample for other analyses.

7.7 Refer to the calculations for the correction for crystal water of gypsum in gysiferous soils.

8. CALCULATIONS

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AD/OD ratio = AD/OD
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where:
AD = air-dry weight
OD = oven-dry weight

$$H_2O = \frac{(AD - OD) \times 100}{OD}$$

where:
H_2O = % Water content

$$AD = \frac{OD \text{ required}}{[1 - (H_2O/100)]}$$

$$AD/OD_c = \frac{AD/OD_{uc}}{[1 + (Gypsum \times 0.001942)]}$$

where:
AD/OD$_c$ = Air-dry/oven-dry ratio, corrected basis, gysiferous soils
AD/OD$_{uc}$ = Air-dry/oven-dry ratio, uncorrected basis
Gypsum   = % Gypsum uncorrected (procedure 6F1a)

$$H_2O = \frac{[\% \ H_2O - (Gypsum \ x \ 0.1942)]}{[1 + (Gypsum \ x \ 0.001942)]}$$

where:
H$_2$O   = % Water content, corrected basis, gypsiferous soils
Gypsum   = % Gypsum uncorrected (procedure 6F1a)

9. REPORT

Report the AD/OD ratio as a dimensionless value to the nearest 0.01 unit.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

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FABRIC-RELATED ANALYSES
WATER RETENTION DIFFERENCE (WRD) (4C)

The calculation of the water retention difference (WRD) is considered the initial step in the approximation of the AWC. The WRD, as defined by the SSL Staff (1992), is a calculated value that denotes the volume fraction for water in the whole soil that is retained between 15-bar suction and an upper limit of usually 1/3 or 1/10 bar suction. The upper limit (lower suction) is selected so that the volume of water retained approximates the volume of water held at field capacity. The 1/10-, 1/3- and 15-bar gravimetric water contents are then converted to a whole soil volume basis by multiplying by the bulk density ($Db_{1/3}$) and adjusting downward for the volume fraction of rock fragments, if present in the soil. The lower suctions, e.g., 0.1 or 0.05 bar, are used for coarse materials. Refer to Soil Survey Staff Division Staff (1993) and Grossman et al. (1994) for additional discussion on coarse materials and the significance of soil water content at lower suctions, e.g., 0.05 and 0.1 bar, as well as suggestions for the selection of these lower suctions for the determination of water retention difference (WRD).

FABRIC-RELATED ANALYSES
WATER RETENTION DIFFERENCE (4C)
BETWEEN 1/3-BAR AND 15-BAR TENSION (4C1)

The SSL calculates the WRD between 1/3- and 15-bar suctions in the whole soil by procedure 4C1. The WRD is reported as centimeters of water per centimeter of depth of soil (cm cm^{-1}), but the numbers do not change when other units, e.g., in in^{-1} or ft ft^{-1} are needed. The WRD with $W_{1/3}$ as the upper limit as determined by procedure 4C1 is reported as cm cm^{-1}. This WRD is calculated on a whole-soil base as follows:

$$WRD_{ws} = \frac{(W_{1/3<2mm} - W_{15<2mm}) \ x \ (Db_{1/3<2mm}) \ x \ Cm \ x \ P_w}{100}$$

where:
WRD_{ws} = Volume fraction (cm^3 cm^{-3}) of water retained in the whole soil between 1/3-bar and 15-bar suction reported in cm cm^{-1}. This is numerically equivalent to inches of water per inch of soil (in in^{-1}).
$W_{1/3<2mm}$ = Weight percentage of water retained at 1/3-bar suction on a <2-mm base (g H$_2$O   100 g^{-1}) soil.
$W_{15<2mm}$ = Weight percentage of water retained at 15-bar suction on a <2-mm base (g H$_2$O   100 g^{-1}) soil. If available, moist 15-bar (procedure 4B2b) is the first option in the WRD calculation; otherwise, dry 15-bar (procedure 4B2a) is used.
$Db_{1/3<2mm}$ = Bulk density at 1/3-bar water content on a <2-mm base (g cc^{-1}).
P_w = Density of water (1 cm^3 H$_2$O 1 g^{-1} H$_2$O).
Cm   = Coarse fragment conversion factor. If no coarse fragments, Cm = 1. If coarse fragments are present, calculate Cm as follows:

$$Cm = \frac{Vol \ moist \ <2\text{-}mm \ fabric \ (cm^3)}{Vol \ moist \ whole \ soil \ (cm_3)}$$

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$$Cm = \frac{100 - \text{Vol}>2mm}{100}$$

where:

Vol>2mm = Volume percentage of the >2-mm fraction.

FABRIC-RELATED ANALYSES
WATER RETENTION DIFFERENCE (WRD) (4C)
BETWEEN 1/10-BAR AND 15-BAR TENSION (4C2)

The SSL also calculates the WRD between 1/10-bar ($W_{1/10}$) and 15-bar suctions (W_{15}) by procedure 4C2. This WRD value can be calculated by substituting the $W_{1/10}$ in place of $W_{1/3}$ in the equation for procedure 4C1. The $W_{1/10}$ may be used as the upper limit of plant available water for coarse soil materials.

FABRIC-RELATED ANALYSES
WATER RETENTION DIFFERENCE (WRD) (4C)
BETWEEEN 1/3-BAR REWET AND 15-BAR (AIR-DRY) TENSION (4C3)

The SSL also calculates the WRD between 1/3-bar rewet (W_r) and W_{15} by procedure 4C3. This WRD value can be calculated by substituting the W_r in place of $W_{1/3}$ in the equation for 4C1. The W_r is used for organic materials.

REFERENCES

Grossman, R.B., T. Sobecki, and P. Schoeneberger. 1994. Soil interpretations for resource soil scientists. Soil water. Tech. Workbook. USDA-SCS, Lincoln, NE.

Soil Survey Division Staff. 1993. Soil survey manual. USDA. Handb. No. 18. U.S. Govt. Print. Office, Washington, DC.

FABRIC-RELATED ANALYSES
COEFFICIENT OF LINEAR EXTENSIBILITY (COLE) (4D)

Coefficient of linear extensibility (COLE) is a derived value that denotes the fractional change in the clod dimension from a dry to a moist state (Franzmeier and Ross, 1968; Grossman et al., 1968; Holmgren, 1968). COLE may be used to make inferences about shrink-swell capacity and clay mineralogy. The COLE concept does not include irreversible shrinkage such as that occurring in organic and some andic soils. Certain soils with relatively high contents of montmorillonite clay have the capacity to swell significantly when moist and to shrink and crack when dry. This shrink-swell potential is important for soil physical qualities (large, deep cracks in dry seasons) as well as for genetic processes and soil classification (Buol et al., 1980).

COLE can also be expressed as percent, i.e., linear extensibility percent (LEP). LEP = COLE x 100. The LEP is not the same as LE. In the *Keys to Soil Taxonomy* (Soil Survey Staff, 1994), linear extensibility (LE) of a soil layer is the product of the thickness, in centimeters, multiplied by the COLE of the layer in question. The LE of a soil is defined as the sum of these products for all soil horizons (Soil Survey Staff, 1994). Refer to Soil Survey Staff (1994) for additional discussion of LE.

FABRIC-RELATED ANALYSES
COEFFICIENT OF LINEAR EXTENSIBILITY (COLE) (4D)
AIR-DRY OR OVEN-DRY TO 1/3-BAR TENSION (4D1)

The SSL calculates the COLE for the whole soil by procedure 4D1 (air-dry or ovendry to 1/3-bar suction). The COLE value is reported in cm cm^{-1}. Calculate COLE when coarse fragments are present as follows:

$$\text{COLE}_{ws} = \{1/[\text{Cm} \times (\text{Db}_{1/3<2mm}/\text{Db}_{d<2mm}) + (1 - \text{Cm})]\}^{1/3} - 1$$

COLLE_{ws} = Coefficient of linear extensibility on a whole-soil base.
$\text{Db}_{1/3<2mm}$ = Bulk density at 1/3-bar water content on a <2-mm base (g cc^{-1}).
$\text{Db}_{d<2mm}$ = Bulk Density, oven-dry or air-dry, on a <2-mm base (g cc^{-1}).
Cm = Coarse fragment (moist) conversion factor. If no coarse fragments, Cm = 1. If coarse fragments are present, calculate Cm as follows:

$$\text{Cm} = \frac{\text{Vol moist <2-mm fabric (cm}^3\text{)}}{\text{Vol moist whole soil (cm}_3\text{)}}$$

OR (alternatively)

$$Cm = \frac{100 - Vol>2mm}{100}$$

where:
Vol>2mm = Volume percentage of the >2-mm fraction.

If no coarse fragments, Cm = 1, the previous equation reduces as follows:

$$COLE_{ws} = (Db_{1/3<2mm}/Db_{1/3<2mm})^{1/3} - 1$$

COLE   = Coefficient of linear extensibility on a whole-soil base.
$Db_{d<2mm}$ = Bulk Density, oven-dry or air-dry, on a <2-mm base (g cc^{-1}).
$Db_{1/3<2mm}$ = Bulk Density at 1/3 water content on a <2-mm base (g cc^{-1}).

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Franzmeier, D.P., and S.J. Ross, Jr. 1968. Soil swelling: Laboratory measurement and relation to other soil properties. Soil Sci. Soc. Amer. Proc. 32:573-577.
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FABRIC-RELATED ANALYSES
MICROMORPHOLOGY (4E)
THIN SECTIONS (4E1)
PREPARATION (4E1a)

1. APPLICATION

Micromorphology is used to identify fabric types, skeleton grains, weathering intensity, illuviation of argillans, and to investigate genesis of soil or pedological features.

2. SUMMARY OF METHOD

A soil clod is impregnated with a polymer resin (Innes and Pluth, 1970). A flat surface of the soil sample is glued to a glass slide. The soil sample is cut and ground to a thickness of ≈ 30 μm. The thin section is examined with a petrographic microscope (Anon. 1987; Cady, et al., 1986).

3. INTERFERENCES

Impregnation of the soil sample must be complete, or the sample will disintegrate during

7. PROCEDURE

Sample Collection

7.1 Collect samples by any procedure that does not disturb the natural structure. Core samplers are commonly used. A satisfactory procedure for some soils is to use a knife or trowel to carve a clod that fits in bulk density box cells, a tin box, matchbox, or a round ice-cream container.

7.2 Place clods in an upright position in the container. Mark the top of clod with a thumb tack, staple, or pin to ensure proper orientation.

7.3 Select clods from bulk samples if orientation is of no interest. Avoid coated clods with Saran or other plastic because coatings interfere with the grinding after the clod is sectioned.

7.4 Place clods in small plastic bags to avoid contamination from other samples during transit. Pack irregular clods in box cells or containers with light weight material to avoid breakage. Unless fragility is affected, the prevention of moisture loss is usually unnecessary as most samples are usually dried before impregnation.

7.5 The whole core or clod can be impregnated, but better results are generally obtained with specimens that are 5 cm^3 or smaller. Remove specimens from the sample with a small chisel, a probe (ice pick), an ordinary hacksaw, or a jeweler's hacksaw.

Sample Preparation

7.6 Place the soil sample in a disposable heat- and chemical-resistant beaker and place in a glass desiccator. Evacuate the air from the desiccator and dry the sample overnight at 80°C. The natural structure of the soil samples is better preserved by the technique of freeze-drying. Impregnation of the freeze-dried samples may be an improvement over oven-dried samples. In preparation for the proceeding step, bring the freeze-dried or oven-dried sample to ~ 80°C.

Mixing plastic solution

7.7 Many good resins are on the market. The NSSL uses Scotchcast. Add two parts of part A by weight to three parts of part B. For best results, raise part A and part B to ~ 80°C before mixing. Weigh parts to an accuracy of 2% before mixing. Mix until a uniform color is obtained.

Impregnation

7.8 Open the desiccator which contains the dry samples, add the heated plastic solution, and evacuate all the air from the sample. Release the vacuum and again evacuate the air. Do not mistake boiling solution under evacuated conditions for escaping air bubbles from the sample material.

7.9 Cure the impregnated soil overnight in the oven at 105°C. After curing, the block is ready for sectioning. Disposable containers can be cut with the cooled samples during sectioning.

Cutting and Rough Grinding

7.10 With a diamond saw blade, cut the sample block into 13-mm thick chips that are small enough to fit on a regular petrographic slide.

7.11 With a slurry of successively finer abrasives, grind one surface smooth on the revolving lap until the surface is highly polished. Experience is required to determine the mixture of abrasive and water that gives the best results for each grade of abrasive. If the sample surface tends to pull apart or to

react with water, dry and reimpregnate the small chip or polish it by hand on a glass plate. Alternatively, grind the block with an abrasive and lubricate with ethylene glycol.

7.12 Clean the sample free of all abrasive material. An ultrasonic bath is recommended. Dry thoroughly.

Mounting
7.13 Burnish petrographic slides to a uniform thickness.

7.14 Firmly attach the chip to the burnished slide with a strong, transparent bonding agent. Use a thermoplastic cement or epoxide. Mix the resin and hardener according to the product instructions. Allow entrapped air to rise to the top. Apply a thin layer of epoxide to the slide and to the chip. Place the chip obliquely on the slide and lower slowly. Move the chip back and forth with moderate pressure to remove entrapped air bubbles and excess epoxide. Clamp with a spring clamp and cure at ~ 50°C for 1 h.

Final Grinding
7.15 Consult the Petro-thin operation and maintenance instructions for proper operation.

7.16 Clean the glass of excess cement.

7.17 Use the Petro-thin to cut off the excess sample and grind the sample to ≈ 30 μm with the diamond lap. Examine the section frequently under a polarizing microscope during the final stages of grinding. If quartz is present in the sample, use it to judge thickness. If the sample is ~ 0.030 mm thick, the quartz interference colors are of the first order, i.e., white, gray, and pale yellow.

7.18 If a Petro-thin is not available, trim the mounted sample with a diamond saw blade to a thickness of 50 to 100 μm. Begin with the coarse abrasive and lap by hand until the sample is relatively thin. Use successively finer abrasives.

7.19 Care and considerable practice are needed to develop the dexterity required to handle an almost finished section without overgrinding. Use the finest abrasive to finish grinding on ground-glass plates. Wash the section free of abrasive and dry thoroughly.

Seating Cover Glass
7.20 Heat the finished section and the cover slip to ≈ 40°C. Spread a small quantity of epoxide over the surface of the thin section and the cover slip. Wait a few seconds for the air bubbles to escape. Place the cover glass obliquely on one end of the section and lower very slowly. If any air bubbles remain, remove them by pressing lightly on the cover glass with a soft eraser. As the section cools, but before the plastic hardens, remove excess epoxy with a razor blade. After the epoxy hardens, remove the final thin film with a razor blade. A thick film may cause the slide to break when the epoxy is removed.

7.21 Very dense soils and soils with clay fractions that have 30% or more montmorillonite require special handling. Use either a dry-grinding technique or a more penetrating impregnation procedure. Without using water, cut the sample to the appropriate size. Sprinkle a coarse abrasive (American Optical No. 190) on the ground-glass plate and commence to dry-grind one face of the sample by hand. Use a figure "8" or a counterclockwise motion for best results. Use successively finer abrasives and continue to grind until the surface is highly polished. Proceed with the standard mounting technique.

7.22 Aroclor 5460, a thermoplastic chlorinated diphenyl resin (Monsanto), seems to give better impregnation of dense soils. Place pieces of air-dry soil material in xylene and evacuate. Submerge the xylene-saturated soil material in molten Aroclor 5460. Hold the sample in the Aroclor at $\approx 200°C$ for 1 to 2 days. Remove impregnated soil material, allow to cool, and prepare thin sections by dry-grinding.

8. CALCULATIONS
None

9. REPORT
Describe the thin section as outlined in procedure 4E1b.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES

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Innes, R.P., and D.J. Pluth. 1970. Thin section preparation using an epoxy impregnation for petrographic and electron microprobe analysis. Soil Sci. Soc. Amer. Proc. 34:483-485.

FABRIC-RELATED ANALYSES
MICROMORPHOLOGY (4E)[1]
THIN SECTIONS (4E1)
INTERPRETATION (4E1b)

BACKGROUND

Micromorphology may be defined as the study of microfabrics of soils in their natural undisturbed arrangement (Cady, 1986). Examination of thin sections with a polarizing light microscope can be considered an extension of field morphological studies. The results of micromorphological studies are most useful when they are combined with other field and laboratory information (Cady, 1965). Micromorphology is used to identify illuviation of argillans, fabric types, skeleton grains, weathering intensity, and to investigate genesis of soil or pedological features.

Initially, the investigator should scan the overall features of a thin section and determine those features that require emphasis. This initial scanning may include all the thin sections from a soil profile or all those related to a particular problem. Different kinds of illumination should be used with each magnification. Strong convergent light with crossed polarizers elucidates structures in dense or weakly birefringent material that may appear opaque or isotropic. Structures in translucent specimens become more clearly visible if plain light is used, and the condensers are stopped down. Everything should be viewed in several positions of the stage or during slow rotation with crossed polarized light.

A thin section is a two-dimensional slice through a three-dimensional body. The shapes of mineral grains and structural features are viewed in one plane, and the true shapes must be extrapolated. A grain that appears needle-shaped may be a needle or the edge of a flat plate. An elliptical pore may be an angular slice through a tube. A circular unit is probably part of a sphere. With a three-dimensional perspective in mind as well as an awareness of section thickness, repeated viewing of similar features that appear to be cut at different angles is the best way to accustom oneself to a volume rather than a planar interpretation of shape. A well-prepared section is 20- to 30-μm thick. Grains smaller in thickness are stacked and cannot be viewed as individual grains. Similarly, pores smaller than 20 to 30 μm cannot be seen clearly. A pore size of 20-μm diameter equates to a soil moisture tension of 0.15 bar (15 kPa) (Rode, 1969) so that visible pores in thin section are mostly drained at water contents below field capacity.

Sand and silt grains in thin sections are identified by standard methods presented in petrography texts. The general analytical approach is the same for grain studies (procedure 7B1) as it is for thin sections. However, in grain studies, the refractive index is used only as a relative indicator, and other optical and morphological properties are more important. Furthermore, in thin sections, a concern with minerals that occur in small quantities or an attempt to quantify mineralogical analysis is seldom necessary. The separate particle-size fractions should be used for the identification and mineralogical analyses that are important to a study, whereas the thin sections should be used mainly for information about component arrangement. Recognition of aggregates, concretions, secondary pseudomorphs, and weathered grains is more important in thin section studies than in sand and silt petrography. Recognition of these components in thin section are easier because interior structures are exposed. Although grain studies are important in soil genesis studies, the arrangement of components is destroyed or eliminated by sample preparation procedures that separate the sand, silt, and clay.

In the United States, emphasis in micromorphology has been on clay arrangement. Clay occurs not only in the form of aggregates but also in massive interstitial fillings, coatings, bridges, and general groundmass. Even though the clay particles are submicroscopic, they can be described, characterized and sometimes identified, e.g., the 1:1 and 2:1 lattice clays can be distinguished. Completely dispersed, randomly arranged clay of less than 1 µm exhibits no birefringence and appears isotropic in crossed polarized light. Clay in a soil is seldom all random and isotropic. Clay develops in oriented bodies, either during formation or as a result of pressure or translocation. If enough plate-shaped particles are oriented together in a body that is large enough to see, birefringence can be observed.

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[1] W. Dennis Nettleton, Research Soil Scientist, NSSC, NRCS, Lincoln, NE wrote the procedure for description and interpretation of soil micromoropmhology as seen in thin sections.

FABRIC-RELATED ANALYSES
MICROMORPHOLOGY (4E)[1]
THIN SECTIONS (4E1)
INTERPRETATION (4E1b)

With the exception of halloysite, the silicate clay minerals in soils are platy. The a and b crystallographic axes are within the plane of the plate, and the c axis is almost perpendicular to this plane. Even though the crystals are monoclinic, the minerals are pseudohexagonal, as the distribution of stems along the a and b axes is so nearly the same, and the c axis is so nearly perpendicular to the other axes. The optical properties, crystal structure, and general habit of clay are analogous to those of the micas, which can be used as models to analyze and describe clay properties.

The speed of light that travels in the direction of the c axis and vibrates parallel to the a axis is almost the same as that light that vibrates parallel to the b axis. Therefore, the refractive indices are very close, and the interference effects in crossed polarized light are small when observed along the c axis. Light that vibrates parallel to the c axis travels faster than in other directions. Hence, the refractive index is lower. If the edge of the crystal or aggregate of crystals is viewed along the a-b plane between crossed polarizers, two straight extinction positions are viewed, and interference colors are manifested in other positions. If a clay concentration is organized so that most of the plates are parallel, the optical effects can be observed. The degree and quality of optical effects depend on the purity, continuity, and the orientation process of the clay body.

Kaolinite has low birefringence and has refractive indices slightly higher than quartz. In the average thin section, interference colors for kaolinite are gray to pale yellow. In residual soils that are derived from coarse-grained igneous rocks, kaolinite occurs as book-like and accordion-like aggregates of silt and sand size.

Even though halloysite can form oriented aggregates, it should not show birefringence because of its tubular habit. Halloysite may show very faint, patternless birefringence, which is caused by impurities or by refraction of light at the interfaces between particles.

The 2:1 lattice minerals have high birefringence and show bright, intermediate-order, interference colors if the edges of aggregates are viewed. In the clay-size range, distinctions among smectite, mica, vermiculite, and chlorite in thin section are seldom possible. These clay minerals are usually mixed in the soil and seldom occur pure. In many soils, these clay minerals are stained and mixed with iron oxide and organic matter.

Residual clay has been in place since its formation by weathering. Although it may have been transported within fragments of weathered material, it remains in place relative to the fabric of these fragments. This clay may be random, have no orientation, and thus be isotropic; however, more often, it shows some birefringence. In transported materials, silt-size flakes and other small aggregates are common. In many residual materials, clay is arranged either in forms that are pseudomorphs of rock minerals or in definite bodies of crystal aggregates, e.g., vermicular or accordion-like kaolin books. The regular, intact arrangement of these materials is usually diagnostic of residual material.

Clay rearrangement may result from differentially applied stress that produces shear. Platy particles become oriented by slippage along a plane, e.g., slickenside faces in a Vertisol or in clayey layers. Platy particles also are oriented inside the blocks. Root pressure, mass movement, slump, and creep can produce stress orientation. If the faces on structural units are smooth and do not have separate coatings, stress orientation can be inferred. Otherwise, in plain light, stress orientation cannot be observed. In plain light, clay in the thin section may be homogeneous and featureless. In crossed polarized light, the orientation pattern is reticulate, consisting of bright lines showing aggregate birefringence, often intersecting at regular angles. The effect is that of a network in a plaid pattern. There may be numerous sets of these slippage planes, which appear in different positions as the stage is turned. Stress-oriented clay may be near rigid bodies, e.g., quartz grains, or along root channels. Stress-oriented clay is often strongly developed on ped faces. Stress can also orient mica flakes and any other small platy grain.

Location features that distinguish translocated clay from residual clay are its occurrence in separate bodies, usually with distinct boundaries, and its location on present or former pore walls, channel linings, or ped faces. Translocated clay may have a different composition than matrix clay, especially if its origin is another horizon. This clay is more homogeneous and is usually finer than the matrix clay. Translocated clay displays lamination, indicating deposition in successive increments, and

manifests birefringence and extinction, indicating that these translocated clay bodies are oriented aggregates. If these bodies are straight, they have parallel extinction. If these bodies are curved, a dark band is present wherever the composite c axis and the composite a and b axes are parallel to the vibration planes of the polarizers. When the stage is rotated, these dark bands sweep through the clay aggregate.

Other substances such as goethite, gibbsite, carbonate minerals, and gypsum may form pore linings and ped coatings. These substances can be identified by their mineralogical properties.

Amorphous coatings of organic matter, with or without admixed Fe and Al, are common, especially in spodic horizons. This material is dark brown to black, isotropic or faintly birefringent, and often flecked with minute opaque grains. Amorphous coatings of organic matter occur as the bridging and coating material in B horizons of sandy Spodosols and as thin coatings or stains on pore and ped faces in other soils.

DESCRIPTION

Terms have been defined for distribution patterns of the components of soil thin sections (Brewer, 1964 and 1976; Brewer et al., 1983; Stoops and Jongerius, 1975; and Bullock et al., 1985). As these terms have become more widely adopted in the literature, the SSL increasingly uses them in Soil Survey Investigations Reports (SSIR's) and in soil project correspondence. At this time, the five "coarse-fine related distribution patterns" of Stoops and Jongerius (1975) are in common usage. The nomenclature of these distribution patterns, as described by Stoops and Jongerius (1975), are intended to be broadly defined. There are no restrictions on material type, absolute size, orientation, granulation, or origin. The system may be used to describe the distribution of primary particles, e.g., quartz grains, as well as compound units, e.g., humic micro-aggregates. The coarser particles may be silt, sand, or gravel, whereas the finer material may be clay, silt, or sand.

The monic type (granic type of Brewer et al., 1983) consists of fabric units of only one size group, e.g., pebbles, sand, or lithic fragments. In the gefuric type, the coarser units are linked by bridges of finer material but are not surrounded by this material. In the chitonic type (chlamydic type of Brewer et al., 1983), the coarser units are surrounded by coatings of finer material. In the enaulic type, the larger units support one another, and the interstitial spaces are partially filled with finer material. The enaulic fabric consists of material finer than is found in either the gefuric or chitonic type but is not so fine as is found in the porphyric type. In the end member of the sequence, the porphyric type, the large fabric units occur in a dense groundmass of smaller units, and there is an absence of interstitial pores. This type is equivalent to the earlier porphyroskelic class of Brewer (1964) or to the current porphyric class (Brewer et al., 1983). The class may be divided into types based on the spacing of the coarser units.

The s-matrix is the material within which pedological features occur (Brewer, 1976). Skeleton grains of a soil material are individual grains that are larger than colloidal size. The soil plasma includes all the colloidal size material as well as the relatively soluble material that is not bound in skeleton grains. The description of plasmic fabrics is based on the interpretations of optical properties under crossed-Nicols, especially extinction phenomena. Plasma concentrated or crystallized into pedological features is not included in the description of plasmic fabrics. In general, the descriptive terms for the s-matrix are those as defined by Brewer (1976). The s-matrix plasma fabrics are divided into two groups, the asepic and sepic types. The asepic fabrics are those with anisotropic plasma in which the domains, i.e., the plasma separations, are not oriented relative to each other. The sepic fabrics are those with anisotropic domains with various orientation patterns. Using a scanning electron microscope (SEM), Eswaran (1983) characterized the $<25\text{-}\mu m^2$ size domains of monomineralic soils. These features are smaller than some domains described by Brewer (1976). However, these small features provide the detail expected of the interparticle relationships present in the larger separations. The domains in allophanic soils are composed of globular aggregates. The halloysitic soils differ in that the halloysite tubes generally may be seen as protrusions from globular forms. The domains in micaceous soils retain the face-to-face

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packing that is common in micas and may retain some of the book-like forms as well. The domains in montmorillonitic soils are bent to conform to the shape of skeletan grains. However, the packing is essentially face-to-face and, upon drying, the fabric is very dense and compact. In kaolinitic soils, the domains frequently are present as booklets that are packed face-to-face, unless iron hydrous oxide has disrupted the platelets, in which case, the platelets may still be packed face-to-face in subparallel stacks. The asepic plasmic fabrics are subdivided into two groups, argillasepic and silasepic types. Argillasepic fabrics are dominated by anisotropic clay minerals and have a random orientation pattern of clay-size domains. Overall, the asepic fabrics have flecked extension patterns. Silasepic fabrics have a wider range of particle sizes than argillasepic types. However, a careful observer may view silt-size domains or plasma bodies that give the matrix an overall flecked extinction pattern.

The sepic plasmic fabrics have recognizable domains with various patterns of orientation. Internally, the domains, i.e., plasma separations, have striated extinction patterns. Brewer (1964) recognizes seven kinds, most of which are widely adopted.

Insepic fabrics consist of isolated, striated plasma domains within a flecked plasma matrix. Mosepic fabrics consist of plasma domains with striated orientation that may adjoin each other or be separated by small plasma areas with flecked orientation that are not oriented relative to each other. The fabric is vosepic when the plasma separations with striated orientation are associated with channel or pore (void) walls. The fabric is skelsepic when the plasma separations occur at the skeleton grain s-matrix contact.

The remaining three sepic plasmic fabrics are most common in fine-textured soils. In masepic fabrics, the plasma separations occur as elongated zones within the s-matrix and apparently are not associated with void walls or skeleton grains. The striations have parallel orientations to zone length. Lattisepic fabrics are similar to masepic fabrics except that the acicular and prolate domains occur in lattice-like patterns. In omnisepic fabrics, all of the plasma has a complex striated orientation pattern.

Three other kinds of plasmic fabrics are characteristic of particular minerals or kinds of soils. Undulic plasmic fabrics have practically isotropic extinction patterns at low magnification, and the domains are indistinct even at high magnification. Isotic plasmic fabrics have isotropic plasma, even at highest magnifications with high light intensity. The crystic plasmic fabrics have anisotropic plasma with recognizable crystals, usually of soluble materials.

The term, cutan, and definitions of its respective types (Brewer, 1964) have been widely adopted by soil scientists. Cutan is defined as a modification of the texture, structure, or fabric at natural surfaces in soil materials due to the concentration of particular soil constituents or as in-place modification of the plasma. Generally, the cutans are subdivided on the basis of their location, composition, and internal fabric. The cutan locations are surfaces of grains, peds, channels, or voids. The mineralogical nature of cutans is characterized, e.g., argillans, ferri-argillans, or organo-argillans. Argillans are composed dominantly of clay minerals; ferri-argillans have iron oxides as a significant part of their composition; and organo-argillans have significant color addition by addition of organic matter.

Sesquan is a general term used for a cutan of sesquioxides or hydroxides. Sesquans that are specific for goethite, hematite, or gibbsite are called goethans, hematans, or gibbsans, respectively. Similarly, cutans of gypsum, carbonate, calcite, halite, quartz, silica, and chalcedony are called gypsans, calcans, calcitans, halans, quartzans, silans, and chalcedans, respectively. Skeleton grains that adhere to the cutanic surface are called skeletans.

Glaebules (Brewer, 1964) are pedological units within the s-matrix whose morphology is incompatible with their present occurrence. They are usually prolate to equant. A glaebule is recognized as a unit either because of a greater concentration of a constituent, or difference in the s-matrix fabric, or because of the presence of distinct boundaries of a constituent within the enclosing s-matrix. Glaebules include papules, nodules, concretions, and pedodes. Papules are pedogenic features composed of clay minerals with continuous and/or laminar fabric, sharp external boundaries, and commonly prolate to equant, somewhat rounded shapes. Nodules are pedological features with undifferentiated internal fabric. Concretions are pedological features with concentrically laminated

structures about a center. Pedodes are pedological features with hollow interiors, often lined with crystals.

Voids are the empty spaces within the s-fabric. Those voids with diameters of 20 μm to ~ 2 mm can be studied and measured in thin section. Brewer (1976) classifies these voids as follows: (1) simple packing voids (empty spaces due to random packing of single skeleton grains); (2) compound packing voids (empty spaces between peds or other compound individuals); (3) vughs (relatively large spaces that are not formed by packing of skeleton grains; (4) vesicles (relatively large empty spaces with smooth, regular outlines); (5) chambers (empty spaces with smooth, regular outlines that connect to other voids); (6) joint planes (plane-shaped, empty spaces that traverse the s-matrix in a regular pattern); (7) skew planes (plane-shaped, empty spaces that traverse the s-matrix in an irregular pattern); (8) craze planes (plane-shaped, empty spaces that traverse the s-matrix in a highly irregular pattern of short flat or curved planes); and (9) channels (mostly cylindrical-shaped, empty spaces that are larger than packing voids).

INTERPRETATIONS
Related Distribution Patterns

Usually, the basic descriptive terms for soil fabrics do not imply any specific genesis of the feature. However, modifiers commonly are added when fabric descriptions are complete enough to understand the means of formation, i.e., stress cutan, or in-place plasma modification, is the result of differential forces, e.g., shearing, whereas an illuviation cutan is formed by movement of material in solution or suspension and later deposited (Brewer, 1964). In an experimental study of soil microfabrics by anisotropic stresses of confined swelling and shrinking, Jim (1986) showed that with an increase in the activity and proportion of the clay fraction, the related distribution patterns alter from dominantly matrigranic (monic, with the units being aggregates) to matrigranodic (enaulic) to porphyric.

Some monic fabrics are inherited, and include soil fabrics formed in sand dunes, sandy sediments deposited by streams and rivers, beach deposits, and gruss. Fauna can produce monic fabrics that are mostly fecal pellets. Monic fabrics also can form by fracturing and flaking of organic coatings in the upper B horizons of the Spodosols (Flach, 1960) and by freezing and thawing (Brewer and Pawluk, 1975).

Several kinds of finer material (plasma) can bridge the coarser particles (skeleton grains) to form gefuric related distribution patterns. Gefuric patterns are common in weakly developed argillic and spodic horizons and in duripans. Silicate clays can bridge skeleton grains in some argillic horizons; the organic matter, iron, and aluminum complexes in some kinds of spodic horizons; and the amorphous silica in some kinds of duripans.

In soils that are slightly more developed than those with gefuric patterns, chitonic related distribution patterns form. These are common in argillic and spodic horizons and in duripans. Bridges as well as complete coatings of skeleton grains are present. Usually, the cement or plasma is material that adheres to skeleton grains. These cements have covalent bonds and commonly include silica, iron, aluminum, and organic matter (Chadwick and Nettleton, 1990).

The enaulic related distribution patterns are more common in soil material in which the cement bonds to itself more strongly than to skeleton grains. In sandy soils, ionic-bonded calcite and gypsum tend to bond to themselves more strongly than to skeleton grains, thereby producing open porphyric related distribution patterns (Chadwick and Nettleton, 1990). Even though organic matter has covalent bonds and usually surrounds grains, organic material forms pellets in void spaces between skeleton grains in some spodic horizons.

Porphyric related patterns form from the normal packing of grains in materials with a high proportion of fine material. These patterns can be the end member of several kinds of sequences (Brewer et al., 1983). In porphyric related patterns, there may or may not be skeleton grains of primary minerals, pedorelicts, organics, lithic fragments of shale, sandstone, or other rocks. In the porphyric related patterns, the material consists of silt and clay, and the interstices tend to be filled with minimal

formation of coatings. In precursors of the porphyric related distribution patterns, the silt to clay ratio is used to identify the kind of sequences by which the porphyric pattern forms (Brewer et al., 1983). The porphyric patterns are common in loessial soils, especially in argillic and petrocalcic horizons, duripans, and orstein.

Plasmic Fabrics

The asepic plasmic fabrics differ in composition mainly in silt to clay ratios. Argillasepic fabrics have the higher clay contents, usually <30 percent but may have as much as 70 percent (Brewer et al., 1983). The birefringence of the plasma is masked by organic matter or iron stains, resulting in a flecked distribution pattern. Argillasepic fabrics are important fabrics in many fine-textured B horizons. Silasepic plasmic fabrics have low clay contents and have more silt than clay. The silasepic fabrics are common in porphyric related distribution patterns in A and B horizons of Solonetz; Solodized Solonetz and Solodic Soils; Soloths; Red Podzolic Soils; Lateritic Podzolic Soils; and are also associated with some sedimentary deposits (Brewer et al., 1983). Silasepic plasma fabrics are common in A and B horizons of loessial soils in association other kinds of plasma separations. Even if there is high clay content, the horizons with asepic plasmic fabrics have low effective linear extensibilities (LE) either because the clays are low-swelling types or because the soils do not dry enough to undergo the full range of laboratory-measured LE.

In soils that form in the same climate, the kind of sepic plasmic fabrics form a sequence relative to increasing linear extensibility (Nettleton et al., 1969; Holzhey et al., 1974). In increasing order of shrink-swell stress, the plasmic fabric sequence is insepic, mosepic, lattisepic, omnisepic, and masepic. Using X-ray diffraction (Clark, 1970) and scanning electron microscopy (Edil and Krizek, 1976), observations of deformation experiments indicate that the degree of clay orientation increases with an increase in applied stress. In an experimental study of soil microfabrics by anisotropic stresses of confined swelling and shrinking, Jim (1986) shows that with an increase in the activity and content of the clay fraction, there is an increase in the long and narrow plasma separations, i.e., a progression from insepic to mosepic to masepic plasmic fabrics.

Insepic plasmic fabrics are very common in finer-grained porphyric B horizons of a wide range of soil groups (Brewer et al., 1983). Soil horizons with insepic fabrics generally have an LE of <4 percent. In some insepic plasmic fabrics, the plasma islands or papules are pseudomorphs of some weatherable mineral, whereas in other insepic fabrics, the papules are clay skin fragments or are eolian sand-size clay aggregates (Butler, 1974). In some samples, the pseudomorphs do not disperse well in particle-size analysis (PSA).

Mosepic plasmic fabrics commonly have more clay than insepic fabrics because they contain more islands of plasma. However, in mosepic plasmic fabrics, LE also remains low. Shrink-swell forces have not been sufficient or have not operated long enough to have homogenized the islands of plasma into the soil matrix.

Vosepic plasmic fabrics occur in soil horizons that have undergone stress either due to shrink-swell forces or to tillage. Even though root growth is adequate to increase the percentage of oriented clay near the root-soil interface (Blevins et al., 1970), root growth does not appear adequate to form vosepic or other highly stressed plasmic fabrics. Usually, vosepic fabrics are present in soil horizons in which the main fabric type is masepic or skelsepic. The vosepic plasmic fabric rarely occurs as the only fabric in a soil horizon.

There are at least two types of origins for orientation of plasma on sands. One is a result of clay illuviation. By definition, this type would not be included with skelsepic fabric. The related distribution patterns associated with this fabric commonly are monic, gefuric, or enaulic. The other origin is commonly the porphyric related distribution patterns with LE's that are >4 percent for dryland soils, i.e., soils in aridic, xeric, or ustic soil moisture regimes. These are the true skelsepic fabrics. Shrink-swell forces have been involved in their formation as shown by relatively few papules or clay skins remaining, and there are vosepic areas.

FABRIC-RELATED ANALYSES
MICROMORPHOLOGY (4E)[1]
THIN SECTIONS (4E1)
INTERPRETATION (4E1b)

Masepic, lattisepic, and omnisepic plasmic fabrics are evidence of stress >4 percent in dryland soils. Clay contents are usually >35 percent, but the threshold amount is dependent on clay mineral type and on degree of dryness common to the environment. In masepic, lattisepic, and omnisepic plasmic fabrics, papules and clay skins rarely are found, but areas of skelsepic and vosepic areas commonly are present.

Undulic plasmic fabrics seem to be associated with basic parent materials, especially basalt, and with moderate to strong weathering (Brewer et al., 1983). The fabric commonly is stained deeply by iron minerals, and kaolinite and halloysite are the important clay minerals. Clays in these horizons do not disperse well in PSA, but high 15-bar (1500-kPa) water contents suggest that the horizons belong in clayey families. Some papules and clay skins commonly are present, but these plasma separations also are stained deeply by iron.

Isotic plasmic fabrics are common in spodic horizons and in Andisols. The clays in these horizons are amorphous and disperse poorly in PSA. The water-holding capacities of these soil horizons are relatively high. Some unweathered volcanic ash may be present.

Crystic plasmic fabrics are common in B horizons of soils formed in dryland areas. In soil horizons with large areas of interlocking crystals, there is restricted soil permeability, increased unconfined compressive strength, and limited particle dispersion, depending on the degree of cementation.

Cutans and Pedogenic features

Most argillans are formed, at least in part, by illuviation. The content of strongly oriented clay (usually argillans plus papules), in texture-contrast soils (soils with argillic horizons) is usually <5 percent of the soil volume (Brewer et al., 1983). In some sandy soils that are low in silt, the argillans and papules are as much as 30 percent of the soil material (Brewer et al., 1983). The measured illuviated clay rarely accounts for the difference in clay content between the A and B horizons. Some of the clay may originate from weathering in place and some from a destruction of argillans and papules.

If argillans and papules are present in argillic horizons in dryland soils, the soil LE is usually <4 percent (Nettleton et al., 1969). In some humid environments, argillans and papules may be present even where the LE is >4 percent. As soils in humid environments do not dry to the same degree as those in the desert, the clay skins may survive because only part of the linear extensibility is effective.

Papules may originate by the weathering of primary minerals, the isolation of clay skins by the channel and void migration within the soil matrix (Nettleton et al., 1968; Nettleton et al., 1990) or by the introduction of eolian sands and silts that are composed of clays (Butler, 1974; Brewer and Blackmore, 1976). The comparison of size and shape of papules and minerals, as well as of parent material, may help to determine if the papules are pseudomorphs of one of the primary minerals. Internal fabric resemblances and residual parts of the primary mineral within the papules help to determine if a papule is a pseudomorph.

The determination of whether or not a papule is an illuvial feature is important for classification purposes. Arcuate forms and laminar internal fabrics are evidence that the feature is illuvial. If the feature partially surrounds an oval body of silt, illuvial origin of the feature is relatively certain (Nettleton et al., 1968).

The origin of the papule as eolian may be determined by studying its size and shape; its internal fabric; and the number and degree of its alterations relative to other particles. Microlaminae may suggest an origin as sediment. Unlike soil pedorelicts or rock fabrics (lithorelicts), nodules, or glaebules rich in soluble plasma, probably form by accretion (Brewer, 1976). Most concretions, as well as pedodes, are accretionary and usually form in place.

A study of soil voids may be useful in predicting the clay activity and shrink-swell behavior of soils. In an experimental study of soil microfabrics by anisotropic stresses of confined swelling and shrinking, Jim (1986) shows that with an increase in the activity and content of the clay fraction, there is a drastic decrease in void volume, especially the >30μm. Furthermore, the void shapes change from

compound packing voids to planar voids and vughs. With an increase in stress from shrink-swell forces, aggregates become flattened at contacts, resulting in more angular and eventually fused compound units.

A possible objective of micromorphological studies may be the measurement of porosity and the prediction not only of soil water content at various suctions but also of hydraulic conductivity. In thin section studies of voids in sands and sandy soils, there is a close correlation between microscopic and suction methods (Swanson and Peterson, 1942). However, in those soils whose volumes change with changes in water content, pore size distribution is undefined, and no constant void size distribution exists (Brewer, 1976). Furthermore, there are several unvalidated assumptions that commonly are made in relating porosity to permeability (Nielsen et al., 1972 p. 11). The assumptions that especially relate to soil fabric are that no pores are sealed off; pores are distributed at random; and pores are generally uniform in size. A more serious difficulty may be that a thin section, even if reduced to a 20-μm thickness, may make the examination of the <20-μm diameter pores impossible, if these pores pass through the section at an angle of $\leq$45°. This means that many voids that are involved in unsaturated water flow in soils will not be visible in thin section (Baver, 1956 p. 271).

The size, shape, and arrangement of skeleton grains determine the nature of simple packing voids, but the origin of compound packing voids is not so straightforward. The unaccommodated peds of the compound packing voids may be formed by faunal excreta, shrink-swell action, man's activities, or by other unknown causes.

Vughs usually occur in soil materials with a wide range in size of particles, including silicate clays. Some vughs form by the weathering and removal of carbonate, and others form by faunal activity or the normal packing of plasma and skeleton grains. The very regular outline of vesicles is of interest (Nettleton and Peterson, 1983). Lapham (1932) states that in Sierozems (Aridisols), the vesicles that are near the surface are the result of air entrapment by rainfall following dry dusty periods. Laboratory studies verify this phenomenon (Springer, 1958). If high silt soils are allowed to dry before each irrigation, the vesicle size increases with the number of irrigations (Miller, 1971). As a result of studies of infiltration rates and sediment production in rangelands in central and eastern Nevada, Blackburn and Skau (1974) and
Rostagno (1989) conclude that the infiltration rates are the lowest and the sediment yields are the highest on sites that have vesicular surface horizons. The failure of most vesicles to connect to other voids and the low strength of the crust in which vesicles occur help to explain the low infiltration rates and the high sediment yields that commonly are found on these soils.

Joint planes are produced in relatively uniform fine-textured soils by a relatively regular system of cracking upon drying (Brewer, 1976). Once formed, these joint planes tend to open in the same place during successive drying cycles. Skew planes are produced in more heterogeneous materials or by irregular drying (Brewer, 1976). Craze planes often occur in Chernozems (Mollisols), possibly as a result of the high humic acid content (Brewer, 1976). Because of their size, cross-sectional shape, and kind of branching pattern, channels probably form by faunal activity, plant root systems, or by certain geological processes (Brewer and Sleeman, 1963).

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FABRIC-RELATED ANALYSES
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THIN SECTIONS (4E1)
INTERPRETATION (4E1b)

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FABRIC-RELATED ANALYSES
PLASTICITY INDEX (4F)

The PI is the range of water content over which a soil behaves plastically. Numerically, the PI is the difference in the water content between the LL and the plastic limit (PL). Refer to procedure 4F1 for the definition of LL. The PL is the percent water content of a soil at the boundary between the plastic and brittle states. The boundary is the water content at which a soil can no longer be deformed by rolling into 3.2-mm (1/8-in) threads without crumbling. Refer to ASTM method D 4318 (American Society for Testing and Materials, 1993). The PI is reported as percent water on a <0.4-mm base (procedure 4F).

FABRIC-RELATED ANALYSES
LIQUID LIMIT (4F1)

The LL is the percent water content of a soil at the arbitrarily defined boundary between the liquid and plastic states. This water content is defined as the water content at which a pat of soil placed in a standard cup and cut by a groove of standard dimensions will flow together at the base of the groove for a distance of 13 mm (1/2 in) when subjected to 25 shocks from the cup being dropped 10 mm in a standard LL apparatus operated at a rate of 2 shocks s^{-1}. Refer to ASTM method D 4318 (American Society for Testing and Materials, 1993). The LL is reported as percent water on a <0.4-mm base (40-mesh) (procedure 4F1).

FABRIC-RELATED ANALYSES
PLASTICITY INDEX (4F2)

The PI is the range of water content over which a soil behaves plastically. Numerically, the PI is the difference in the water content between the LL and the plastic limit (PL). Refer to procedure 4F1 for the definition of LL. The PL is the percent water content of a soil at the boundary between the plastic and brittle states. The boundary is the water content at which a soil can no longer be deformed by rolling into 3.2-mm (1/8-in) threads without crumbling. Refer to ASTM method D 4318 (American Society for Testing and Materials, 1993). The PL is reported as percent water on a <0.4-mm base (procedure 4F2).

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FABRIC-RELATED ANALYSES
AGGREGATE STABILITY (4G)
WET SIEVING AIR-DRY 2 to 1 mm (4G1)
(2- to 0.5-mm Aggregates Retained)

1. APPLICATION

An aggregate is a group of primary particles that cohere to each other more strongly than to other surrrounding soil particles (Kemper and Rosenau, 1986). Disintegration of soil mass into aggregates requires the application of a disrupting force. Aggregate stability is a function of whether the cohesive forces between particles can withstand the applied disruptive force. Erodibility of soils increases as aggregate stability decreases (Kemper and Rosenau, 1986). The datum can serve as a predictor of soil erosion potential. Procedure 4G1 provides a measure of aggregate stability following a disruption of aggregates by wet sieving. This procedure was developed for use by the Soil Conservation Service, Soil Survey field offices.

2. SUMMARY OF METHOD

This method measures the retention of air-dry aggregates (2 to 1 mm) on a 0.5-mm sieve after sample has been submerged in distilled water overnight followed by agitation of sample.

3. INTERFERENCES

Air bubbles in the sieve can create tension in the water, thereby reducing the percentage of aggregates that are retained on the 0.5-mm sieve. Variation in the moisture content of air-dry soils can affect results. For those samples with sand (>0.5 mm), dispersion in sodium hexametaphosphate solution can affect aggregate weight results.

4. SAFETY

If ovens are used, hot surfaces can be a hazard. Follow standard laboratory saftey precautions.

5. EQUIPMENT

5.1 Bowls, Rubbermaid or equivalent, 1800 mL

5.2 Electronic balance, ±0.01-g sensitivity and 500-g capacity

5.3 Sieves, square-hole

5.3.1 0.5 mm, stainless steel, no.35, 125-mm diameter, 50-mm height

5.3.2 1 mm, brass, 203-mm diameter, 50-mm height

5.3.3 2 mm, brass, 203-mm diameter, 50-mm height

5.4 Oven, 105°C

5.5 Camping plate, Coleman, stainless steel, 152-mm diameter, Peak 1, Model 8553-462.

5.6 Aluminum foil dish, 57-mm diameter x 15-mm deep, with lifting tab

6. REAGENTS

6.1 Distilled water

6.2 Sodium hexametaphosphate solution. Dissolve 35.7 g of sodium hexametaphosphate ($Na_4P_2O_7$) and 7.94 g of sodium carbonate (Na_2CO_3) in 1 L of distilled water. Alternatively, use Calgon, water softener.

7. PROCEDURE

7.1 Use natural fabric (NF) samples in pint containers. Assemble a 2-mm sieve on top of a 1-mm sieve. Crush the NF sample by hand or with mortar and pestle. Crush sample so as to pass the 2-mm sieve with a minimum reduction in size. Sieve entire NF sample.

7.2 Place the material that is retained on 1-mm sieve in pint container and discard the remaining material.

FABRIC-RELATED ANALYSES
AGGREGATE STABILITY (4G)
WET SIEVING AIR-DRY 2 to 1 mm (4G1)
(2- to 0.5-mm Aggregates Retained)

7.3 Sieve the material again with 1-mm sieve to remove dust and other small particles. Weigh a 3.00 ± 0.05 g sample of the 2- to 1-mm material in aluminum foil dishes.

7.4 Place 0.5-mm sieve in plastic bowl and fill bowl so that the water level is at a 20-mm height above the base of screen. Remove air bubbles with a syringe.

7.5 Distribute the 3.00-g sample (2 to 1 mm) on the 0.5-mm sieve. Aggregates should not touch. Allow sample to sit overnight.

7.6 Agitate the sample by raising and lowering the sieve in the water bowl 20 times in 40 s. On the upward strokes, drain sieve but do not raise so high that air enters from beneath the sieve.

7.7 Remove sieve from water bowl, place on Coleman plate, and dry in oven for 2 to 2.5 h at 105°C. During drying process, the plate retains the soil that drops through the sieve.

7.8 Remove the sample from the oven. Weigh sieve, plate, and sample. Sample is those aggregates retained on 0.5 mm sieve. Record weight. If no sand (>0.5 mm) is present, discard sample from sieve and plate. Weigh sieve and plate. Record weight.

7.9 If there is sand (>0.5 mm), discard sample on plate and disperse the sample on sieve with sodium hexametaphosphate solution. Alternatively, place 3 g of Calgon in plastic bowl and stir until dissolved. Place the 0.5-mm sieve with sample in sodium hexametaphosphate (or Calgon) solution so that the solution line is at a 35-mm height above the base of screen. Agitate until aggregates are soft. Remove sieve from sodium hexametaphosphate (or Calgon) solution and rinse with distilled water until all sodium hexametaphosphate (or Calgon) solution has passed through sieve, and only the sand (>0.5 mm) is left on sieve. Place sieve on Coleman plate, place in oven, and dry for for 2 to 2.5 h at 105°C.

7.10 Remove sample from oven. Weigh the sieve, plate, and sample. Record weight. Discard sample and brush sieve and plate. Weigh sieve and plate. Record weight.

7.11 Thoroughly wash sieve and plate with distilled water, especially those sieves with Sodium hexametaphosphate solution.

8. CALCULATIONS

$$\text{Aggregates (\%)} = \frac{W_R - S_W}{3.00 - S_W} \times 100$$

where:
W_R = Total weight of aggregates retained on 0.5-mm sieve
S_W = Weight of 2- to 0.5-mm sand

9. REPORT

Report aggregate stability as a percentage of aggregates (2- to 0.5-mm) retained after wet sieving. Do not report determinations if the 2- to 0.5-mm fraction is $\geq$50% of the 2- to 1-mm sample.

10. PRECISION

Precision data are not available for this procedure.

FABRIC-RELATED ANALYSES
AGGREGATE STABILITY (4G)
WET SIEVING AIR-DRY 2 to 1 mm (4G1)
(2- to 0.5-mm Aggregates Retained)

11. REFERENCES

Kemper, W.D., and Rosenau, R.C. 1986. Aggregate stability and size distribution. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:425-422.

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)

INTRODUCTION

Cation-exchange capacity (CEC) is defined as the sum total of exchangeable cations that a soil can adsorb. The CEC is a reversible reaction in the soil solution and may arise from permanently charged or pH-dependent sites on organic and mineral colloid surfaces. The CEC is commonly expressed in units of meq 100 g^{-1} soil and can range from less than 1.0 to greater than 100 meq 100 g^{-1} soil. Common CEC values for some soil components are as follows:

Soil Component	meq 100 g^{-1}	
Organic matter	200	- 400
Vermiculite	100	- 150
Montmorillonite	60	- 100
Illite	20	- 40
Kaolinite	2	- 16
Sesquioxides		- 0

The CEC is dependent upon negative charges of soil components. The mechanisms for these charges are isomorphic substitution within layered silicate minerals; broken bonds at mineral edges and external surfaces; dissociation of acidic functional groups in organic compounds; and preferential adsorption of certain ions on particle surfaces (Rhoades, 1982). Ihic substitution withinrfac these

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other pH values or by other cations may result in different data. Knowledge of the operational definition (procedure, pH, cation, and concentration) is necessary before evaluating the CEC measurement.

REFERENCES

Rhoades, J.D. Cation exchange capacity. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:149-157.

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
BY SUMMATION (5A3)
SUM OF CATIONS (CEC-8.2) (5A3a)
(sum of NH$_4$OAc extractable bases plus BaCl$_2$ extractable acidity)

Compute CEC-8.2 from the sum of NH$_4$OAc extractable bases plus the BaCl$_2$ extractable acidity. The NH$_4$OAc extractable bases are determined in procedures 6N2, 6O2, 6P2, and 6Q2. The extractable acidity is determined by titrating the BaCl$_2$-TEA extract buffered at pH 8.2 in procedure 6H5a. The CEC values by this method are not valid if significant quantities of soluble salts or carbonates are present in the soil. Calculate CEC by sum of cations as follows:

CEC-8.2 = NH$_4$OAc extractable bases + Extractable acidity

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
BY SUMMATION (5A3)
EFFECTIVE CATION CAPACITY (ECEC) (5A3b)
(sum of NH$_4$OAc extractable bases plus KCl extractable Al)

Compute ECEC from the sum of NH$_4$OAc extractable bases plus the KCl extractable Al. The NH$_4$OAc extractable bases are determined in procedures 6N2, 6O2, 6P2, and 6Q2. The KCl extractable Al is determined in procedure 6G9. The KCl extractable Al represents a major constituent in strongly acid soils (pH <5). The KCl extractant is an unbuffered salt and usually affects the soil one pH unit or less. Therefore, extraction is performed at or near soil pH. The ECEC is not reported for soils with soluble salts. Calculate ECEC as follows:

ECEC = NH$_4$OAc extractable bases + KCl extractable Al

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH$_4$OAc, pH 7.0 (5A8)
AUTOMATIC EXTRACTOR (CEC-7)
STEAM DISTILLATION
KJELTEC AUTO 1035 ANALYZER (5A8c)

1. APPLICATION

The CEC determined with 1 *N* NH$_4$OAc buffered at pH 7.0, is a commonly used method and has become a standard reference to which other methods are compared (Peech et al., 1947). The advantages of using this method are that the extractant is highly buffered so that the extraction is performed at a constant, known pH (7.0) and that the NH4$^+$ on the exchange complex is easily determined.

2. SUMMARY OF METHOD

Displacement after washing is the basis for this procedure. The CEC is determined by saturating the exchange sites with an index cation (NH4$^+$); washing the soil free of excess saturated salt; displacing the index cation (NH4$^+$) adsorbed by the soil; and measuring the amount of the index cation (NH4$^+$). A sample is leached using 1 *N* NH$_4$OAc and a mechanical vacuum extractor (Holmgren et al., 1977). The extract is weighed and saved for analyses of the cations. The NH$_4^+$ saturated soil is rinsed with ethanol to remove the NH$_4^+$ that was not adsorbed. Steam distillation and titration are used to determine the NH$_4^+$ adsorbed on the soil exchange complex. The CEC by NH$_4$OAc, pH 7 is reported in meq 100 g^{-1} oven-dry soil in procedure 5A8c.

3. INTERFERENCES

Incomplete saturation of the soil with NH$_4^+$ and insufficient removal of NH$_4^+$ are the greatest interferences to this method. Ethanol removes some adsorbed NH$_4^+$ from the exchange sites of some soils. Isopropanol rinses has been used for some soils in which ethanol removes adsorbed NH$_4^+$. Soils that contain large amounts of vermiculite can irreversibly "fix" NH$_4^+$. Soils that contain large amounts of soluble carbonates can change the extractant pH and/or can contribute to erroneously high cation levels in the extract.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Nessler's reagent contains mercury which is toxic. Proper disposal of the Nessler's reagent and clean-up of equipment in contact with the reagent is necessary.

Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the vacuum extractor and the Kjeltec Auto 1035 Analyzer.

5. EQUIPMENT
5.1 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE
5.2 Mechanical vacuum extractor, Mavco Sampletex, 5300 N. 57th St., Lincoln, NE
5.3 Syringes, polypropylene, disposable, 60 mL, for extraction vessel, extractant reservoir and tared extraction syringe
5.4 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (1/8 ID x 1/4 OD x 1 in) for connecting syringe barrels.
5.5 Polycons, Richards Mfg. Co.
5.6 Kjeltec Auto 1035/1038 Sampler System, Tecator, Perstorp Analytical Inc.
5.7 Digestion tubes, straight neck, 250 mL
5.8 Analytical filter pulp, ash-free, Schleicher and Schuell, No. 289

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH₄OAc, pH 7.0 (5A8)
AUTOMATIC EXTRACTOR (CEC-7)
STEAM DISTILLATION
KJELTEC AUTO 1035 ANALYZER (5A8c)

5.9 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.
5.10 Electronic balance, ±1-mg sensitivity

6. REAGENTS

6.1 Distilled deionized (DDI) water
6.2 Ammonium acetate solution (NH_4OAc), 1 *N*, pH 7.0. Add 1026 mL of glacial acetic acid (CH_3COOH) to 15 L DDI water. Add 1224 mL of concentrated ammonium hydroxide (NH_4OH). Mix and cool. Dilute with DDI water to 18 L and adjust to pH 7.0 with CH_3COOH or NH_4OH.
6.3 Ethanol (CH_3CH_2OH), 95%, U.S.P.
6.4 Nessler's reagent. Add 4.56 g of potassium iodide (KI) to 30 mL DDI water. Add 5.68 g of mercuric iodide (HgI_2). Stir until dissolved. Dissolve 10 g of sodium hydroxide (NaOH) in 200 mL of DDI water. Transfer NaOH solution to a 250-mL volumetric flask and slowly add K-Hg-I solution. Dilute to volume with DDI water and thoroughly mix. Solution should not contain a precipitate. Solution can be used immediately. Store in brown bottle to protect from light.
6.5 Sodium chloride (NaCl), reagent, crystal.
6.6 Antifoam agent, slipicone release spray, Dow Chemical Corp. Alternatively, use n-octyl alcohol.
6.7 Boric acid, 4% (w:v), with bromcresol green-methyl red indicator (0.075 % bromcresol green and 0.05% methyl red), Chempure Brand
6.8 Hydrochloric acid (HCl), 0.05 *N*, standardized. Dilute 83 mL of concentrated HCl in 20 L of DDI water. Refer to Appendix VIII, Standardization of Acids.
6.9 NaOH, 1 *M*. Add 500 mL of 50% NaOH solution to 8 L of DDI water. Dilute to 9 L with DDI water.

7. PROCEDURE

Extraction of Bases

7.1   Prepare extraction vessel by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 2.50 g of <2-mm, air-dry soil and place in an extraction vessel. Weigh a smaller amount of sample, if the soil is highly organic. Prepare one quality control check sample per 48 samples.

7.3 Place extraction vessel on upper disk of the extractor and connect a tared extraction syringe. Use a 25.4-mm (1 in) length rubber tubing and insert the plunger in the slot of the stationary disk of the extractor.

7.4 Use a squeeze bottle to fill extraction vessel to the 20-mL mark with NH_4OAc solution ($\approx$ 10 mL). Thoroughly wet the sample. Let stand for at least 20 min.

7.5 Put reservoir tube on top of the extraction vessel. Rapidly extract the NH_4OAc solution to a 0.5- to 1.0-cm height above sample. Turn off extractor. Add $\approx$ 45 mL of NH_4OAc solution to the reservoir tube. Set extractor for an overnight (12 to 16 h) extraction. Refer to Appendix III and IV for operation and calibration of mechanical vacuum extractors.

7.6 Next morning turn off the extractor. Pull the plunger of the syringe down. Do not pull plunger from the barrel of the syringe. Carefully remove the syringe containing the extract. Leave the rubber tubing on the extraction vessel. Weigh each syringe containing the NH_4OAc extract to the nearest 0.01 g.

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH$_4$OAc, pH 7.0 (5A8)
AUTOMATIC EXTRACTOR (CEC-7)
STEAM DISTILLATION
KJELTEC AUTO 1035 ANALYZER (5A8c)

7.7 Mix the extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. The solution in the polycon is reserved for analyses of extracted cations (procedures 6N2, 6O2, 6P2, and 6Q2).

Removal of Excess Ammonium Acetate

7.8 Return the extractor to starting position. Attach syringe to the extraction vessel and rinse the sides of the extraction vessel with ethanol from a wash bottle. Fill the extraction vessel to the 20-mL mark with ethanol and let stand for 15 to 20 min.

7.9 Place reservoir tube on the extraction vessel. Rapidly extract the ethanol level to a 0.5- to 1.0-cm height above the sample. Turn off the extractor and add 55 to 60 mL of ethanol to the reservoir. Extract at a 45-min rate. Refer to Appendix III and IV for operation and calibration of mechanical vacuum extractors.

7.10 After the extractor has stopped, turn off the switch. Pull the plunger of the syringe down. Do not pull the plunger from the syringe barrel. Remove the syringe and discard the ethanol.

7.11 Repeat the ethanol wash.

7.12 After the second wash, collect a few drops of ethanol extract from the extraction vessel on a spot plate. Test for NH_4^+ by using Nessler's reagent. A yellow, red to reddish brown precipitate is a positive test. If the test is positive, repeat the ethanol wash and retest with Nessler's reagent. Repeat until a negative test is obtained.

Steam Distillation: Samples and Reagent Blanks

7.13 Remove the extraction vessel and transfer the sample to a 250-mL digestion tube. Add 6 to 7 g of NaCl to the digestion tube.

7.14 Perform the same transfer and addition of reagents for blanks as for samples.

7.15 Spray silicone antifoam agent (or 2 drops of n-octyl alcohol solution) into the digestion tubes for each of the samples and reagent blanks.

7.16 When using new reagents, e.g., boric acid, reagent blanks are distilled in 2 sets of 6, one set per Kjeltec machine. Each set of 6 is averaged and recorded on bench worksheet and manually set on each machine. During the steam distillation, the mean reagent blank titer is automatically subtracted from the sample titer. Refer to Appendix IX for operation and calibration of Kjeltec Auto 1035 Analyzer.

7.17 On bench worksheet, record the normality of standardized acid, i.e., ≈ 0.05 *N* HCl.

7.18 Connect the tube to the distillation unit. Close the safety door. Distillation and titration are performed automatically. Record the titer in mL of titrant. Refer to Appendix IX for operation and calibration of Kjeltec Auto 1035 Analyzer.

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH_4OAc, pH 7.0 (5A8)
AUTOMATIC EXTRACTOR (CEC-7)
STEAM DISTILLATION
KJELTEC AUTO 1035 ANALYZER (5A8c)

8. CALCULATIONS

```
CEC = Titer x N x 100 x AD/OD
      _____

          Sample Weight (g)
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where:
CEC   = Cation Exchange Capacity (meq 100 g^{-1})
Titer   = Titer of sample (mL)
N   = Normality of HCl titrant
100   = Conversion factor to 100-g basis
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)

9. REPORT
Report CEC-7 in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq 100 g^{-1}.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.
Peech, M., L.T. Alexander, L.A. Dean, and J.F. Reed. 1947. Methods of soil analysis for soil fertility investigations. U.S. Dept. Agr. Circ. 757, 25 pp.

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH_4Cl, pH 7.0 (5A9)
AUTOMATIC EXTRACTOR
STEAM DISTILLATION (5A9c)
KJELTEC AUTO 1035 ANALYZER (5A9c)

1. APPLICATION

The CEC determined with a neutral unbuffered salt, e.g., 1 N NH_4Cl, is an estimate of the "effective" CEC (ECEC) of the soil (Peech et al., 1947). For a soil with a pH of <7.0, the ECEC value should be < CEC measured with a buffered solution at pH 7.0. The NH_4Cl CEC is $\approx$ equal to the NH_4OAc extractable bases plus the KCl extractable Al for noncalcareous soils.

2. SUMMARY OF METHOD

Displacement after washing is the basis for this procedure. The CEC is determined by saturating the exchange sites with an index cation ($NH4^+$); washing the soil free of excess saturated salt; displacing the index cation ($NH4^+$) adsorbed by the soil; and measuring the amount of the index cation ($NH4^+$). A sample is leached using 1 N NH_4Cl and a mechanical vacuum extractor (Holmgren et al., 1977). The extract is weighed and saved for analyses of the cations. The NH_4^+ saturated soil is rinsed with ethanol to remove the NH_4^+ that was not adsorbed. Steam distillation and titration are used to determine the NH_4^+ adsorbed on the soil exchange complex. The CEC by NH_4Cl is reported in meq 100 g^{-1} oven-dry soil in procedure 5A9c.

3. INTERFERENCES

Incomplete saturation of the soil with NH_4^+ and insufficient removal of NH_4^+ are the greatest interferences to this method. Ethanol removes some adsorbed NH_4^+ from the exchange sites of some soils. Isopropanol rinses has been used for some soils in which ethanol removes adsorbed NH_4^+. Soils that contain large amounts of vermiculite can irreversibly "fix" NH_4^+. Soils that contain large amounts of soluble carbonates can change the extractant pH and/or can contribute to erroneously high cation levels in the extract.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. Nessler's reagent contains mercury which is toxic. Proper disposal of the Nessler's reagent and clean-up of equipment in contact with the reagent is necessary. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the vacuum extractor and the Kjeltec Auto 1030 Analyzer.

5. EQUIPMENT
5.1 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE
5.2 Mechanical vacuum extractor, Mavco Sampletex, 5300 N. 57th St., Lincoln, NE
5.3 Syringes, polypropylene, disposable, 60 mL, for extraction vessel, extractant reservoir, and tared extraction syringe
5.4 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (1/8 ID x 1/4 OD x 1 in), for connecting syringe barrels.
5.5 Polycons, Richards Mfg. Co.
5.6 Kjeltec Auto 1035/1038 Sampler System, Tecator, Perstorp Analytical Inc.
5.7 Digestion tubes, straight neck, 250 mL
5.8 Analytical filter pulp, ash-free, Schleicher and Schuell, No. 289
5.9 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.
5.10 Electronic balance, ±1-mg sensitivity

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH$_4$Cl, pH 7.0 (5A9)
AUTOMATIC EXTRACTOR
STEAM DISTILLATION (5A9c)
KJELTEC AUTO 1035 ANALYZER (5A9c)

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Ammonium chloride solution (NH$_4$Cl), 1 *N*. Dissolve 535 g of NH$_4$Cl reagent in DDI water and dilute to 10 L.

6.3 Ethanol (CH$_3$CH$_2$OH), 95%, U.S.P.

6.4 Nessler's reagent. Add 4.56 g of potassium iodide (KI) to 30 mL DDI water. Add 5.68 g of mercuric iodide (HgI$_2$). Stir until dissolved. Dissolve 10 g of sodium hydroxide (NaOH) in 200 mL DDI water. Transfer NaOH solution to a 250-mL volumetric flask and slowly add K-Hg-I solution. Dilute to volume with DDI water and thoroughly mix. Solution should not contain a precipitate. Solution can be used immediately. Store the reagent in a brown bottle to protect from light.

6.5 Sodium chloride (NaCl), reagent, crystal.

6.6 Antifoam agent, slipicone release spray, Dow Chemical Corp. Alternatively, use n-octyl alcohol

6.7 Boric acid, 4% (w:v), with bromcresol green-methyl red indicator (0.075 % bromcresol green and 0.05% methyl red), Chempure Brand

6.8 Hydrochloric acid (HCl), 0.05 *N*, standardized. Dilute 83 mL of concentrated HCl in 16 L of DDI water. Refer to Appendix VIII, Standardization of Acids.

6.9 NaOH, 1 *M*. Add 500 mL of 50% NaOH solution to 8 L of DDI water. Dilute to 9 L with DDI water.

7. PROCEDURE

Extraction of Bases

7.1 Prepare extraction vessel by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 2.50 g of <2-mm, air-dry soil and place in an extraction vessel. Weigh a smaller amount of sample, if the soil is highly organic. Prepare one quality control check sample per 48 samples.

7.3 Place extraction vessel on upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1 in) length rubber tubing and insert the plunger in the slot of the stationary disk of the extractor.

7.4 Use a squeeze bottle to fill extraction vessel to the 20-mL mark with NH$_4$Cl solution ($\approx$ 10 mL). Thoroughly wet the sample. Let stand for at least 20 min.

7.5 Put reservoir tube on top of the extraction vessel. Rapidly extract the NH$_4$Cl solution to a 0.5- to 1.0-cm height above sample. Turn off extractor. Add $\approx$ 45 mL of NH$_4$Cl solution to the reservoir tube. Set extractor for an overnight (12 to 16 h) extraction. Refer to Appendix III and IV for operation and calibration of mechanical vacuum extractors.

7.6 Next morning turn off the extractor. Pull the plunger of the syringe down. Do not pull plunger from the barrel of the syringe. Carefully remove the syringe containing the extract. Leave the rubber tubing on the extraction vessel. Weigh each syringe containing the NH$_4$Cl extract to the nearest 0.01 g.

7.7 Mix the extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. The solution in the polycon is reserved for analyses of extracted cations (procedures 6N2, 6O2, 6P2, and 6Q2).

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH$_4$Cl, pH 7.0 (5A9)
AUTOMATIC EXTRACTOR
STEAM DISTILLATION (5A9c)
KJELTEC AUTO 1035 ANALYZER (5A9c)

Removal of Excess Ammonium Chloride

7.8 Return the extractor to starting position. Attach syringe to the extraction vessel and rinse the sides of the extraction vessel with ethanol from a wash bottle. Fill the extraction vessel to the 20-mL mark with ethanol and let stand for 15 to 20 min.

7.9 Place reservoir tube on the extraction vessel. Rapidly extract the ethanol level to a 0.5- to 1.0-cm height above the sample. Turn off the extractor and add 55 to 60 mL of ethanol to the reservoir. Extract at a 45-min rate. Refer to Appendix III and IV for operation and calibration of mechanical vacuum extractors.

7.10 After the extractor has stopped, turn off the switch. Pull the plunger of the syringe down. Do not pull the plunger from the syringe barrel. Remove the syringe and discard the ethanol.

7.11 Repeat the ethanol wash.

7.12 After the second wash, collect a few drops of ethanol extract from the extraction vessel on a spot plate. Test for NH$_4^+$ by using Nessler's reagent. A yellow, red to reddish brown precipitate is a positive test. If the test is positive, repeat the ethanol wash and retest with Nessler's reagent. Repeat until a negative test is obtained.

Steam Distillation: Samples and Reagent Blanks

7.13 Remove the extraction vessel and transfer the sample to a 250-mL digestion tube. Add 6 to 7 g of NaCl to the sample.

7.14 Perform the same transfer and addition of reagents for blanks as for samples.

7.15 Spray silicone antifoam agent (or 2 drops of n-octyl alcohol solution) into the digestion tubes for each of the samples and reagent blanks.

7.16 When using new reagents, e.g., boric acid, reagent blanks are distilled in 2 sets of 6, one set per Kjeltec machine. Each set of 6 is averaged and recorded on bench worksheet and manually set on each machine. During the steam distillation, the mean reagent blank titer is automatically subtracted from the sample titer. Refer to Appendix IX for operation and calibration of Kjeltec Auto 1035 Analyzer.

7.17 On bench worksheet, record the normality of standardized acid, i.e., ~ 0.05 *N* HCl.

7.18 Connect the tube to the distillation unit. Close the safety door. Distillation and titration are performed automatically. Record the titer in mL of titrant. Refer to Appendix IX for operation and calibration of Kjeltec Auto 1035 Analyzer.

8. CALCULATIONS

```
CEC = Titer x N x 100 x AD/OD
      _____

            Sample Weight(g)
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ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH₄Cl, pH 7.0 (5A9)
AUTOMATIC EXTRACTOR
STEAM DISTILLATION (5A9c)
KJELTEC AUTO 1035 ANALYZER (5A9c)

where:

CEC	= Cation Exchange Capacity (meq 100 g^{-1})
Titer	= Titer of sample (mL)
N	= Normality of HCl titrant
100	= Conversion factor to 100-g basis
AD/OD	= Air-dry/oven-dry ratio (procedure 4B5)

9. REPORT

Report neutral salts CEC in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq 100 g^{-1}.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.

Peech, M., L.T. Alexander, L.A. Dean, and J.F. Reed. 1947. Methods of soil analysis for soil fertility investigations. U.S. Dept. Agr. Circ. 757, 25 pp.

ION EXCHANGE ANALYSES
EXTRACTABLE BASES (5B)
NH$_4$OAc, pH 7.0, AUTOMATIC EXTRACTOR (5B5)

Analyze the NH$_4$OAc leachate from procedure 5A8b for Ca^{2+}, Mg^{2+}, Na$^+$, and K$^+$ in procedures 6N2, 6O2, 6P2, and 6Q2, respectively.

ION EXCHANGE ANALYSES
EXTRACTABLE BASES (5B)
NH$_4$OAc, pH 7.0, AUTOMATIC EXTRACTOR (5B5)
UNCORRECTED (extractable) (5B5a)

If a soil does not contain soluble salts or carbonates, the extractable bases, i.e., those bases extracted in procedure 5A8b and analyzed in procedures 6N2, 6O2, 6P2, and 6Q2 are presumed to equal the exchangeable bases. These bases are reported as extractable bases.

ION EXCHANGE ANALYSES
BASE SATURATION (5C)
NH$_4$OAc, pH 7.0 (5C1)

Compute base saturation by dividing the sum of NH$_4$OAc extractable bases by the CEC by the NH$_4$OAc, pH 7.0 (CEC-7) and multiplying by 100. The NH$_4$OAc extractable bases are determined in procedures 6N2, 6O2, 6P2, and 6Q2. The CEC-7 is determined in procedure 5A8b. If extractable Ca is not reported because of the influence of carbonates or soluble salts, then the base saturation is usually reported as 100%. In *Soil Taxonomy*, base saturation determined by CEC-7 is used in mollic, umbric, and eutro-dystro criteria in (Soil Survey Staff, 1975). Calculate base saturation by CEC-7 as follows:

```
Base saturation (%) =
```

$$
\frac{\text{Sum of NH}_4\text{OAc extractable bases}}{\text{CEC-7}} \times 100
$$

ION EXCHANGE ANALYSES
BASE SATURATION (5C)
SUM OF CATIONS, TEA, pH 8.2 (5C3)

Compute base saturation by dividing the sum of NH$_4$OAc extractable bases by the CEC by sum of cations (CEC-8.2) and multiplying by 100. The NH$_4$OAc extractable bases are determined in procedures 6N2, 6O2, 6P2, and 6Q2. The CEC-8.2 is computed in procedure 5A3a. This value is not reported if either extractable Ca or extractable acidity is omitted. In *Soil Taxonomy*, base saturation determined by sum of cations (CEC-8.2) is used in most alfic-ultic criteria (Soil Survey Staff, 1975). Calculate base saturation by sum cations as follows:

```
Base saturation (%) =
```

$$
\frac{\text{Sum of NH}_4\text{OAc extractable bases}}{\text{CEC-8.2}} \times 100
$$

REFERENCES
Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys, USDA-SCS Agric. Handb. No. 436. U.S. Govt. Print. Office, Washington, DC.

ION EXCHANGE ANALYSES
EXCHANGEABLE SODIUM PERCENTAGE (ESP) (5D)
NH$_4$OAc, pH 7.0 (5D2)

Compute the exchangeable sodium percentage (ESP) by dividing the exchangeable sodium (ES) by the CEC by NH$_4$OAc, pH 7.0 (CEC-7) and multiplying by 100. The ES is calculated by subtracting the water soluble Na$^+$ determined in procedure 6P1 from the NH$_4$OAc extractable Na$^+$ determined in procedure 6P2 (U.S. Salinity Laboratory Staff, 1954). The CEC-7 is determined in procedure 5A8c. In *Soil Taxonomy*, an ESP >15% is a criterion for natric horizons (Soil Survey Staff, 1975). When the saturation extract is not prepared, the ESP is calculated as follows:

$$ESP = \frac{ES}{CEC-7} \times 100$$

where:
ESP   = Exchangeable sodium percentage
ES   = Extractable sodium (NH$_4$OAc extractable Na$^+$, meq 100 g^{-1}).
CEC-7   = CEC by NH$_4$OAc, pH 7.0 (meq 100 g^{-1}).

When the saturation extract is prepared, the SSL calculates the ESP by procedure 5D2 as follows:

$$ESP = 100 \times \frac{[Na_{ex} - (Na_{ex} \times (H_2O_{ws}/1000))]}{CEC-7}$$

where:
ESP   = Exchangeable sodium percentage
Na$_{ex}$ = Extractable Na (NH$_4$OAc extractable Na$^+$, meq 100 g^{-1}).
Na$_{ws}$ = Water-soluble Na (meq L^{-1}).
H$_2$O$_{ws}$ = Water saturation percentage.
CEC-7   = CEC by NH$_4$OAc, pH 7.0 (meq 100 g^{-1}).

ION EXCHANGE ANALYSES
SODIUM-ADSORPTION RATIO (SAR) (5E)

Compute the SAR by dividing the molar concentration of the monovalent cation Na$^+$ by the square root of the molar concentration of the divalent cations Ca^{2+} and Mg^{2+} (U.S. Salinity Laboratory Staff, 1954). The water soluble Ca^{2+}, Mg^{2+}, and Na$^+$ are determined in procedures 6N1, 6O1, and 6P1, respectively. The SAR was developed as a measurement of the quality of irrigation water, particularly when the water is used for irrigating soils that are salt or Na affected (U.S. Salinity Laboratory Staff, 1954). In *Soil Taxonomy*, an SAR $\geq$13 is a criterion for natric horizons (Soil Survey Staff, 1975). The SSL calculates the SAR by procedure 5E. The SAR is calculated as follows:

$$\text{SAR} = \frac{\left[Na^+\right]}{\left[\right]}$$

CHEMICAL ANALYSIS
ORGANIC CARBON (6A)

INTRODUCTION

Soil organic matter has been defined as the organic fraction of the soil exclusive of undecayed plant and animal residues and has been used synonymously with "humus" (Soil Science Society of America, 1987). However, for laboratory analyses, the soil organic matter generally includes only those organic materials that accompany soil particles through a 2-mm sieve (Nelson and Sommers, 1982). The organic matter content influences many soil properties, e.g., water retention capacity; extractable bases; capacity to supply N, P, and micronutrients; stability of soil aggregates; and soil aeration (Nelson and Sommers, 1982).

Organic C is a major component of soil organic matter. Organic C consists of the cells of microorganisms; plant and animal residues at various stages of decomposition; stable "humus" synthesized from residues; and nearly inert and highly carbonized compounds, e.g., charcoal, graphite, and coal (Nelson and Sommers, 1982). As organic C is the major component of soil organic matter, a measurement of organic C can serve as an indirect determination of organic matter. Organic C determination is either by wet or dry combustion. The SSL uses the wet combustion method, Walkley-Black modified acid-dichromate digestion, $FeSO_4$ titration, automatic titrator (procedure 6A1c).

Values for organic C are multiplied by the "Van Bemmelen factor" of 1.724 to calculate organic matter. This factor is based on the assumption that organic matter contains 58% organic C. The proportion of organic C in soil organic matter for a range of soils is highly variable. Any constant factor that is selected is only an approximation. Studies have indicated that subsoils have a higher factor than surface soils (Broadbent, 1953). Surface soils rarely have a factor <1.8 and usually range from 1.8 to 2.0. The subsoil factor may average ~ 2.5. The preference is to report organic C rather than to convert the organic C to organic matter through use of an approximate correction factor.

The SSL also uses a direct determination of soil organic matter. The organic matter is destroyed, after which the loss in weight of the soil is taken as a measure of the organic matter content (procedure 8F1). The percent organic matter lost on ignition (400°C) can be used in place of organic matter estimates by the Walkley-Black organic C method.

Total C in soils is the sum of organic and inorganic C. Most of the organic C is associated with the organic matter fraction, whereas the inorganic C is usually associated with the carbonate minerals. Total C is quantified by two basic methods, i.e., wet or dry combustion. The SSL uses a dry combustion (procedure 6A2d). In the total C determination, the conversion of all forms of soil C to CO_2 is followed by a quantification of the evolved CO_2. Total C can be used to estimate organic C content of a soil. The difference between total and inorganic C is the organic C. The inorganic C is equivalent to carbonate values measured by CO_2 evolution with strong acid (Nelson and Sommers, 1982). In procedure 6E1g, the amount of carbonate in a soil is determined by treating a sample with HCl followed by manometrically measuring the evolved CO_2. The amount of carbonate is then calculated as a $CaCO_3$ equivalent basis.

REFERENCES

Broadbent, F.E. 1953. The soil organic fraction. Adv. Agron. 5:153-183.
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Soil Science Society of America. 1987. Glossary of soil science terms. Rev. ed. Soil Sci. Soc. of Am., Madison, WI.

CHEMICAL ANALYSES
ORGANIC CARBON (6A)
WALKLEY-BLACK MODIFIED ACID-DICHROMATE ORGANIC CARBON (6A1)
$FeSO_4$ TITRATION, AUTOMATIC TITRATOR
METROHM 686 TITROPROCESSOR (6A1c)

1. APPLICATION

Organic C by the Walkley-Black method is a wet combustion technique to estimate organic C. A correction factor is used to convert the Walkley-Black value to an organic matter content. A common value for the factor is 1.724 based upon the assumption that soil organic matter contains 58% organic C. A review of the literature reveals that the factor is highly variable, not only among soils but also between horizons in the same soil (Broadbent, 1953). In addition, a recovery factor is used because the Walkley-Black method does not completely oxidize all the organic C.

2. SUMMARY OF METHOD

The SSL uses the Walkley-Black modified acid-dichromate $FeSO_4$ titration organic carbon procedure. A sample is oxidized with 1 *N* potassium dichromate and concentrated sulfuric acid (1:2 volume ratio). After 30 min, the reaction is halted by dilution with water. The excess dichromate is potentiometrically back-titrated with ferrous sulfate. A blank is carried throughout the procedure to standardize the ferrous sulfate. Percent organic C is reported on an oven-dry soil basis.

3. INTERFERENCES

Dichromate methods that do not use additional heating do not give complete oxidation of organic matter. Even with heating, the recovery may not be complete. Walkley and Black (1934) determined an average recovery factor of 76%. Other studies have found recovery factors ranging from 60% to 86%. Thus, an average correction factor yields erroneous values for many soils. The Walkley-Black method is only an approximate or semiquantitative estimate of organic C.

Maintain the ratio of dichromate solution to concentrated H_2SO_4 at 1:2 to help maintain uniform heating of the mixture.

The presence of significant amounts of chloride in the soil results in a positive error. If the chloride in the soil is known, use the following correction factor (Walkley, 1947) for the organic C.

Organic C (%) = Apparent soil C % - (Soil Cl$^-$ %)/12

The presence of significant amounts of ferrous ions results in a positive error (Walkley, 1947). The dichromate oxidizes ferrous to ferric iron.

$$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14\ H^+ = 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$$
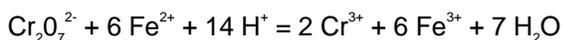
The presence of manganese dioxide results in a negative error (Walkley, 1947). When heated in an acidic medium, the higher oxides of manganese, e.g., MnO_2, compete with dichromate for oxidizable substances.

$$2\ MnO_2 + C^o + 4\ H^+ = CO_2 + 2\ Mn^{2+} + 2\ H_2O$$
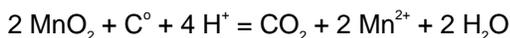
All dichromate methods assume that the organic C in the soil has an average oxidation state of zero and an equivalent weight of 3 g per equivalent when reacting with dichromate. When the soil has carbonized material, e.g., charcoal, graphite, coal and soot, the Walkley-Black method gives low recovery of this material, i.e., recovery range is from 2 to 36%.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing acids and dichromate. Toxic chromyl chloride may be released from the sample, if high concentrations of chloride are present. Use the fume hood to contain the gases released by this procedure. Use the safety showers and eyewash stations to dilute

CHEMICAL ANALYSES
ORGANIC CARBON (6A)
WALKLEY-BLACK MODIFIED ACID-DICHROMATE ORGANIC CARBON (6A1)
FeSO$_4$ TITRATION, AUTOMATIC TITRATOR
METROHM 686 TITROPROCESSOR (6A1c)

spilled acids. Use sodium bicarbonate and water to neutralize and dilute spilled acids and dichromate. Follow the manufacturer's safety precautions when using the automatic titrator.

5. EQUIPMENT
5.1 Electronic balance, ±1-mg sensitivity
5.2 Titration beakers, borosilicate glass, 250 mL
5.3 Automatic dispenser, 5 to 20 mL, Oxford no. 470 or equivalent, for K$_2$Cr$_2$O$_7$, capable of volume adjustment to 10.00 ± 0.01 mL, 0.5% reproducibility.
5.4 Dispenser, Zippette 30 mL or equivalent, for concentrated H$_2$SO$_4$, Brinkmann Instruments, Inc.
5.5 Shaker, Eberbach 6000 power unit, fitted with spring holders for titration beakers, reciprocating speed of 60 to 260 epm, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI.
5.6 Automatic titrator, Metrohm 686 Titroprocessor Series 04, 664 Control Unit, 674 Sample Changer Series 5, and 665 Dosimat Series 14, Metrohm Ltd., Brinkmann Instruments, Inc.
5.7 Platinum electrode, Metrohm part no. 6.0412.000

6. REAGENTS
6.1 Distilled deionized (DDI) water
6.2 Potassium dichromate, 1.000 *N*, primary standard. Dissolve 49.035 g of K$_2$Cr$_2$O$_7$ reagent, dried @ 105°C, in 1-L volumetric flask with DDI water.
6.3 Sulfuric acid (H$_2$SO$_4$), concentrated, reagent
6.4 Ferrous sulfate, 1 *N*, acidic. Dissolve 1 kg of FeSO$_4$·7H$_2$O in 6 L of DDI water. Carefully add 640 mL of concentrated H$_2$SO$_4$ with stirring. Cool and dilute to 8 L with DDI water.

7. PROCEDURE

Digestion of Organic C
7.1 Weigh 1.000 g air-dry soil and place in a titration beaker. If the sample contains >3% of organic C, use a smaller sample size. Refer to Table 1 for sample weight guide. If sample size is <0.5 g, use <80-mesh soil. If sample size is >0.5 g, use <2-mm soil.

7.2 With automatic dispenser, add 10.00 mL of K$_2$Cr$_2$O$_7$ solution to the titration beaker. Mix by swirling the sample.

7.3 Use the dispenser to carefully add 20 mL of concentrated H$_2$SO$_4$ to the beaker. Mix by swirling solution. Adjustment in the amount of K$_2$Cr$_2$O$_7$ added to sample requires appropriate adjustment in the amount of H$_2$SO$_4$ so that a 1:2 volume is maintained.

7.4 Place titration beaker on the reciprocating shaker and shake 1 min. If the dichromate-acid mixture turns a blue-green color, all the dichromate has been reduced. Add more dichromate and acid to maintain a 1:2 volume. Refer to Table 1 for dichromate:acid volumes.

ORGANIC CARBON (6A)
WALKLEY-BLACK MODIFIED ACID-DICHROMATE ORGANIC CARBON (6A1)
FeSO$_4$ TITRATION, AUTOMATIC TITRATOR
METROHM 686 TITROPROCESSOR (6A1c)

Table 1. Digestion of organic C. Guide for sample weight and dichromate:acid volumes.

```
 OC       Sample  K₂Cr₂O₇  H₂SO₄
(%)       ( g)    (mL)     (mL)


0 - 3     1.000   10.00    20
3 - 6     0.500   10.00    20
3 - 6     1.000   20.00    40
6 - 12    0.500   20.00    40
12 - 24   0.250   20.00    40
24 - 50   0.100   30.00    60
```

7.5 Place the beaker on a heat resistant surface for 30 min.

7.6 Add ~ 180 mL DDI water to the beaker to stop the reaction.

Titration of Excess Dichromate

7.7 Titrate eight reagent blanks at the start of each batch to determine the normality of the ferrous sulfate. A blank is 10.00 mL K$_2$Cr$_2$O$_7$ plus H$_2$SO$_4$ without soil. The average titer is used for the blank titer value.

7.8 Place the appropriate blanks and samples in the sample holder magazines and place on the sample changer.

7.9 Refer to the Appendix XV, Automatic Titrator, and the manufacturer's instruction manual for operation of automatic titrator.

7.10 Set the endpoint to 700 mV. Set the controls of the 664 Control Unit to the appropriate settings.

7.11 Prime the buret with 50 mL of ferrous sulfate solution before starting the titrations.

7.12 When a long series of samples are being titrated, intersperse blank samples throughout the titrations. The blank titer drifts over time, mainly because of the temperature change of the solution. Any sample with a titer of less one milliter and/or endpoint of less than 620 millivolts should be reanalyzed.

7.13 Press "Start" on the titrator.

8. CALCULATIONS

OC (%) =
$$\frac{(\text{Blank x Volume}) - (10 \text{ x Titer}) \text{ x } 3 \text{ x } 100 \text{ x AD/OD}}{\text{Blank x Sample Weight (g) x } 0.77 \text{ x } 1000}$$

where:
OC (%)   = Organic C (%)
Blank   = Average titer of reagent blanks (mL)
Volume   = Volume of 1 N K$_2$Cr$_2$O$_4$ (mL)
Titer   = Titer of FeSO$_4$ (mL)
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)
3   = Equivalents per C (assumed)
1000   = Meq eq^{-1}
100   = Convert to 100-g basis
0.77   = Assumed C oxidation factor.

9. REPORT

Report organic C percentage to two decimal places, e.g., 0.95% OC, on an oven-dry basis.

10. PRECISION

Precision data are not available for this procedure.   A quality control check sample is run in every batch of 20 samples. With 251 observations of the quality control check sample, the mean, standard deviation, and C.V. for organic carbon are 1.47, 0.025, and 1.7%, respectively.

11. REFERENCES

Broadbent, F.E. 1953. The soil organic fraction. Adv. Agron. 5:153-183.

Walkley, A. 1946. A critical examination of a rapid method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. Soil Sci. 63:251-263.

Walkley, A., and Black, I.A. 1934. An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37:29-38.

CHEMICAL ANALYSES
TOTAL CARBON (6A)
DRY COMBUSTION (6A2)
LECO SC-444 CARBON ANALYZER (6A2e)

1. APPLICATION

Total C in soils is the sum of organic and inorganic C. Most of the organic C is associated with the organic matter fraction, and the inorganic C is generally found with carbonate minerals. The organic C in mineral soils generally ranges from 0 to 12 percent.

Total C is quantified by two basic methods, i.e., wet or dry combustion. The SSL uses dry combustion. In total C determinations, all forms of C in a soil are converted to CO_2 followed by a quantification of the evolved CO_2. Total C can be used to estimate the organic C content of a soil. The difference between total and inorganic C is an estimate of the organic C. Organic C also can be determined directly (procedure 6A1c). The inorganic C should be equivalent to carbonate values measured by CO_2 evolution with strong acid (Nelson and Sommers, 1982).

Organic C defines mineral and organic soils. In *Soil Taxonomy*, organic C is also used at lower taxonomic levels, e.g., ustollic and fluventic subgroups (Soil Survey Staff, 1975).

2. SUMMARY OF METHOD

A fine-ground (<80-mesh) soil sample is oxidized at high temperatures. The released gases are scrubbed, and the CO_2 in the combustion gases is measured by using an infrared detector. The microprocessor formulates the analytical results (C_i) by combining the outputs of the infrared detector and the system ambient sensors with pre-programmed calibration, linearization and weight compensation factors. Percent total C is reported on an oven-dry soil basis.

3. INTERFERENCES

This procedure simultaneously measures inorganic and organic C. A high rate of combustion can oversaturate the carbon detection cell. The rate of combustion can be retarded by adding a solid/powder combustion controller.

4. SAFETY

Wear protective clothing and safety glasses. Magnesium perchlorate may form explosive mixtures. Magnesium perchlorate may contain traces of perchloric acid, which remain from manufacturer's operations. This acid is anhydrous because of the strong desiccating capability of the salt. Avoid prolonged contact with oxidizable material or material capable of forming unstable perchlorate esters or salts. Remove magnesium perchlorate by using an excess of water to thoroughly dilute the material.

The use of high temperatures in the oxidation of samples requires that extreme caution be used to prevent burns and fires. Follow standard laboratory procedures when handling compressed gases. Oxygen is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the carbon analyzer.

5. EQUIPMENT
5.1 Carbon analyzer, Leco Model SC-444, Sulfur and Carbon Analyzers, Leco Corp., St. Joseph, MI
5.2 Combustion boats, part no. 529-203, Leco Corp., St. Joseph, MI
5.3 Single-stage regulator, oxygen service, part no. E11-W-N115Box, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105
5.4 Electronic balance, ±1-mg sensitivity

6. REAGENTS
6.1 Anhydrous magnesium perchlorate, granular
6.2 Glass wool
6.3 Compressed oxygen, >99.5% @ 30 psi
6.4 Calcium carbonate, $CaCO_3$, reagent grade.

CHEMICAL ANALYSES
TOTAL CARBON (6A)
DRY COMBUSTION (6A2)
LECO SC-444 CARBON ANALYZER (6A2e)

6.5 Solid/Powder Combustion Controller, part no. 501-426, Leco Corp., St. Joseph, MI

6.6 Soil Calibration Sample, part no. 502-062, Leco Corp., St. Joseph, MI

7. PROCEDURE

7.1 Use a fine-ground 80-mesh, air-dry soil

7.2 Prepare instrument as outlined in the operator's instruction manual (Leco, 1994; Leco, 1993) and Appendix V.

7.3 Methods are created with the method menu and stored in the instrument memory. System parameters are set as follows:

Furnace operating temperature: 1450°C
Lance delay: 20 s
Analysis time settings: 70 to 180 s
Comparator level settings: 0.1%

7.3 Condition instrument by analyzing a few soil samples, until readings are stable.

7.4 Calibrate instrument by analyzing at least three replicates of each calibration standard. Use the soil calibration standard for samples with less than three to four percent total carbon and calcium carbonate for samples with more than four percent total carbon. Weigh standards in a range from 0.2 to 0.7 g.

7.5 Load samples on autoload rack, place in the analyzer, and press analyze key.

7.6 Weigh 0.2 to 0.5 g sample in a tared combustion boat.

7.7 Load samples on autoload rack, place in the analyzer, and press analyze key.

7.8 If results exceed calibration range, reduced weight of sample. If carbon detection cell is saturated, add approximately 1 g of solid/powder combustion controller to sample.

7.9 Repack the reagent (anhydrous magnesium perchlorate) tubes whenever the reagent becomes caked or moist or the warning alarm displays.

8. CALCULATIONS

C (%) = C_i x AD/OD

where:
C (%)   = C (%), oven-dry basis
C_i = C (%) instrument
AD/OD   = air-dry/oven-dry ratio (procedure 4B5)

9. REPORT
Report total C percentage on an oven-dry basis to the nearest 0.1%.

CHEMICAL ANALYSES
TOTAL CARBON (6A)
DRY COMBUSTION (6A2)
LECO SC-444 CARBON ANALYZER (6A2e)

10. PRECISION
A quality control check sample is included in every batch of ten samples. For 191 observations of calcium carbonate (actual total C = 12%), the mean, standard deviation, and C.V. for total carbon are 12.04, 0.31, and 2.5%, respectively. For 86 observations of soil calibration standard (reported total C = 0.77%), the mean, standard deviation, and C.V. for total carbon are 0.79, 0.02, and 2.2%, respectively.

11. REFERENCES
Leco Corp. 1993. Sulfur and carbon in cements, soils, rock, ceramic and similar materials. Application Bulletin. Leco Corp., 3000 Lakeview Ave., St. Joseph, MI.

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Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:539-579.

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA-SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

CHEMICAL ANALYSIS
TOTAL NITROGEN (6B)
DRY COMBUSTION (6B4)
LECO FP-438 ANALYZER (6B4a)

1. APPLICATION

The total N content of the soil may range from <0.02% in subsoils, 2.5% in peats, and 0.06 to 0.5% in surface layers of many cultivated soils (Bremmer and Mulvaney, 1982). The total N data may be used to determine the soil C:N ratio, the soil potential to supply N for plant growth, and the N distribution in the soil profile. The C:N ratio generally ranges between 10 to 12. Variations in the C:N ratio may serve as an indicator of the amount of soil inorganic N. Uncultivated soils usually have higher C:N ratios than do cultivated soils.

Soils with large amounts of illites or vermiculites can "fix" significant amounts of N compared to those soils dominated by smectites or kaolinites (Young and Aldag, 1982; Nommik and Vahtras, 1982). Since the organic C of many soils diminishes with depth while the level of "fixed" N remains constant or increases, the C:N ratio narrows (Young and Aldag, 1982). The potential to "fix" N has important fertility implications as the "fixed" N is slowly available for plant growth.

2. SUMMARY OF METHOD

A soil sample is combusted at high temperature with oxygen to release NO_x. The gases released are scrubbed to remove interferences (e.g., CO_2 and H_2O), and the NO_x is reduced to N_2. The N_2 is measured by thermal conductivity detection and reported as percent N.

3. INTERFERENCES

The total N that is measured by the combustion method does not distinguish among the types of N that are present in the soil. The purity of the helium and oxygen gases used in the instrument may affect the results of the analysis. The highest purity gases available are required to assure low detection limits and consistent results.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (goggles or safety glasses) when handling hot crucibles. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary.

5. EQUIPMENT

5.1 Electronic balance, ±0.001-g sensitivity

6. REAGENTS
None

7. PROCEDURE

7.1 Weigh 0.200 g of 80-mesh, air-dry soil into a tin foil cup.

7.2 Close the tin foil cup by twisting the top closed as to fit the sample holder.

7.3 Place the enclosed sample in the sample holder.

7.4 When all the samples are in the sample holder, place the sample holder on the instrument.

7.5 Refer to Appendix VII for operation and calibration of the LECO FP-438 Analyzer.

7.6 On the bench worksheet, record the percent N for the samples.

8. CALCULATIONS

N (%) = Instrument Reading x AD/OD

where:
AD/OD = Air-dry/Ovendry ratio (procedure 4B5)

9. REPORT
Report total N as a dimensionless value to the nearest 0.001 unit on an ovendry basis.

10. PRECISION
Precision data are not available for this procedure. For 105 observations of the quality control check sample for total N, the mean, standard deviation, and C.V. are 0.143, 0.004, and 2.7 percent, respectively.

11. REFERENCES

Bremmer, J.M., and C.S. Mulvaney. 1982. Nitrogen - Total. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:595-624.

Nommik, H., and K. Vahtras. 1982. Retention and fixation of ammonium and ammonia in soils. *In* F.J. Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22:123-171.

Young, J.L., and R.W. Aldag. 1982. Inorganic forms of nitrogen in soil. *In* F.J. Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22:43-66.

CHEMICAL ANALYSES
MINERALIZABLE NITROGEN (6B)
STEAM DISTILLATION (6B5)
KJELTEC AUTO 1035 SAMPLER (6B5A)

1. APPLICATION

The most satisfactory methods currently available for obtaining an index for the availability of soil N are those involving the estimation of the N formed when soil is incubated under conditions which promote mineralization of organic N by soil microorganisms (Environmental Protection Agency, 1992). The method described herein for estimating mineralizable N is one of anaerobic incubation and is suitable for routine analysis of soils. This method involves estimation of the ammonium produced by a 1-week period of incubation of soil at 40°C (Keeney and Bremner, 1966) under anaerobic conditions to provide an index of N availability.

2. METHOD SUMMARY

An aliquot of air-dry homogenized soil is placed in a test tube with water, stoppered, and incubated at 40°C for 1 week. The contents are transferred to a steam distillation, rinsed with 4 *N* KCl. The amount of ammonium-N is determined by steam distillation and titration for the KCl:soil mixture.

3. INTERFERENCES

There are no known interferences. The temperature and incubation period must remain constant for all samples. The test can be performed on field-moist or air-dry soil samples.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Follow the manufacturer's safety precautions when using the incubator and Kjeltec Auto 1035 Analyzer.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity
5.2 Test tubes, 16-mm x 150-mm
5.3 PVC stoppers
5.4 Incubator, Model 10-140, Quality Lab Inc., Chicago, IL
5.5 Digestion tubes, straight neck, 250 mL
5.6 Kjeltec Auto 1035/1038 Sampler System, Tecator, Perstorp Analytical Inc.

6. REAGENTS

6.1 Distilled deionized (DDI) water
6.2 Potassium chloride (KCl), 4 *N*. Dissolve 298.24 g KCl in DDI water and dilute to 1-L volume.
6.3 Hydrochloric acid (HCl), 0.05 *N*, standardized. Dilute 83 mL of concentrated HCl in 20 L of DDI water. Refer to Appendix VIII, Standardization of Acids.
6.4 Antifoam agent, slipicone release spray, Dow Chemical Corp. Alternatively, use n-octyl alcohol.
6.5 Boric acid, 4% (w:v), with bromcresol green-methyl red indicator (0.075 % bromcresol green and 0.05% methyl red), Chempure Brand

7. PROCEDURE

Anaerobic Incubation of Soil Sample
7.1 Place 5.00 g of mineral soil (or 1.25 g of organic soil) into a 16-mm x 150-mm test tube. Record the soil sample weight to the nearest 0.00 g.

7.2 Add 12.5 ±1 mL of DDI water. Do not add ethanol to overcome any wetting difficulties as ethanol may act as an interference with microbial activity. Stopper the tube, shake, and place in a 40°C constant-temperature incubator for 7 days. Refer to the manufacturer's instructions for set-up and operation of the incubator.

7.3 At the end of 7 days, remove the tube and shake for 15 s.

7.4 Transfer the contents of the test tube to a 250-mL digestion tube. Complete the transfer by rinsing the tube with 3 times with 4 ml of 4 *N* KCl, using a total of 12.5 ±1 mL of the KCl.

Steam Distillation: Samples and Reagent Blanks
7.5 Remove the extraction vessel and transfer the sample to a 250-mL digestion tube.

7.6 Perform the same transfer and addition of reagents for blanks as for samples.

7.7 Spray silicone antifoam agent (or 2 drops of n-octyl alcohol solution) into the digestion tubes for each of the samples and reagent blanks.

7.8 When using new reagents, e.g., boric acid, reagent blanks are distilled in 2 sets of 6, one set per Kjeltec machine. Each set of 6 is averaged and recorded on bench worksheet and manually set on each machine. During the steam distillation, the mean reagent blank titer is automatically subtracted from the sample titer. Refer to Appendix IX for operation and calibration of Kjeltec Auto 1035 Analyzer.

7.9 On bench worksheet, record the normality of standardized acid, i.e., $\approx$ 0.0500 *N* HCl.

7.10 Load samples in racks of 20. Distillation and titration are performed automatically. Record the titer in mL of titrant. Refer to Appendix IX for operation and calibration of Kjeltec Auto 1035 Analyzer.

8. CALCULATIONS

$$\text{N} = \frac{\text{Titer x } N \text{ x 100 x AD/OD}}{\text{Sample Weight (g)}}$$

where:
N   = Mineralizable N (meq 100 g^{-1})
Titer   = Titer of sample (mL)
N   = Normality of HCl titrant
100   = Conversion factor to 100-g basis
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)

9. REPORT
Report mineralizable N in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.001 meq 100 g^{-1}.

10. PRECISION
No precision data are available for this procedure.

11. REFERENCES

Environmental Protection Agency. 1992. Handbook of laboratory methods for forest health monitoring. G.E. Byers, R.D. Van Remortel, T.E. Lewis, and M. Baldwin (eds.). Part III. Soil analytical laboratory. Section 10. Mineralizable N. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

Keeney, D.R. and J.M. Bremner. 1966. Comparison and evaluation of laboratory methods of obtaining an index of soil nitrogen availability. Agron. J. 58:498-503.

CHEMICAL ANALYSES
IRON, MANGANESE, AND ALUMINUM (6C, 6D, and 6G)
DITHIONITE-CITRATE EXTRACTION (6C2, 6D2, and 6G7)
ATOMIC ABSORPTION
PERKIN-ELMER AA 5000
(6C2b, 6D2a, and 6G7a)

1. APPLICATION

Dithionite-citrate (CD) is used as a selective dissolution extractant for organically complexed Fe and Al, noncrystalline hydrous oxides of Fe and Al, and amorphous aluminosilicates (Wada, 1989). The CD solution is a poor extractant of crystalline hydrous oxides of Al, allophane, and imogolite. The CD solution does not extract opal, Si, or other constituents of crystalline silicate minerals (Wada, 1989). In *Soil Taxonomy*, the CD extractable Fe and Al are criteria for spodic placement (Soil Survey Staff, 1975).

2. SUMMARY OF METHOD

A soil sample is mixed with sodium dithionite, sodium citrate, and distilled deionized water, and shaken overnight. Superfloc 16 is added, and the mixture is made to volume. Solution is allowed to settle, and a clear extract is obtained. The CD extract is diluted with distilled deionized (DDI) water. The analytes are by an atomic absorption spectrophotometer (AA). The data are automatically recorded by a microcomputer and printer. The percent CD extractable Fe, Mn, and Al are reported in procedures 6C2b, 6D2a, and 6G7a, respectively.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AA analyses of these elements. These interferences vary in importance, depending upon the particular analyze selected.

The redo potential of the extractant is dependent upon the pH of the extracting solution and the soil system. Sodium citrate complexes the reduced Fe and usually buffers the system to a pH of 6.5 to 7.3. Some soils may lower the pH, resulting in the precipitation of Fe sulfides. The SSL has not had significant problems with this interference.

Filtered extracts can yield different recoveries of Fe, Mn, and Al, relative to unfiltered extracts.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves); eye protection (face shields, goggles, or safety glasses); and a breathing filter when handling dry sodium dithionite. Sodium dithionite may spontaneously ignite if allowed to become moist, even by atmospheric moisture. Keep dithionite in a fume hood.

Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity
5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell
5.3 Atomic absorption spectrophotometer (AA), model 5000, Perkin-Elmer Corp., Norwalk, CT
5.4 Automatic burner control, model 5000, Perkin-Elmer Corp., Norwalk, CT
5.5 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT
5.6 Dot matrix printer, P-132, Interdigital Data Systems,Inc.
5.7 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA
5.8 Digital diluter/dispenser, MicroLab 500, Hamilton Co., P.O. Box 10030, Reno, NV
5.9 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

CHEMICAL ANALYSES
IRON, MANGANESE, AND ALUMINUM (6C, 6D, and 6G)
DITHIONITE-CITRATE EXTRACTION (6C2, 6D2, and 6G7)
ATOMIC ABSORPTION
PERKIN-ELMER AA 5000
(6C2b, 6D2a, and 6G7a)

5.10 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.11 Containers, polypropylene

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Sodium dithionite ($Na_2S_2O_4$), purified powder

6.3 Sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), crystal, reagent

6.4 Hydrochloric acid (HCl), concentrated 12 *N*

6.5 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.6 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.7 Superfloc 16, 0.2% solution (w:v). Dissolve 2 g of Superfloc 16 in 1 liter of DDI water. Do not shake the mixture as this breaks the polymer chains of the Superfloc. Gently swirl the mixture occasionally over the several days that the solution requires to completely dissolve the Superfloc. Suggested source is American Cyanamid Co., P.O. Box 32787, Charlotte, NC.

6.8 Primary mixed standard, 4000 mg L^{-1} (4000 ppm) Fe, 600 mg L^{-1} (600 ppm) Mn, and 3000 mg L^{-1} (3000 ppm) Al. Dissolve 4.000 g of Fe wire, 0.6000 g of Mn metal powder, and 3.000 g of Al wire with 1:1 HCl in a glass beaker. When dissolved transfer to a 1-L volumetric flask and make to volume with 1% HCl solution. Store in a polypropylene bottle.

6.9 High calibration standard, 240 mg/8 oz (1012 ppm) Fe; 36 mg/8 oz (152 ppm) Mn; and 180 mg/8 oz (759 ppm) Al. Pipet 60 mL of primary mixed standard into 8 oz bottle. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.10 Low calibration standard, 120 mg/8 oz (506 ppm) Fe; 18 mg/8 oz (76 ppm) Mn; and 90 mg/8 oz (380 ppm) Al. Pipet 30 mL of primary mixed standard into 8 oz bottle. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards and reagent blanks, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.11 Calibration reagent blank solution. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards and reagent blanks, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.12 Acetylene gas, purity 99.6%

6.13 Compressed air with water and oil traps

7. PROCEDURE

Extraction of Fe, Mn, and Al

7.1 Weigh 4.00 g of <2-mm, air-dry soil sample and place in an 8-oz nursing bottle.

7.2 Add 2 g of sodium dithionite and 20 to 25 g of sodium citrate dihydrate.

7.3 Add DDI water to 4-oz level on bottle and securely stopper bottle.

7.4 Shake overnight (12 to 16 h) in a reciprocating shaker. After shaking, use a dispenser to add 2 ml of Superfloc 16 solution.

CHEMICAL ANALYSES
IRON, MANGANESE, AND ALUMINUM (6C, 6D, and 6G)
DITHIONITE-CITRATE EXTRACTION (6C2, 6D2, and 6G7)
ATOMIC ABSORPTION
PERKIN-ELMER AA 5000
(6C2b, 6D2a, and 6G7a)

7.5 Fill bottle to 8-oz volume with DDI water. Stopper and shake thoroughly for ~ 15 s.

7.6 Allow to settle for at least 3 day (3 to 5 days typical). The Fe, Mn, and Al are determined from a clear aliquot of solution.

Dilution of Sample Extracts and Standards

7.7 No ionization suppressant is required as the Na in the extractant is present in sufficient quantity. Set the digital diluter at 66 for diluent and 35 for CD extracts, calibration reagent blanks, and calibration standards for a 1:20 dilution as follows:

7.8 Dilute 1 part CD sample extract with 19 parts of DDI water (1:20 dilution).

7.9 Dilute 1 part calibration reagent blank with 19 parts of DDI water (1:20 dilution).

7.10 Dilute 1 part low calibration standard with 19 parts of DDI water (1:20 dilution).

7.11 Dilute 1 part high calibration standard with 19 parts of DDI water (1:20 dilution).

7.12 Dispense the reagent blanks and calibration standards in polycons from which the solutions are transferred to test tubes. Dispense the diluted sample solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration

7.13 Use the calibration reagent blank and high calibration standard to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

7.14 Use the low calibration standard (120 mg/8 oz Fe; 18 mg/8 oz Mn; and 90 mg/8 oz Al) as a check sample. Use high calibration standard for Fe check sample and low calibration standard for Mn and Al check sample.

AA Set-up and Operation

7.15 Refer to Appendix X, Atomic Absorption, and manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Wavelength (nm)	Burner Head	Fuel/Oxidant
Fe	248.8	5-cm parallel	10 C_2H_2/25 Air
Mn	280.1	5-cm parallel	10 C_2H_2/25 Air
Al	309.3	5-cm parallel	30 C_2H_2/17 N_2O

Typical read delay is 6 s, and integration time is 8 s.

7.16 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

CHEMICAL ANALYSES
IRON, MANGANESE, AND ALUMINUM (6C, 6D, and 6G)
DITHIONITE-CITRATE EXTRACTION (6C2, 6D2, and 6G7)
ATOMIC ABSORPTION
PERKIN-ELMER AA 5000
(6C2b, 6D2a, and 6G7a)

7.17 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with DDI water (1:20 dilution).

7.18 The instrument readings are usually programmed to display analyte concentration in mg/8 oz.

8. CALCULATIONS

$$\text{Fe (\%)} = \frac{(\text{Fe} \times \text{DR} \times 100 \times \text{AD/OD})}{\text{Sample} \times 1000}$$

$$\text{Fe}_2\text{O}_3 \text{ (\%)} = \frac{(\text{Fe} \times \text{DR} \times 1.43 \times 100 \times \text{AD/OD})}{\text{Sample} \times 1000}$$

$$\text{Mn (\%)} = \frac{(\text{Mn} \times \text{DR} \times 100 \times \text{AD/OD})}{\text{Sample} \times 1000}$$

$$\text{Al (\%)} = \frac{(\text{Al} \times \text{DR} \times 100 \times \text{AD/OD})}{\text{Sample} \times 1000}$$

where:
Fe   = mg/8 oz
Mn   = mg/8 oz
Al   = mg/8 oz
DR   = Dilution Ratio
Sample = Sample weight (g)
1.43   = Conversion factor from Fe to Fe_2O_3
100   = Conversion factor to percent
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)
1000   = Conversion factor (mg g^{-1})

9. REPORT
Report percent CD extractable Fe, Mn, and Al on oven-dry soil basis to the nearest whole number.

CHEMICAL ANALYSES
IRON, MANGANESE, AND ALUMINUM (6C, 6D, and 6G)
DITHIONITE-CITRATE EXTRACTION (6C2, 6D2, and 6G7)
ATOMIC ABSORPTION
PERKIN-ELMER AA 5000
(6C2b, 6D2a, and 6G7a)

10. PRECISION

Precision data are not available for this procedure. A quality control check sample is run with every batch of samples. For the quality control check sample, the mean, standard deviation, and CV for Fe, Mn, and Al are as follows:

Element	Mean	n	Std. Dev.	C.V.
Fe	2.5	35	0.05	2.2%
Mn	0.01	19	0.00	0.0%
Al	0.26	33	0.01	5.4%

11. REFERENCES

Wada, K. 1989. Allophane and imogolite. *In* J.B. Dixon and S.B. Weed (eds.). Minerals in soil environment. 2nd ed. Soil Sci. Soc. Amer. No. 1. p. 1051-1087.

Soil Survey Staff. 1975. Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA-SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

CHEMICAL ANALYSES
IRON, MANGANESE, AND ALUMINUM (6C, 6D, and 6G)
DITHIONITE-CITRATE EXTRACTION (6C2, 6D2, and 6G7)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE 4000
(6C2c, 6D2b, and 6G7b)

1. APPLICATION

Dithionite-citrate (CD) is used as a selective dissolution extractant for organically complexed Fe and Al, noncrystalline hydrous oxides of Fe and Al, and amorphous aluminosilicates (Wada, 1989). The CD solution is a poor extractant of crystalline hydrous oxides of Al, allophane, and imogolite. The CD solution does not extract opal, Si, or other constituents of crystalline silicate minerals (Wada, 1989). In *Soil Taxonomy*, the CD extractable Fe and Al are criteria for spodic placement (Soil Survey Staff, 1975).

2. SUMMARY OF METHOD

A soil sample is mixed with sodium dithionite, sodium citrate, and distilled deionized water, and shaken overnight. Superfloc 16 is added, and the mixture is made to volume. Solution is allowed to settle, and a clear extract is obtained. The CD extract is diluted with distilled deionized (DDI) water. The analytes are measured by an atomic absorption spectrophotometer (AA). The data are automatically recorded by a microcomputer and printer. The percent CD extractable Fe, Mn, and Al are reported in procedures 6C2c, 6D2b, and 6G7b, respectively.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AA analyses of these elements. These interferences vary in importance, depending upon the particular analyte selected.

The redox potential of the extractant is dependent upon the pH of the extracting solution and the soil system. Sodium citrate complexes the reduced Fe and usually buffers the system to a pH of 6.5 to 7.3. Some soils may lower the pH, resulting in the precipitation of Fe sulfides. The SSL has not had significant problems with this interference.

Filtered extracts can yield different recoveries of Fe, Mn, and Al, relative to unfiltered extracts.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves); eye protection (face shields, goggles, or safety glasses); and a breathing filter when handling dry sodium dithionite. Sodium dithionite may spontaneously ignite if allowed to become moist, even by atmospheric moisture. Keep dithionite in a fume hood.

Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity

5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell

5.3 Atomic absorption spectrophotometer (AA), Smith-Hieftje Model 4000, Thermo Jarrell Ash Corp., Franklin, MA

5.4 Autosampler, Model 150, Thermo Jarrell Ash Corp., Franklin, MA

5.5 ThermoSpec software, Version 3.01, Enable 4.0, DOS 5.0, Thermo Jarrell Ash Corp., Franklin, MA

5.6 Computer, CUi Advantage 486, Thermo Jarrell Ash Corp., Franklin, MA

5.7 Printer, NEC Pinwriter P3200

5.8 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.9 Digital diluter/dispenser, MicroLab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.10 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

CHEMICAL ANALYSES
IRON, MANGANESE, AND ALUMINUM (6C, 6D, and 6G)
DITHIONITE-CITRATE EXTRACTION (6C2, 6D2, and 6G7)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE 4000
(6C2c, 6D2b, and 6G7b)

5.11 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.12 Containers, polypropylene

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Sodium dithionite ($Na_2S_2O_4$), purified powder

6.3 Sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), crystal, reagent

6.4 Hydrochloric acid (HCl), concentrated 12 *N*

6.5 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.6 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.7 Superfloc 16, 0.2% solution (w:v). Dissolve 2 g of Superfloc 16 in 1 liter of DDI water. Do not shake the mixture as this breaks the polymer chains of the Superfloc. Gently swirl the mixture occasionally over the several days that the solution requires to completely dissolve the Superfloc. Suggested source is American Cyanamid Co., P.O. Box 32787, Charlotte, NC.

6.8 Primary mixed standard, 4000 mg L^{-1} (4000 ppm) Fe, 600 mg L^{-1} (600 ppm) Mn, and 3000 mg L^{-1} (3000 ppm) Al. Dissolve 4.000 g of Fe wire, 0.6000 g of Mn metal powder, and 3.000 g of Al wire with 1:1 HCl in a glass beaker. When dissolved transfer to a 1-L volumetric flask and make to volume with 1% HCl solution. Store in a polypropylene bottle.

6.9 High calibration standard, 240 mg/8 oz (1012 ppm) Fe; 36 mg/8 oz (152 ppm) Mn; and 180 mg/8 oz (759 ppm) Al. Pipet 60 mL of primary mixed standard into 8 oz bottle. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.10 Low calibration standard, 120 mg/8 oz (506 ppm) Fe; 18 mg/8 oz (76 ppm) Mn; and 90 mg/8 oz (380 ppm) Al. Pipet 30 mL of primary mixed standard into 8 oz bottle. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards and reagent blanks, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.11 Calibration reagent blank solution. Add 20 g of sodium citrate dihydrate, 1.24 mL of concentrated H_2SO_4, and 2 mL of Superfloc 16 solution. In standards and reagent blanks, the H_2SO_4 substitutes for the dithionite. Fill to 8-oz volume with DDI water and mix thoroughly. After dissolution, transfer solution to a plastic bottle.

6.12 Acetylene gas, purity 99.6%

6.13 Compressed air with water and oil traps

7. PROCEDURE

Extraction of Fe, Mn, and Al

7.1 Weigh 4.00 g of <2-mm, air-dry soil sample and place in an 8-oz nursing bottle.

7.2 Add 2 g of sodium dithionite and 20 to 25 g of sodium citrate dihydrate.

7.3 Add DDI water to 4-oz level on bottle and securely stopper bottle.

7.4 Shake overnight (12 to 16 h) in a reciprocating shaker. After shaking, use a dispenser to add 2 ml of Superfloc 16 solution.

7.5 Fill bottle to 8-oz volume with DDI water. Stopper and shake thoroughly for ~ 15 s.

CHEMICAL ANALYSES
IRON, MANGANESE, AND ALUMINUM (6C, 6D, and 6G)
DITHIONITE-CITRATE EXTRACTION (6C2, 6D2, and 6G7)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE 4000
(6C2c, 6D2b, and 6G7b)

7.6 Allow to settle for at least 3 day (3 to 5 days typical). The Fe, Mn, and Al are determined from a clear aliquot of solution.

Dilution of Sample Extracts and Standards

7.7 No ionization suppressant is required as the Na in the extractant is present in sufficient quantity. Set the digital diluter at 66 for diluent and 35 for CD extracts, calibration reagent blanks, and calibration standards for a 1:20 dilution as follows:

7.8 Dilute 1 part CD sample extract with 19 parts of DDI water (1:20 dilution).

7.9 Dilute 1 part calibration reagent blank with 19 parts of DDI water (1:20 dilution).

7.10 Dilute 1 part low calibration standard with 19 parts of DDI water (1:20 dilution).

7.11 Dilute 1 part high calibration standard with 19 parts of DDI water (1:20 dilution).

7.12 Dispense the reagent blanks and calibration standards in polycons from which the solutions are transferred to test tubes. Dispense the diluted sample solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration

7.13 Use the calibration reagent blank and high calibration standard to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

7.14 Use the low calibration standard (120 mg/8 oz Fe; 18 mg/8 oz Mn; and 90 mg/8 oz Al) as a check sample. Use high calibration standard for Fe check sample and low calibration standard for Mn and Al check sample.

AA Set-up and Operation

7.15 Refer to Appendix X, Atomic Absorption, and manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Wavelength (nm)	Burner Head	Fuel/Oxidant
Fe	248.8	5-cm parallel	4 C_2H_2/16 Air
Mn	280.1	5-cm parallel	4 C_2H_2/16 Air
Al	309.3	5-cm parallel	20 C_2H_2/10 N_2O

Typical read delay is 6 s, and integration time is 8 s.

7.16 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.17 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with DDI water (1:20 dilution).

CHEMICAL ANALYSES
IRON, MANGANESE, AND ALUMINUM (6C, 6D, and 6G)
DITHIONITE-CITRATE EXTRACTION (6C2, 6D2, and 6G7)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE 4000
(6C2c, 6D2b, and 6G7b)

7.18 The instrument readings are usually programmed to display analyte concentration in mg/8 oz.

8. CALCULATIONS

$$\text{Fe (\%)} = \frac{(\text{Fe x DR x 100 x AD/OD})}{\text{Sample x 1000}}$$

$$\text{Fe}_2\text{O}_3 \text{ (\%)} = \frac{(\text{Fe X DR x 1.43 x 100 x AD/OD})}{\text{Sample x 1000}}$$

$$\text{Mn (\%)} = \frac{(\text{Mn x DR x 100 x AD/OD})}{\text{Sample x 1000}}$$

$$\text{Al (\%)} = \frac{(\text{Al x DR x 100 x AD/OD})}{\text{Sample x 1000}}$$

where:
Fe   = mg/8 oz
Mn   = mg/8 oz
Al   = mg/8 oz
DR   = Dilution Ratio
Sample   = Sample weight (g)
1.43   = Conversion factor from Fe to Fe_2O_3
100   = Conversion factor to percent
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)
1000   = Conversion factor (mg g^{-1})

9. REPORT
Report percent CD extractable Fe, Mn, and Al on oven-dry soil basis to the nearest whole number.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is run with every batch of samples.

11. REFERENCES
Wada, K. 1989. Allophane and imogolite. *In* J.B. Dixon and S.B. Weed (eds.). Minerals in soil environment. 2nd ed. Soil Sci. Soc. Amer. No. 1. p. 1051-1087.
Soil Survey Staff. 1975. Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA-SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

CHEMICAL ANALYSIS
IRON, MANGANESE, ALUMINUM, CALCIUM, MAGNESIUM, SODIUM, POTASSIUM, PHOSPHORUS, SILICON, ZIRCONIUM, COPPER, ZINC, ARSENATE, TITANTIUM, SELENIUM, CADMIUM, AND LEAD
HF PLUS AQUA REGIA (HF + HNO$_3$ + HCl) DISSOLUTION
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH ICAP 61E
(6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a, 8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a)

1. APPLICATION

This procedure is an integral part of total analysis (procedure 7C4a) and represents the spectroscopic analysis of elements in the digestate.

2. SUMMARY OF METHOD

High and low calibration standards are prepared for Ca, K, Mg, Mn, Cu, Zn, Cd, and Pb (mixed standards CALO and CAHI); Al, Fe, Ti, Zr, and Na (mixed standards ALLO and ALHI); and Si, P, Se, and As (mixed standards SILO and SIHI). A blank of HF, HNO$_3$, HCl, and H$_3$BO$_3$ is prepared. A Thermo Jarrell Ash ICAP 61E spectrometer is used for analysis. The concentration of Fe, Mn, Al, Ca, Mg, Na, K, P, Si, Zr, Cu, Zn, As, Ti, Se, Cd, and Pb are determined by ICP analysis by procedures 6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a, 8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a, respectively. Data are reported in procedure 7C4a.

3. INTERFERENCES

None.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated acids to the fume hood. Keep HF acid refrigerated and avoid contact with skin of all acids. Wash hands thoroughly after handling reagents.

5. EQUIPMENT

5.1 Volumetrics, 500-mL, polypropylene

5.2 Containers, 500-mL, polypropylene, with screw caps

5.3 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 µL and 10 mL

5.4 Inductively coupled plasma spectrometer, ICAP 61E, Thermo Jarrell Ash Corp., Franklin, MA

5.5 RF generator, floor mounted power unit, Model 7/90, Thermo Jarrell Ash Corp., Franklin, MA

5.6 Computer, AT&T 386 Starstation, Model CPU-G72, and printer, NEC Pinwriter, P2200XE, Dot Matrix

5.7 ThermoSpec software, Thermo Jarrell Ash Corp., Franklin, MA

5.9 Line conditioner, Unity/I, Model UT8K, Best Power Technology, Inc., Necedah, WI

5.10 Compressed argon gas

5.11 Autosampler, Thermo Jarrell Ash Corp., Franklin, MA

5.12 High flow torch, Part No. 126440-01; Saffire (HF-resistant) tip, Part No. 127190-00; Polypropylene spray chamber, Part 131129-00, Thermo Jarrell Ash Corp., Franklin, MA

6. REAGENTS

6.1 Deionized distilled (DDI) water

6.2 Hydrofluoric acid (HF), 48%, low trace metal content

6.3 Concentrated hydrochloric acid (HCl), 12 *N*. Use instrumental grade which contains low levels of impurities.

6.4 Concentrated nitric acid (HNO$_3$), 16 *N*. Use instrumental grade which contains low levels of impurities.

6.5 Boric acid solution. Dissolve 25.0 g low trace metal, granular boric acid (H$_3$BO$_3$) in 1000 mL DDI water.

CHEMICAL ANALYSIS
IRON, MANGANESE, ALUMINUM, CALCIUM, MAGNESIUM, SODIUM, POTASSIUM, PHOSPHORUS, SILICON, ZIRCONIUM, COPPER, ZINC, ARSENATE, TITANTIUM, SELENIUM, CADMIUM, AND LEAD
HF PLUS AQUA REGIA (HF + HNO$_3$ + HCl) DISSOLUTION
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH ICAP 61E
(6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a, 8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a)

6.6 Standards, 1000 ppm, suitable for atomic absorption spectroscopy for all elements

7. PROCEDURE

7.1 Instrument calibration standards for analysis are limited to specific combinations of elements because of chemical incompatibilities of certain elements. Specific combinations of elements in calibration standards are based on suggestions by Thermo Jarell Ash (TJA), Inc. Each working standard is used in two concentrations, high and low. The concentrations of elements in the low standards (CALO, ALLO, and SILO) are 50 percent of the concentrations in the high standards (CAHI, ALHI, and SIHI). Refer to Tables 1-3 for the amounts of primary standards (1000 ppm) to make 500-mL volume of the low and high calibration standards, at the specified concentrations, for ICP analysis.

Table 1. Calibration standards for CALO and CAHI[1]

| Element | -- Concentration -- | | Primary Std Required for | |
	CALO	CAHI	CALO	CAHI
	------- ppm -------		---- mL ----	
Ca	75	150	37.5	75.0
K	25	50	12.5	25.0
Mg	20	40	10.0	20.0
Mn	10	20	5.0	10.0
Cu	5	10	2.5	5.0
Zn	5	10	2.5	5.0
Cd	5	10	2.5	5.0
Pb	5	10	2.5	5.0

[1] All calibration standards are made to a final 500-mL volume.

CHEMICAL ANALYSIS
IRON, MANGANESE, ALUMINUM, CALCIUM, MAGNESIUM, SODIUM, POTASSIUM, PHOSPHORUS, SILICON, ZIRCONIUM, COPPER, ZINC, ARSENATE, TITANTIUM, SELENIUM, CADMIUM, AND LEAD
HF PLUS AQUA REGIA (HF + HNO_3 + HCl) DISSOLUTION
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH ICAP 61E
(6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a, 8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a)

Table 2. Calibration standards ALLO and ALHI[1]

| Element | -- Concentration -- | | Primary Std Required for | |
	ALLO	ALHI	ALLO	ALHI
	------- ppm --------		---- mL ----	
Al	100	200	50.0	100.0
Fe	75	150	37.5	75.0
Ti	5	10	2.5	5.0
Zr	5	10	2.5	5.0
Na	25	50	12.5	25.0

Table 3. Calibration standards SILO and SIHI[1]

| Element | -- Concentration -- | | Primary Std Required for | |
	SILO	SIHI	SILO	SIHI
	------- ppm --------		---- mL ----	
Si	225	450	112.5	225.0
P	5	10	2.5	5.0
Se	5	10	2.5	5.0
As	5	10	2.5	5.0

[1]All calibration standards are made to a final 500-mL volume.

7.2 To the calibration standards and a blank, also add the following chemicals: 25.0 mL HF; 3.75 mL HNO_3; 1.25 mL HCl; and 12.5 g granular Boric Acid. Make all standards and the blank to a final 500-mL volume with DDI water.

7.3 Use the TJA ICAP 61E spectrophotometer and analyze for the following elements: Fe, Mn, Al, Ca, Mg, Na, K, P, Si, Zr, Cu, Zn, As, Ti, Se, Cd, and Pb. No initial dilutions of samples are necessary prior to analysis. Use polypropylene spray chamber and HF resistant torch on ICP. Check instrument alignment and gas pressures to obtain optimum readings with maximum signal to noise ratio. The torch tip used for HF digestions should not be run dry or used with RF powers exceeding 1350. The HF torch tip should only be used with the high flow torch.

CHEMICAL ANALYSIS
IRON, MANGANESE, ALUMINUM, CALCIUM, MAGNESIUM, SODIUM,
POTASSIUM, PHOSPHORUS, SILICON, ZIRCONIUM, COPPER, ZINC,
ARSENATE, TITANTIUM, SELENIUM, CADMIUM, AND LEAD
HF PLUS AQUA REGIA (HF + HNO$_3$ + HCl) DISSOLUTION
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH ICAP 61E
(6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a,
8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a)

7.4 Use the HF blank standard solution to dilute those samples with concentrations greater than the high standard. Rerun all elements and use only the data needed from the diluted analysis.

7.5 Run the detection limits daily using the blank standard solution. These values establish the lower detection limits for each element. Analyzed values lower than the detection limits are set equal to zero.

7.6 When ICP analyses are completed, transfer data from the hard drive storage to a 3.5 inch floppy disk as an ASCII file via the "Report Writer" in the TJA software Thermospec, Version 5.06. These data are imported into a LOTUS 123, Version 3.1 spreadsheet for data analysis. Refer to procedure 7C4a.

8. CALCULATIONS
Refer to procedure 7C4a.

9. REPORT
Refer to procedure 7C4a.

10. PRECISION
No precision data are available for this procedure.

CHEMICAL ANALYSES
ORGANIC CARBON, IRON, MANGANESE, AND ALUMINUM
(6A, 6C, 6D, and 6G)
SODIUM PYROPHOSPHATE EXTRACTION (6A4)
CO_2 EVOLUTION, GRAVIMETRIC (6A4a)
SODIUM PYROPHOSPHATE EXTRACTION II (6C8, 6D4, and 6G10)
ATOMIC ABSORPTION
PERKIN-ELMER 5000 AA (6C8a, 6D4a, and 6G10a)

1. APPLICATION

Sodium pyrophosphate (0.1 M $Na_4P_2O_7$) is used as a selective dissolution extractant for organically complexed Fe and Al (Wada, 1989). The $Na_4P_2O_7$ solution is a poor extractant for allophane, imogolite, amorphous aluminosilicates, and noncrystalline hydrous oxides of Fe and Al. The $Na_4P_2O_7$ solution does not extract opal, crystalline silicates, layer silicates, and crystalline hydrous oxides of Fe and Al (Wada, 1989). In *Soil Taxonomy*, sodium pyrophosphate extractable organic C, Fe, and Al are criteria for spodic placement (Soil Survey Staff, 1975).

2. SUMMARY OF METHOD

The soil sample is mixed with 0.1 M $Na_4P_2O_7$ and shaken overnight. Superfloc 16 is added, and the mixture is made to volume. The solution is allowed to settle and a clear extract is obtained. The $Na_4P_2O_7$ extracted solution is diluted with distilled deionized (DDI) water. The diluted extract is aspirated into an atomic absorption spectrophotometer (AA). The analyte is measured by absorption of the light from a hollow cathode lamp. An automatic sample changer is used to aspirate a series of samples. The AA converts absorption to analyte concentration. Percent sodium pyrophosphate extractable Fe, Mn, and Al are reported in procedures 6C8a, 6D4a, and 6G10a, respectively. The organic C in the sodium pyrophosphate extract is wet oxidized and gravimetrically measured in procedure 6A4a.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AA analyses of these elements. These interferences vary in importance, depending upon the particular analyte selected. Refer to Appendix X, Atomic Absorption Spectroscopy, for an explanation of these interferences.

The concentration of $Na_4P_2O_7$ solution must be close to 0.1 M. Variable amounts of Fe, Al, Mn, and organic C may be extracted by varying the pyrophosphate concentration.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. EQUIPMENT
5.1 Electronic balance, ±0.0001 g
5.2 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 epm, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI
5.3 Nursing bottle, 240 mL (8 fl. oz.), graduated
5.4 Rubber stoppers, No. 2, to fit nursing bottles
5.5 Dispenser/diluters, Repipet, 0 to 10 mL, Labindustries, 1802 2nd St., Berkeley, CA
5.6 Atomic absorption spectrophotometer (AA), model 5000, Perkin-Elmer Corp., Norwalk, CT
5.7 Automatic burner control, model 5000, Perkin-Elmer Corp., Norwalk, CT
5.8 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

CHEMICAL ANALYSES
ORGANIC CARBON, IRON, MANGANESE, AND ALUMINUM
(6A, 6C, 6D, and 6G)
SODIUM PYROPHOSPHATE EXTRACTION (6A4)
CO$_2$ EVOLUTION, GRAVIMETRIC (6A4a)
SODIUM PYROPHOSPHATE EXTRACTION II (6C8, 6D4, and 6G10)
ATOMIC ABSORPTION
PERKIN-ELMER 5000 AA (6C8a, 6D4a, and 6G10a)

5.9 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.10 Heated regulator, single-stage, nitrous oxide, stock number 808 8039, Airco Welding Products, P.O. Box 486, Union, NJ

5.11 Diluter/dispenser, Microlab 500, Catalogue No. 69052, Hamilton Co., Bonaduz, GR, Switzerland

5.12 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.13 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.14 Absorption bulb, Nesbitt with stopper

5.15 Absorption bulb, Stetser-Norton

5.16 Flask, boiling, round bottom, short neck

5.17 Condenser, Allihn

5.18 Funnel, separatory, cylindrical, open top, with stopcock

5.19 Tube, drying, Schwartz

5.20 Containers, polypropylene

5.21 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated, 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI H$_2$O.

6.4 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI H$_2$O.

6.5 Superfloc 16, 0.2% solution (w:v). Dissolve 2 g of Superfloc 16 in 1 liter of DDI H$_2$O. Do not shake the mixture as this breaks the polymer chains of the Superfloc. Gently swirl the mixture occasionally over the several days that the solution requires to completely dissolve the Superfloc. Suggested source is American Cyanamid Co., P.O. Box 32787, Charlotte, NC

6.6 Sodium pyrophosphate solution, 0.1 *M*. Dissolve 800 g of Na$_4$P$_2$O$_7 \cdot$H$_2$O in 16 L of DDI H$_2$O. Dilute to 18 L with DDI H$_2$O.

6.7 Primary mixed standard, 4000 mg L^{-1} (4000 ppm) Fe; 2000 mg L^{-1} (3000 ppm) Al; and 600 mg L^{-1} (600 ppm) Mn. Dissolve 4.000 g of Fe wire, 3.000 g of Al wire, and 0.600 g of Mn metal powder in 1:1 HCl:DDI in a glass beaker. When dissolved transfer to a 1-L volumetric flask and fill with 1% HCl solution. Store in a polypropylene bottle.

6.8 High calibration mixed standards solution (HCMSS), 80 mg/8 oz (80 ppm) Fe; 12 mg/8 oz (12 ppm) Mn; and 60 mg/8 oz (60 ppm) Al. Pipet 20 mL of primary mixed standard into an 8-oz bottle. Add 10.55 g of Na$_4$P$_2$O$_7 \cdot$H$_2$O and 3.5 mL of concentrated H$_3$PO$_4$. Dilute to 8 oz with DDI H$_2$O. Store in a polypropylene bottle.

6.9 Low calibration mixed standards solution (LCMSS), 40 mg/8 oz (40 ppm) Fe; 6 mg/8 oz (6 ppm) Mn; and 30 mg/8 oz (30 ppm) Al. Pipet 10 mL of primary mixed standard into an 8-oz bottle. Add 10.55 g of Na$_4$P$_2$O$_7 \cdot$H$_2$O and 3.5 mL of concentrated H$_3$PO$_4$. Dilute to 8 oz with DDI H$_2$O. Store in a polypropylene bottle.

6.10 Calibration reagent blank solution (CRBS). Add 10.55 g of Na$_4$P$_2$O$_7 \cdot$H$_2$O and 3.5 mL of concentrated H$_3$PO$_4$. Dilute to 8 oz with DDI H$_2$O. Store in a polypropylene bottle.

6.11 Potassium dichromate (K$_2$Cr$_2$O$_7$), reagent

6.12 Potassium iodide solution. Dissolve 100 g of KI in 100 mL of DDI H$_2$O.

6.13 Silver sulfate, saturated aqueous solution.

CHEMICAL ANALYSES
ORGANIC CARBON, IRON, MANGANESE, AND ALUMINUM
(6A, 6C, 6D, and 6G)
SODIUM PYROPHOSPHATE EXTRACTION (6A4)
CO_2 EVOLUTION, GRAVIMETRIC (6A4a)
SODIUM PYROPHOSPHATE EXTRACTION II (6C8, 6D4, and 6G10)
ATOMIC ABSORPTION
PERKIN-ELMER 5000 AA (6C8a, 6D4a, and 6G10a)

6.14 Digestion acid mixture. Mix 600 mL of concentrated H_2SO_4 and 400 mL of 85% H_3PO_4.

6.15 Indicarb or Mikohlbite

6.16 Soda lime

6.17 Zinc granules, 300 mesh

6.18 Anhydrone

6.19 Acetylene gas, purity 99.6%

6.20 Nitrous oxide gas, compressed

6.21 Compressed air with water and oil traps

7. PROCEDURE

Extraction of Fe, Mn, and Al

7.1 Weigh 2.00 g of <2-mm, air-dry soil sample and place in an 8-oz nursing bottle.

7.2 Add 0.1 M $Na_4P_2O_7$ solution to 7-oz level on bottle and securely stopper bottle.

7.3 Shake overnight (12 to 16 h) in a reciprocating shaker. After shaking, use a dispenser to add 4 mL of Superfloc 16 solution.

7.4 Fill bottle to 8-oz volume with $Na_4P_2O_7$ solution.

7.5 Stopper and shake vigorously for ~ 15 s.

7.6 Allow to settle for at least 3 days (4 to 6 days typical). The Fe, Mn, and Al are determined from a clear aliquot of solution.

Dilution of Sample Extracts and Standards

7.7 No ionization suppressant is required as the Na in the extractant is present in sufficient quantity. Set the digital diluter on Hamilton diluter to 66 for diluent and 35 for sodium pyrophosphate sample extracts, calibration reagent blanks, and calibration standards for a 1:20 dilution as follows:

7.8 Dilute 1 part sample sodium pyrophosphate sample extract with 19 parts of DDI H_2O (1:20 dilution).

7.9 Dilute 1 part CRBS with 19 parts of DDI H_2O (1:20 dilution).

7.10 Dilute 1 part LCMSS with 19 parts of DDI H_2O (1:20 dilution).

7.11 Dilute 1 part HCMSS with 19 parts of DDI H_2O (1:20 dilution).

7.12 Dispense the diluted solutions into test tubes which have been placed in the sample holder of the sample changer.

AA Calibration

7.13 Use the calibration reagent blank and high calibration standard to calibrate the AA. The AA requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

CHEMICAL ANALYSES
ORGANIC CARBON, IRON, MANGANESE, AND ALUMINUM
(6A, 6C, 6D, and 6G)
SODIUM PYROPHOSPHATE EXTRACTION (6A4)
CO$_2$ EVOLUTION, GRAVIMETRIC (6A4a)
SODIUM PYROPHOSPHATE EXTRACTION II (6C8, 6D4, and 6G10)
ATOMIC ABSORPTION
PERKIN-ELMER 5000 AA (6C8a, 6D4a, and 6G10a)

7.14 Use the low calibration standard as a check sample.

AA Set-up and Operation

7.15 Refer to Appendix XI and to the manufacturer's manual for operation of the Perkin-Elmer 5000 AA. The following are only very general guidelines for instrument conditions for the various analytes.

```
Analyte        Wavelength
                   nm

Fe               248.8
Mn               280.1
Al               309.3


Analyte        Burner Head

Fe             5-cm parallel
Mn             5-cm parallel
Al             5-cm parallel


Analyte        Fuel/Oxidant

Fe             10  C2H2/25 Air
Mn             10  C2H2/25 Air
Al             30  C2H2/17 Air
```

Typical read delay is 6 s, and the integration by peak area is 8 s.

7.16 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.17 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep matrix the same after dilution by diluting with DDI H$_2$O (1:20 dilution).

Organic C Determination

7.18 Pipet 100 mL of the extract into a 100-ml flask.

7.19 Evaporate the extract to near dryness using a 50°C waterbath and a gentle stream of clean, filtered air.

7.20 Construct the wet combustion apparatus. Refer to Appendix VI for figure of the apparatus for gravimetric organic C determination.

CHEMICAL ANALYSES
ORGANIC CARBON, IRON, MANGANESE, AND ALUMINUM
(6A, 6C, 6D, and 6G)
SODIUM PYROPHOSPHATE EXTRACTION (6A4)
CO$_2$ EVOLUTION, GRAVIMETRIC (6A4a)
SODIUM PYROPHOSPHATE EXTRACTION II (6C8, 6D4, and 6G10)
ATOMIC ABSORPTION
PERKIN-ELMER 5000 AA (6C8a, 6D4a, and 6G10a)

7.21 Add 1 to 2 g of potassium dichromate.

7.22 Wash the neck of the flask with 3 mL of DDI H$_2$O and connect to condenser.

7.23 Attach a weighed Nesbitt bulb to the system and open the valve at the top.

7.24 Pour 25 mL of digestion-acid mixture into the funnel. Add the mixture to the flask and immediately close the stopcock. Use the digestion-acid mixture to lubricate the stopcock.

7.25 The tip of the air-delivery tube should be ~ 0.5 cm below the digestion-acid mixture. Adjust the flow of the "carrier stream" to maintain 1 to 2 bubble s^{-1} rate throughout the digestion. Apply suction on the outlet side of the Nesbitt bulb. Gentle air pressure and needle valve on the air pressure line aids flow adjustment.

7.26 With a gas flame or a variable power heating mantle, gently heat the flask until the mixture boils (~ 3 to 4 min). Continue a gentle boiling for 10 min. Heating is too rapid if white fumes of SO$_2$ are visible above the second bulb of the reflux condenser.

7.27 Remove the heat and allow to aerate for 10 additional min at a rate of 6 to 8 bubbles s^{-1}.

7.28 Close the stopcock on the Nesbitt bulb, disconnect the bulb from the system, and weigh to the nearest 0.0001 g.

8. CALCULATIONS

$$\text{Analyte (\%)} = \frac{(\text{AA} \times \text{DR} \times \text{AD/OD} \times 100)}{\text{Sample Weight (g)} \times 1000}$$

where:
Analyte   = Fe, Mn, and Al
AA   = Analyte concentration AA reading
DR   = Dilution ratio of 1 if no additional dilution
Sample   = Sample weight (g)
100   = Factor to convert to percent
1000   = Conversion factor (mg g^{-1})
AD/OD   = Air-dry/oven-dry ratio

$$\text{Organic C (\%)} = \frac{(\text{Wt}_F - \text{Wt}_I) \times 27.3 \times \text{Volume} \times \text{AD/OD}}{\text{Sample Weight (g)} \times 236.6}$$

CHEMICAL ANALYSES
ORGANIC CARBON, IRON, MANGANESE, AND ALUMINUM
(6A, 6C, 6D, and 6G)
SODIUM PYROPHOSPHATE EXTRACTION (6A4)
CO_2 EVOLUTION, GRAVIMETRIC (6A4a)
SODIUM PYROPHOSPHATE EXTRACTION II (6C8, 6D4, and 6G10)
ATOMIC ABSORPTION
PERKIN-ELMER 5000 AA (6C8a, 6D4a, and 6G10a)

where:

Wt_F	= Nesbitt bulb weight after digestion (g)
Wt_i	= Nesbitt bulb weight before digestion (g)
V	= Volume of extract digested (mL)
AD/OD	= Air-dry/oven-dry ratio (procedure 4B5)
27.3	= Conversion factor
236.6	= Total volume of extract (mL)

9. REPORT

Report percent sodium pyrophosphate extractable Fe, Mn, and Al on oven-dry soil basis to the nearest whole number.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Soil Survey Staff. 1975. Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA-SCS Agric. Handb. 436. U.S.Govt. Print. Office, Washington, DC.

Wada, K. 1989. Allophane and imogolite. *In* J.B. Dixon and S.B. Weed (eds.). Minerals in soil environment. 2nd ed. Soil Sci. Soc. Amer. No. 1. p. 1051-1087.

CHEMICAL ANALYSES
IRON, MANGANESE, ALUMINUM, AND SILICON (6C, 6D, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C9, 6D6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6C9b, 6D5b, 6G12b, 6V2b)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

1. APPLICATION

Oxalic acid-ammonium oxalate (acid oxalate) is used as a selective dissolution extractant for organically complexed Fe and Al, noncrystalline hydrous oxides of Fe and Al, allophane, and amorphous aluminosilicates (Wada, 1989). Acid oxalate is a poor extractant of imogolite and layer silicates and does not extract crystalline hydrous oxides of Fe and Al, opal, or crystalline silicate (Wada, 1989). A more reliable and accurate estimation of soil properties and a better understanding of soil exchange complex is provided when acid oxalate extraction is used in conjunction with other selective dissolution procedures, thermal techniques, and chemical tests. In *Soil Taxonomy*, acid oxalate extractable Fe and Al are criteria for andic soil properties (Soil Survey Staff, 1990).

2. SUMMARY OF METHOD

A soil sample is extracted with a mechanical vacuum extractor (Holmgren et al., 1977) in a 0.2 *M* acid oxalate solution buffered at pH 3.0 under darkness. The acid oxalate extract is weighed. The acid oxalate extract is diluted with 0.1 *N* HCl. The analytes are measured by a inductively coupled plasma emission spectrophotometer (ICP). Data are automatically recorded by a microcomputer and printer. The percent acid oxalate extractable Fe, Mn, Al, and Si are reported in procedures 6C9b, 6D5b, 6G12b, and 6V2b, respectively. In procedure 8J, the optical density of the extract is measured with a UV spectrophotometer at 430 nm.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the ICP analyses of these elements. These interferences vary in importance, depending upon the particular analyte chosen.

The acid oxalate buffer extraction is sensitive to light, especially UV light. The exclusion of light reduces the dissolution effect of crystalline oxides and clay minerals. If the sample contains large amounts of amorphous material (>2% Al), an alternate method should be used, i.e., shaking with 0.275 *M* acid oxalate, pH 3.25, 1:100 soil:extractant.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Follow the manufacturer's safety precautions when using the UV spectrophotometer and ICP.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity

5.2 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.3 Mechanical vacuum extractor, Mavco Sampletex, 5300 N. 57th St., Lincoln, NE

5.4 Syringes, polypropylene, disposable, 60 mL, for extractant reservoir, extraction vessel, and tared extraction syringe

5.5 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm, (1/8 ID x 1/4 OD x 1 in) for connecting syringe barrels

5.6 Analytical filter pulp, ash-free, Schleicher and Schuell, No. 289

CHEMICAL ANALYSES
IRON, MANGANESE, ALUMINUM, AND SILICON (6C, 6D, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C9, 6D6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6C9b, 6D5b, 6G12b, 6V2b)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

5.7 Extraction vessel, 60-mL, 10u polypropylene, part no. 6986-6010, Whatman Inc., 9 Bridewell Place, Clifton, NJ

5.8 Polycons, Richards Mfg. Co.

5.9 UV-visible spectrophotometer, DU-7, Beckmann Instruments, Inc.

5.10 Cuvettes, disposable, polystrene, 1-cm light path

5.11 Inductively coupled plasma spectrometer, ICAP 61E, Thermo Jarrell Ash Corp., Franklin, MA

5.12 Nebulizers, Precision Glass, Type A, 2.3 mlpm, 35 psig, Precision Glass Co., 14775 Hinsdale Ave., Englewood, CO.

5.13 RF generator, floor mounted power unit, Model 7/90, Thermo Jarrell Ash Corp., Franklin, MA

5.14 Computer, AT&T 386 Starstation, Model CPU-G72, and printer, NEC Pinwriter, P2200XE, Dot Matrix

5.15 ThermoSpec software, Thermo Jarrell Ash Corp., Franklin, MA

5.16 Line conditioner, Unity/I, Model UT8K, Best Power Technology, Inc., Necedah, WI

5.17 Single-stage regulator, high-purity, high-flow, argon, product no. E11-X-N145DHF, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.18 Autosampler, Thermo Jarrell Ash Corp., Franklin, MA

5.19 Digital diluter/dispenser, MicroLab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.20 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gastight, Hamilton Co., P.O. Box 10030, Reno, NV

5.21 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.22 Containers, polyproylene

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Acid oxalate buffer solution, 0.2 *M*, pH 3.0. *Solution A* (base): Dissolve 284 g of $(NH_4)_2C_2O_4 \cdot 2H_2O$ in 10 L of DDI water. *Solution B* (acid): Dissolve 252 g of $H_2C_2O_4 \cdot H_2O$ in 10 L of DDI water. Mix 4 parts solution A with 3 parts solution B. Adjust acid oxalate solution pH by adding either acid or base solution. Store in a polypropylene bottle.

6.3 pH buffers, pH 4.00 and 7.00, for electrode calibration

6.4 Primary Fe standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, N.J.

6.5 Primary Al standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, N.J.

6.6 Primary Si standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, N.J.

6.7 Primary Mn standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, N.J.

6.8 Dodecylbenzenesulfonic acid (DDBSA), Tech 97%, 0.1 *M*. Dissolve 32.2 g DDBSA in 1-L DDI water.

6.9 DDBSA solution. Dilution solution for acid oxalate extracts. Add 40.0 mL of 0.1 *M* DDBSA and make to 2-L volume with DDI water.

CHEMICAL ANALYSES
IRON, MANGANESE, ALUMINUM, AND SILICON (6C, 6D, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C9, 6D6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6C9b, 6D5b, 6G12b, 6V2b)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

6.10 High calibration standard. Mix 30 mL of each primary standard (Si, Fe, and Al) with 5 mL of primary Mn standard. Add 30 mL of 0.4 M acid oxalate solution and 16.0 mL of 0.1 M DDBSA and make to 1-L volume with DDI water. The elements are added in the above-stated order to avoid element precipitation. Resulting solution contains 30 ppm each of Si, Fe, and Al and 5 ppm Mn. Store in a polypropylene bottle.

6.11 Low calibration standard. Mix 10 mL of each primary standard (Si, Fe, and Al) with 2 mL of primary Mn standard. Add 30 mL of 0.4 M acid oxalate solution and 16.0 mL of 0.1 M DDBSA and make to 1-L volume with DDI water. Resulting solution contains 10 ppm each of Si, Fe, and Si and 2 ppm Mn. Store in a polypropylene bottle.

6.12 Calibration reagent blank solution. Add 50 mL of 0.4 M acid oxalate solution and 16.0 mL of 0.1 M DDBSA and make to 1-L volume with DDI water.

6.13 Argon gas, purity 99.9%

7. PROCEDURE

Extraction of Fe, Mn, Al, and Si

7.1 Prepare extraction vessel by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 0.500 g of <2-mm, air-dry soil and place in an extraction vessel. Prepare two reagent blanks (no sample in tube) per set of 48 samples.

7.3 Place the extraction vessel on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a dispenser to add 15.00 mL of acid oxalate buffer to the extraction vessel. Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Set extractor for 30-min extraction rate and extract until the acid oxalate buffer solution is at a 0.5 to 1.0-cm height above sample. Turn off extractor.

7.6 Put reservoir tube on top of the extraction vessel.

7.7 Add 35 mL of acid oxalate buffer to the reservoir tube.

7.8 Cover the extractor with a black plastic bag to exclude light. Adjust the extraction rate for a 12-h extraction. Refer to Appendix III and IV, Mechanical Vacuum Extractor.

7.9 After the extraction, shut off the extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the extraction vessel.

7.10 Weigh each syringe containing acid oxalate extract to the nearest 0.01 g.

CHEMICAL ANALYSES
IRON, MANGANESE, ALUMINUM, AND SILICON (6C, 6D, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C9, 6D6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6C9b, 6D5b, 6G12b, 6V2b)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

7.11 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution. This solution is reserved for determinations of Fe, Mn, Al, and Si. If optical density is to be measured, fill a disposable cuvette with extract solution. Discard excess solution.

Determination of Optical Density of Extract

7.12 Place 4 mL of acid oxalate extract in disposable cuvette.

7.13 Place 4 mL of acid oxalate reagent blank in disposable cuvette.

7.14 On DU-7 spectrophotometer, select a 430-nm wavelength. Select normal slit width and height. Refer to Appendix XIX, UV-Visible Spectrophotometer, and manufacturer's manual for operation of the spectrophotometer.

7.15 Use the acid oxalate extract reagent blank to set spectrophotometer.

7.16 Record optical density of acid oxalate extract to nearest 0.000.

Dilution of Sample Extracts and Standards

7.17 Dilute acid oxalate extracts (1:10) with DDBSA solution. Add 1 part acid oxalate sample extract with 10 parts dilution solution.

7.18 Set the digital settings of the Hamilton diluter for a 1:10 dilution. Calibration reagent blanks and calibration standards are not diluted.

7.19 Dispense the diluted solutions into test tubes which have been placed in the sample holder of the sample changer.

ICP Calibration

7.20 Use a multipoint calibration for ICP analysis of acid oxalate extracts. The ICP calibrates the blank first, then the low standard, followed by the high standard. Prepare a quality control (QC) standard with analyte concentration between the high and low calibration standards. The ICP reads the QC after the high standard. If the QC falls within the range set by operator, the instrument proceeds to analyze the unknowns. If the QC is outside the range, the instrument restandardizes. The QC is analyzed approximately every 12 samples.

ICP Set-up and Operation

7.21 Refer to the Appendix XIII, Inductively Coupled Plasma (ICP), and the manufacturer's manual for operation of the ICP. The following parameters are only very general guidelines for instrument conditions for the various analytes.

CHEMICAL ANALYSES
IRON, MANGANESE, ALUMINUM, AND SILICON (6C, 6D, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C9, 6D6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6C9b, 6D5b, 6G12b, 6V2b)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

Parameter	Value
Gas Flow	
Torch Gas	High Flow
Auxiliary Gas Flow	Medium 1.0 LPM
Nebulizer Pressure	31 psi
Power	
Approximate RF Power	1150
Peristaltic Pump	
Analysis Pump Rate	150 RPM
Flush Pump Rate	200 RPM
Relaxation Time	10 s
Pumping Tube Type	Silicone-Orange-3stop
Argon Flow Rate	2.0 LPM
Purged Optical Pathway Enclosure Purge	2.0 SLPM Air

Nebulizer pressure depends on the type of nebulizer that is being used, i.e., low flow nebulizer requires a higher nebulizer pressure whereas a higher flow nebulizer requires a lower nebulizer pressure. To check for correct nebulizer pressure, aspirate with 1000.0 ppm yttrium. Adjust pressure to correct yttrium bullet.

7.22 Analyte data are reported at the following wavelengths.

Analyte	Wavelength (nm)	High Standard (ppm)	Low Standard (ppm)
Fe	259.940	30.00	10.00
Al	167.081	30.00	10.00
Si	251.611	30.00	10.00
Mn	257.610	5.00	2.00

7.23 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings. The instrument readings are usually programmed in ppm.

7.24 If sample exceeds calibration standard, dilute the sample (1:5) with 0.2 *M* acid oxalate solution (matrix) and then dilute (1:10) with the DDBSA solution.

CHEMICAL ANALYSES
IRON, MANGANESE, ALUMINUM, AND SILICON (6C, 6D, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C9, 6D6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6C9b, 6D5b, 6G12b, 6V2b)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

8. CALCULATIONS

$$\text{Analyte (\%)} = \frac{\text{ICP} \times (\text{Syr}_{\text{fin}} - \text{Syr}_{\text{init}}) \times \text{D.R.} \times \text{AD/OD}}{\text{Sample Weight (g)} \times 10000 \times \text{Density}}$$

where:
ICP   = ICP analyte concentration (ppm)
Syr_{fin} = Weight of syringe + extract (g)
Syr_{init} = Tare weight of syringe (g)
D.R.   = Dilution ratio of samples over calibration range
Density   = Density of acid oxalate solution (1.007)
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)

9. REPORT
Report the percent acid oxalate extractable Fe, Mn, Al, and Si to the nearest 0.01%. Report the optical density of the acid oxalate extract to the nearest 0.001 unit.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.
Soil Survey Staff. 1990. Keys to soil taxonomy. 4th ed. SMSS technical monograph no. 6. Blacksburg, VA.
Wada, K. 1989. Allophane and imogolite. *In* J.B. Dixon and S.B. Weed (eds.). Minerals in soil environment. 2nd ed. Soil Sci. Soc. Amer. No. 1. p. 1051-1087.

CHEMICAL ANALYSES
MANGANESE AND ALUMINUM (6D and 6G)
KCl, AUTOMATIC EXTRACTOR (6D3 and 6G9)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6D3b and 6G9c)

1. APPLICATION

The Al extracted by 1 N KCl approximates exchangeable Al and is a measure of the "active" acidity present in soils with a 1:1 water pH <5.5. Above pH 5.5, precipitation of Al occurs during analysis. This method does not measure the acidity component of hydronium ions (H_3O^+). If Al is present in measurable amounts, the hydronium is a minor component of the active acidity. Because the 1 N KCl extractant is an unbuffered salt and usually affects the soil pH one unit or less, the extraction is determined at or near the soil pH. The KCl extractable Al is related to the immediate lime requirement and existing CEC of the soil. The "potential" acidity is better measured by the $BaCl_2$-TEA method (procedure 6H5a) (Thomas, 1982).

2. SUMMARY OF METHOD

A soil sample is leached with 1 N KCl using the mechanical vacuum extractor (Holmgren et al., 1977). The extract is weighed. The KCl extracted solution is diluted with distilled deionized water. The anlaytes are measured by inductively coupled plasma emission spectrophotometer (ICP). Data are automatically recorded by a microcomputer and printer. The Mn and Al are reported in mg kg^{-1} (ppm) and meq 100 g^{-1} ovendry soil in procedures 6D3b and 6G9c, respectively.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the ICP analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

The soil:extractant ratio must remain constant. A soil:extractant ratio of 1:10 (w:v) for batch procedures is most commonly used. Using a leaching technique, a 1:20 (w:v) ratio gives comparable results. If the sample size is changed, the amount of extractable Al is changed. No other significant interferences have been identified for this procedure.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Follow the manufacturer's safety precautions when using the ICP.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity

5.2 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.3 Mechanical vacuum extractor, Mavco Sampletex, 5300 N. 57th St., Lincoln, NE

5.4 Syringes, polypropylene, disposable, 60 mL, for extraction vessel, extractant reservoir and tared extraction syringe

5.5 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm, (1/8 ID x 1/4 OD x 1 in) for connecting syringe barrels

5.6 Analytical filter pulp, ash-free, Schleicher and Schuell, No. 289

5.7 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.

5.8 Wash bottle, 20 mL, to dispense KCl.

5.9 Polycons, Richards Mfg. Co.

5.10 Inductively coupled plasma spectrometer, ICAP 61E, Thermo Jarrell Ash Corp., Franklin, MA

5.11 RF generator, floor mounted power unit, Model 7/90, Thermo Jarrell Ash Corp., Franklin, MA

5.12 Computer, AT&T 386 Starstation, Model CPU-G72, and printer, NEC Pinwriter, P2200XE, Dot Matrix

CHEMICAL ANALYSES
MANGANESE AND ALUMINUM (6D and 6G)
KCI, AUTOMATIC EXTRACTOR (6D3 and 6G9)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6D3b and 6G9c)

5.13 ThermoSpec software, Thermo Jarrell Ash Corp., Franklin, MA

5.14 Line conditioner, Unity/I, Model UT8K, Best Power Technology, Inc., Necedah, WI

5.15 Single-stage regulator, high-purity, high-flow, argon, product no. E11-X-N145DHF, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.16 Autosampler, Thermo Jarrell Ash Corp., Franklin, MA

5.17 Nebulizers, Precision Glass, Type A, 2.3 mlpm, 35 psig, Precision Glass Co., 14775 Hinsdale Ave., Englewood, CO.

5.18 Digital diluter/dispenser, MicroLab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.19 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gastight, Hamilton Co., P.O. Box 10030, Reno, NV

5.20 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.21 Containers, polyproylene

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Potassium chloride solution (KCl), 1.0 *N*. Dissolve 1342 g of KCl reagent in 16 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 18 L with DDI water. Use 1.0 *N* KCl for Al and Mn extraction.

6.3 Potassium chloride solution (KCl), 2.0 *N*. Dissolve 298.24 g of KCl reagent in 1.5 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 2 L with DDI water. Use 2.0 *N* KCl for standards.

6.4 Primary Al standard, 1000 ppm (111 meq L^{-1}). Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, N.J.

6.5 Primary Mn standard, 1000 ppm (250 meq L^{-1}). Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, N.J.

6.6 High calibration Al and Mn standard, 10 meq L^{-1} and 8 ppm, respectively. Pipet 22.476 mL of primary Al standard into a 250-mL volumetric flask. Add 125.0 mL 2 *N* KCl solution to the flask and mix. Pipet 2.0 mL of primary Mn standard into flask and mix. Dilute to volume with DDI water.

6.7 Calibration reagent blank solution, 1.0 *N* KCl. Add 125 mL of 2.0 *N* KCl to a volumetric flask and make to 250-mL volume with DDI water. Store in polypropylene container.

6.8 Calibration Al and Mn check standard, 5 meq L^{-1} and 3.0 ppm, respectively. Pipet 11.24 mL of primary Al standard into a 250-mL volumetric flask. Add 125.0 mL 2 *N* KCl solution to the flask and mix. Pipet 0.75 mL of primary Mn standard into flask and mix. Dilute to volume with DDI water.

6.9 Dodecylbenzenesulfonic acid (DDBSA), tech 97%., 0.1 *M*. Dissolve 32.2 g DDBSA in 1-L DDI water.

6.10 DDBSA rinse solution. Dilute 40.0 mL 0.1 *M* DDBSA to 2-L volume with DDI water.

6.11 Argon gas, purity 99.9%

7. PROCEDURE

Extraction of Al and Mn

7.1 Prepare extraction vessel by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh exactly 2.50 g of <2-mm, air-dry soil and place in an extraction vessel. Prepare one quality control check sample per 48 samples.

CHEMICAL ANALYSES
MANGANESE AND ALUMINUM (6D and 6G)
KCl, AUTOMATIC EXTRACTOR (6D3 and 6G9)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6D3b and 6G9c)

7.3 Place the extraction vessel on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a squeeze bottle and fill extraction vessel to the 20-mL mark with 1.0 N KCl solution (~ 10 mL). Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Put reservoir tube on top of the extraction vessel. Set extractor for fast extraction rate and extract until the KCl solution is at a 0.5- to 1.0-cm height above sample. Turn off extractor.

7.6 Add 45 mL KCl solution to reservoir tube. Set extractor for 45-min extraction. Refer to Appendix II and III, Mechanical Vacuum Extractor.

7.7 After the extraction, shut off extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the extraction vessel.

7.8 Weigh each syringe containing KCl extract to the nearest 0.01 g.

7.9 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. This solution is reserved for extractable Al and Mn analyses.

Dilution of Extracts and Standards

7.10 Set the digital settings at a 1:5 dilution for the KCl sample extracts, calibration reagent blanks, calibration standards, and calibration check standards as follows:

7.11 Dilute 1 part KCl sample extract with 4 parts of DDI water (1:5 dilution).

7.12 Dilute 1 part calibration reagent blank with 4 parts of DDI water (1:5 dilution).

7.13 Dilute 1 part calibration standard with 4 parts of DDI water (1:5 dilution).

7.14 Dilute 1 part calibration check standard with 4 parts of DDI water (1:5 dilution).

7.15 Dispense the diluted solutions into test tubes and place in the sample holder of the sample changer.

ICP Calibration

7.16 Use the calibration reagent blank (1.0 N KCl), high standard (10 meq L^{-1} Al and 8 ppm Mn), and the blank to calibrate the ICP.

7.17 Use the calibration check standard (5 meq L^{-1} Al and 3 ppm Mn) as a check sample. Perform a calibration check every 12 samples.

CHEMICAL ANALYSES
MANGANESE AND ALUMINUM (6D and 6G)
KCl, AUTOMATIC EXTRACTOR (6D3 and 6G9)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6D3b and 6G9c)

ICP Set-up and Operation

7.18 Refer to the Appendix XIII, Inductively Coupled Plasma (ICP), and the manufacturer's manual for operation of the ICP. The following parameters are only very general guidelines for instrument conditions for the analytes.

Parameter	Value
Gas Flow	
Torch Gas	High Flow
Auxiliary Gas Flow	Medium 1.0 LPM
Nebulizer Pressure	32 PSI
RF Power	1150

Analyte	Wavelength (nm)	High Peak Offset	Low Peak Offset
Al	167.081	0/-21	-2
Mn	257.610	0/-18	0

7.19 Determine a set of 24 unknown samples for each successful calibration check.

7.20 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.21 If a sample exceeds the calibration standard, dilute the sample (1:5) as follows.

7.22 Analyze 4 quality control check sample for every 48 samples.

8. CALCULATIONS

8.1 The instrument readings are the analyte concentration (meq L^{-1} Al and ppm Mn) in undiluted extract. Use these values to calculate the analyte concentration on an oven-dry soil basis   (meq 100 g^{-1}).

Analyte (meq 100 g^{-1}) =

$$\frac{ICP \times (Wt_{syr+ext} - Wt_{syr}) \times D.R. \times 100 \times AD/OD}{Sample\ Weight \times 1.0412 \times 1000}$$

CHEMICAL ANALYSES
MANGANESE AND ALUMINUM (6D and 6G)
KCl, AUTOMATIC EXTRACTOR (6D3 and 6G9)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY
THERMO JARRELL ASH, ICAP 61E
(6D3b and 6G9c)

where:

ICP	= ICP analyte reading
$Wt_{syr+ext}$	= Weight of extraction syringe & extract (g)
Wt_{syr}	= Weight of tared extraction syringe (g)
D.R.	= Dilution ratio of samples over calibration range
1.0412	= Density of 1 N KCl @ 20°C
1000	= g L^{-1}
100	= Conversion factor (100-g basis)
AD/OD	= Air-dry/oven-dry ratio (procedure 4B5)

9. REPORT

Report KCl extractable Al and Mn in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.01 meq 100 g^{-1}.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Holmgren, George G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.

Thomas, G.W. 1982. Exchangeable cations. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:159-165.

CHEMICAL ANALYSES
MANGANESE AND ALUMINUM (6G)
KCl, AUTOMATIC EXTRACTOR (6G9)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE 4000
(6D3c and 6G9d)

1. APPLICATION

The Al extracted by 1 N KCl approximates exchangeable Al and is a measure of the "active" acidity present in soils with a 1:1 water pH <5.5. Above pH 5.5, precipitation of Al occurs during analysis. This method does not measure the acidity component of hydronium ions (H_3O^+). If Al is present in measurable amounts, the hydronium is a minor component of the active acidity. Because the 1 N KCl extractant is an unbuffered salt and usually affects the soil pH one unit or less, the extraction is determined at or near the soil pH. The KCl extractable Al is related to the immediate lime requirement and existing CEC of the soil. The "potential" acidity is better measured by the $BaCl_2$-TEA method (procedure 6H5a) (Thomas, 1982).

2. SUMMARY OF METHOD

A soil sample is leached with 1 N KCl using the mechanical vacuum extractor (Holmgren et al., 1977). The extract is weighed. The KCl extract is diluted with distilled deionized (DDI) water. The analytes are measured by an atomic absorption spectrophotometer. The data are automatically recorded by a microcomputer and printer. The Al and Mn are reported in meq 100 g-1 and mg kg^{-1} (ppm) ovendry soil in procedure 6D3c and 6G9d.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AA analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected. Refer to the Appendix X, Atomic Absorption Spectroscopy, for an explanation of these interferences.

The soil:extractant ratio must remain constant. A soil:extractant ratio of 1:10 (w:v) for batch procedures is most commonly used. Using a leaching technique, a 1:20 (w:v) ratio gives comparable results. If the sample is changed, the amount of extractable Al is changed. No other significant interferences have been identified for this procedure.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity

5.2 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.3 Mechanical vacuum extractor, Mavco Sampletex, 5300 N. 57th St., Lincoln, NE

5.4 Syringes, polypropylene, disposable, 60 mL, for extraction vessel, extractant reservoir, and tared extraction syringe

5.5 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm, (1/8 ID x 1/4 OD x 1 in) for connecting syringe barrels

5.6 Analytical filter pulp, ash-free, Schleicher and Schuell, No. 289

5.7 Wash bottle, 20 mL, to dispense KCl.

5.8 Polycons, Richards Mfg. Co.

5.9 Atomic absorption spectrophotometer (AA), Smith-Hieftje Model 4000, Thermo Jarrell Ash Corp., Franklin, MA

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5.10 Autosampler, Model 150, Thermo Jarrell Ash Corp., Franklin, MA
5.11 ThermoSpec software, Version 3.01, Enable 4.0, DOS 5.0, Thermo Jarrell Ash Corp., Franklin, MA
5.12 Computer, CUi Advantage 486, Thermo Jarrell Ash Corp., Franklin, MA
5.13 Printer, NEC Pinwriter P3200
5.14 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA
5.15 Digital diluter/dispenser, MicroLab 500, Hamilton Co., P.O. Box 10030, Reno, NV
5.16 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV
5.17 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX
5.18 Containers, polypropylene

6. REAGENTS
6.1 Distilled deionized (DDI) water
6.2 Potassium chloride solution (KCl), 1.0 *N*. Dissolve 1342 g of KCl reagent in 16 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 18 L with DDI water. Use 1.0 *N* KCl solution for Al extraction.
6.3 Potassium chloride solution (KCl), 2.0 *N*. Dissolve 298.24 g of KCl reagent in 1.5 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 2 L with DDI water. Use 2.0 *N* KCl solution for standards.
6.4 Primary Al standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, N.J.
6.5 Primary Mn standard, 1000 ppm. Certified Reference Solution, Fisher Chemical Scientific Co., Fairlawn, N.J.
6.6 High calibration Al (4 meq L^{-1}) and Mn (3 ppm) standard. Mix 9 mL of primary Al standard with 125 mL 2 *N* KCl. Add 0.75 mL of primary Mn standard and make to 250-mL volume with DDI water.
6.7 Low calibration Al (0.2 meq L^{-1}) and Mn (0.2 ppm) standard. Mix 1.8 mL of primary Al standard with 125 mL 2 *N* KCl. Add 0.05 mL of primary Mn standard and make to 250-mL volume with DDI water.
6.8 Calibration Al (2 meq L^{-1}) and Mn (1.5 ppm) check standard. Mix 4.5 mL of primary Al standard with 125 mL 2 *N* KCl. Add 0.375 mL of primary Mn standard and make to 250-mL volume with DDI water.
6.9 Calibration reagent blank solution, 1.0 *N* KCl. Add 125 mL of 2.0 *N* KCl to a volumetric flask and make to 250-mL volume with DDI water.
6.10 Nitrous oxide gas, compressed
6.11 Acetylene gas, compressed, purity 99.6%
6.12 Compressed air with water and oil traps

7. PROCEDURE

Extraction of Al
7.1 Prepare extraction vessel by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh exactly 2.50 g of <2-mm, air-dry soil and place in an extraction vessel. Prepare one quality control check sample per 48 samples.

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7.3 Place the extraction vessel on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a squeeze bottle and fill extraction vessel to the 20-mL mark with 1.0 N KCl solution (~ 10 mL). Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Put reservoir tube on top of the extraction vessel. Set extractor for fast extraction rate and extract until the KCl solution is at a 0.5- to 1.0-cm height above sample. Turn off extractor.

7.6 Add 45 mL KCl solution to reservoir tube. Set extractor for 45-min extraction. Refer to Appendix II and III, Mechanical Vacuum Extractor.

7.7 After the extraction, shut off extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the extraction vessel.

7.8 Weigh each syringe containing KCl extract to the nearest 0.01 g.

7.9 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. This solution is reserved for extractable Al and Mn analyses.

Dilution of Sample Extracts and Standards
7.10 No ionization suppressant is required as the K in the extractant is present in sufficient quantity. Set the digital settings at a 1:2 dilution for the KCl sample extracts, calibration reagent blanks, calibration standards, and calibration check standards as follows:

7.11 Dilute 1 part KCl sample extract with 1 part of DDI water (1:2 dilution).

7.12 Dilute 1 part calibration reagent blank with 1 part of DDI water (1:2 dilution).

7.13 Dilute 1 part calibration standard with 1 part of DDI water (1:2 dilution).

7.14 Dilute 1 part calibration check standard with 1 part of DDI water (1:2 dilution).

7.15 Dispense the diluted solutions into test tubes and place in the sample holder of the sample changer.

AA Calibration
7.16 Use the calibration reagent blank (1.0 N KCl), high standard (4 meq L^{-1} Al and 3 ppm Mn), and the low standard (2 meq L^{-1} Al and 1.5 ppm Mn) to calibrate the AA.

7.17 Use the calibration check standard (2 meq L^{-1} Al and 1.5 ppm Mn) as a check sample. Perform a calibration check every 12 samples.

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AA Set-up and Operation

7.18 Refer to the Appendix XIII, Atomic Absorption (AA), and the manufacturer's manual for operation of the AA. The following parameters are only very general guidelines for instrument conditions for the analyte.

Element	Wavelength (nm)	Burner head & angle	Fuel/Oxidant
Al	309.3	5-cm parallel	20 C_2H_2/10 N_2O
Mn	280.1	5-cm parallel	4 C_2H_2/16 Air

Typical read delay is 6 s, and integration by peak area is 8 s.

7.19 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.20 If a sample exceeds the calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with DDI water (1:2 dilution).

7.21 Analyze one quality control check sample for every 48 samples.

8. CALCULATIONS

8.1 The instrument readings are the analyte concentration (meq L^{-1} Al) in undiluted extract. Use these values to calculate the analyte concentration on an oven-dry soil basis (meq 100 g^{-1}).

$$\text{Al (meq 100 } g^{-1}) = \frac{AA_{Al} \times (Wt_{syr+ext} - Wt_{syr}) \times D.R. \times 100 \times AD/OD}{\text{Sample Weight (g)} \times 1.0412 \times 1000}$$

where:
AA_{Al} = AA Al reading (meq L^{-1})
$Wt_{syr+ext}$ = Weight of extraction syringe and extract (g)
Wt_{syr} = Weight of tared extraction syringe (g)
D.R. = Dilution ratio for samples over calibration range
1.0412 = Density of 1 N KCl @ 20°C
1000 = g L^{-1}
100 = Conversion factor (100-g basis)
AD/OD = Air-dry/oven-dry ratio (procedure 4B5)

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9. REPORT

Report KCl extractable Al in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq 100 g^{-1}.

10. PRECISION

Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples.

11. REFERENCES

Holmgren, George G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.

Thomas, G.W. 1982. Exchangeable cations. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:159-165.

CHEMICAL ANALYSES
CALCIUM CARBONATE (6E)
HCl TREATMENT (6E1)
MANOMETER, ELECTRONIC (6E1g)
<20 mm BASIS (6E4)

1. APPLICATION

The determination of calcium carbonate ($CaCO_3$) equivalent is a criterion in *Soil Taxonomy* (Soil Survey Staff, 1975). Carbonate content of a soil is used to define carbonatic, particle-size, and calcareous soil classes and to define calcic and petrocalcic horizons (Soil Survey Staff, 1975). The distribution and amount of $CaCO_3$ are important for fertility, erosion, available water-holding capacity, and genesis of the soil. The $CaCO_3$ equivalent is most commonly reported on the <2-mm base (procedure 6E1g). However, in some soils with hard carbonate concretions, carbonates are determined on both the <2- and the 2- to 20-mm bases (procedure 6E4).

2. SUMMARY OF METHOD

The amount of carbonate in the soil is measured by treating the samples with HCl. The evolved CO_2 is measured manometrically. The amount of carbonate is then calculated as $CaCO_3$.

3. INTERFERENCES

Chemical interference is the reaction by the acid with other carbonates, e.g., carbonates of Mg, Na, and K, that may be present in soil sample. The calculated $CaCO_3$ is only a semiquantitative measurement (Nelson, 1982).

Analytical interference may be caused by temperature changes within the reaction vessel. When sealing the vessel, the analyst should not hold the vessel any longer than necessary to tighten the cap. The internal pressure must be equalized with the atmosphere. After the septa has been pierced with a needle, ~ 5 to 10 s are required to equalize the internal pressure of the bottle. With extensive use, the septa leak gas under pressure. The septa should be replaced at regular intervals. The analyst should not touch the glass of the vessel when reading the pressure.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when handling acids. Thoroughly wash hands after handling acids. Use the fume hood when diluting concentrated HCl. Use the safety showers and eyewash stations to dilute spilled acids. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

The gelatin capsule may leak acid while being filled. Keep other personnel away from the area when filling capsules.

High pressure may develop inside the bottle if there is a large amount of calcareous sample. Do not use more than 2 g of any sample in the bottles. If high pressure develops in the bottle, release the pressure by venting the gas with a syringe needle. Some bottles may break without shattering. Discard any bottle with hairline cracks or obvious defects.

5. EQUIPMENT

5.1 Electronic balance, ±0.1-mg sensitivity

5.2 Threaded weighing bottles, wide-mouth, clear glass, standard, 120 mL (4 fl. oz.), 48-mm neck size. For best results, grind rim of bottle with 400-600 grit sandpaper on a flat glass plate.

5.3 Machined PVC caps for threaded 120-mL (4 fl. oz.) weighing bottles, 54-mm diameter with 12.7-mm diameter hole drilled in center, O-ring seal.

5.4 O-rings, 3.2 x 50.8 x 57.2 mm (1/8 x 2 x 2 1/4 in) square cross-section

5.5 Flanged stopper No. 03-255-5, Fisher Scientific. Place in machined cap.

5.6 Manometer, hand-held gauge and differential pressure, PCL-200 Series, Omega Engineering, Stamford, CT.

5.7 Hypodermic needle, 25.4 mm (1 in), 23 gauge. Connect needle to pressure tubing on transducer.

CHEMICAL ANALYSES
CALCIUM CARBONATE (6E)
HCl TREATMENT (6E1)
MANOMETER, ELECTRONIC (6E1g)
<20 mm BASIS (6E4)

6. REAGENTS
6.1 Distilled deionized (DDI) water
6.2 Methy red indicator
6.3 Hydrochloric acid (HCl), concentrated., 12 *N*
6.4 HCl, 3 *N*. Dilute 500 mL of concentrated HCl with 1500 mL DDI water. Add a few crystals of methyl red indicator. Methyl red indicator will turn yellow if HCl is consumed by sample. If this reaction occurs, adjust the sample size (smaller).
6.5 Gelatin capsule, 1/2 oz, size 11, Torpac Ltd., 52 Sfton Circle, Piscataway, NJ
6.6 Gylcerine, USP. Put the gylcerine in a small squeeze bottle and use as a lubricant for the O- rings.

7. PROCEDURE

<2-mm Basis
7.1 A $CaCl_2$ pH >6.95 is generally used as an indicator of the presence of carbonates. The presence of carbonates (effervescence with HCl) is also checked during lab preparation (procedure 1B). For trace amounts, add a few drops of 3 or 6 *N* HCl to wet soil on a spot plate and observe under a binocular microscope. Evolution of gas bubbles indicates the presence of carbonates.

7.2 Weigh 0.500 to 2.000 g of <2-mm, air-dry soil sample and place in a 120-mL, wide-mouth bottle. Run 1 or 2 blanks and a quality control check sample with every batch of 24 samples. The quality control check sample serves as a single point check. Vary the sample weight according to the $CaCO_3$ content as follows:

a. Use a 2-g sample weight if effervescence is 0, Trace, or Weak (procedure 1B).

b. Use a 1-g sample weight, if effervescence is Moderate (procedure 1B).

c. Use a 0.5-g sample weight, if effervescence is Strong (procedure 1B).

7.3 Lubricate the O-ring of bottle cap with gylcerine from a squeeze bottle.

7.4 Dispense 10 mL of 3 *N* HCl into a gelatin capsule and carefully place the top on the capsule. The HS may squirt or leak out of capsule. If this happens, discard the capsule.
7.5 Place the capsule in bottle and cap bottle immediately.

7.6 Release any pressure in the bottle by piercing the stopper with a hypodermic needle. Remove the needle after ~ 5 to 10 s.

7.7 After 5 to 10 min, the HCl dissolves through the capsule. After 1 h, measure the pressure in the bottle by piercing the stopper of the cap with a hypodermic needle connected to the manometer.

7.8 Read the pressure on the manometer. Auto zero the manometer before taking pressure readings.

<20-mm Basis
7.9 Determine carbonate content of the 2- to 20-mm fraction by the above method.

7.10 The carbonate in the 2- to 20-mm fraction and in the <2-mm fraction are combined and converted to a <20-mm soil basis.

8. CALCULATIONS

```
CCE = [(A - B) x 0.0916 x AD/OD - 0.0364]
      _____

               Sample Weight (g)
```

where:
CCE   = Calcium Carbonate Equivalent (%)
A   = Manometer reading (torrs)
B   = Reagent blank reading
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)

```
Carbonate = (A x B) + [C x (1-B)]
```

where:
Carbonate   = Carbonate as $CaCO_3$ on a <20-mm basis (%)
A   = $CaCO_3$ in <2-mm fraction (%)
B   = Weight of the <20-mm fraction minus the weight of the 2- to 20-mm fraction divided by
                   the weight of <20-mm fraction (procedures 1B and 3B).
C   = $CaCO_3$ in 2- to 20-mm fraction (%)

9. REPORT
Report $CaCO_3$ equivalent as a percentage of oven-dry soil to the nearest whole number.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Nelson, R.E. 1982. Carbonate and gypsum. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.)
    Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy
    9:181-197.
Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and
    interpreting soil surveys. USDA-SCS
Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

CHEMICAL ANALYSES
GYPSUM (6F)
WATER EXTRACT (6F1)
PRECIPITATION IN ACETONE (6F1a)
(qualitative and quantitative by EC)
(<2-mm Basis) (6F1a)
(<20-mm Basis) (6F4)

1. APPLICATION

Gypsum content of a soil is a criterion for gypsic and petrogypsic horizons and for mineralogical class at the family level (Soil Survey Staff, 1975). Soil subsidence through solution and removal of gypsum can crack building foundations, break irrigation canals, and make roads uneven. Failure can be a problem in soils with as little as 1.5% gypsum (Nelson, 1982). The gypsum content in the soil may be used to determine if reclamation of sodic soils requires chemical amendments. Corrosion of concrete is also associated with soil gypsum.

Gypsum formation by precipitation of calcium sulfate ($CaSO_4$) is usually highest at the surface layers. Gypsum from deposits high in gypsum are usually highest in the lower part of the soil profile. However, leaching may disrupt this sequence. Gypsum is reported on both the <2- and the <20-mm base.

2. SUMMARY OF METHOD

A soil sample is mixed with water to dissolve gypsum. Acetone is added to a portion of the clear extract to precipitate the dissolved gypsum. After centrifuging, the gypsum is redissolved in water. The electrical conductivity (EC) of the solution is read. The EC reading is used to estimate the gypsum content in meq 100 g^{-1}.

In procedure 6F1a, gypsum content (meq 100 g^{-1}) is converted to percent gypsum (uncorrected). The percent gypsum (uncorrected) is used to calculate percent gypsum (corrected). The percent gypsum (corrected) is used to correct the AD/OD (air-dry/oven-dry ratio). The AD/OD and corrected AD/OD are determined in procedures 4B5 and 6F3, respectively. The corrected AD/OD uses the correction for the crystal water of gypsum. Gypsum content on a <2-mm basis is reported in procedure 6F1a.

Gypsum content may also be determined on the 2- to 20-mm fraction prepared by procedure 1B5a. The gypsum determined on the 2- to 20-mm fraction and the gypsum determined on the fine earth (1B1a) are combined and converted to a <20-mm soil basis. Gypsum on a <20-mm basis is reported in procedure 6F4.

3. INTERFERENCES

Loss of the precipitated gypsum is the most significant potential error. Care in handling the precipitated gypsum is required. Incomplete dissolution of gypsum is also possible. In soils with large gypsum crystals, use fine-ground samples to reduce sampling errors.

When present in sufficiently high concentrations, the sulfates of Na and K are also precipitated by acetone. The concentration limits for sulfates of Na and K are 50 and 10 meq L^{-1}, respectively.

4. SAFETY

Acetone is highly flammable. Avoid open flames and sparks. Use a nonsparking centrifuge. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Proper use and appropriate load balance of the centrifuge is required. Follow standard laboratory safety precautions.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity, Mettler PE 360 or equivalent
5.2 Fleakers, 500 mL, with caps.
5.3 Shaker, Eberbach 6000 power unit, with reciprocating speed of 60 to 260 epm, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI
5.4 Dispenser, 100 mL, Universal, OPTIFIX, EM Science

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5.5 Dispenser, Repipet or equivalent, 10 mL,

5.6 Pipettor, Pistolpet, 20 mL, solvent, Manostat

5.7 Pipet, Macro, fixed volume, 5 mL, MLA

5.8 Pipet tips, 5 mL, polypropylene, Oxford

5.9 Centrifuge, Hi-Speed Centricone, 15 mL, 8 tube, Precision

5.10 Centrifuge tubes, 15 mL, plain, conical

5.11 Thermometer, 0° to 100°C

5.12 Conductivity bridge and conductivity cell, Markson Model 1096, Amber Science, Eugene, OR

5.13 Filter paper, folded, 18.5-cm diameter, Whatman No. 12 or Schleicher and Schuell No. 560

5.14 Funnel, 90 cm

5.15 Flask, Erhlenmeyer, 125 mL

5.16 Vortexer, Glas-Col, Terre Haute, IN

6. REAGENTS

6.1 Distilled water

6.2 Potassium chloride (KCl), 0.010 *N*. Dry KCl overnight or at least 4 h in oven (105°C). Dissolve 0.7456 g of dry reagent grade KCl in distilled water and bring to 1-L volume. Conductivity at 25°C is 1.41 mmhos cm^{-1}.

6.3 Acetone, purity 99%

7. PROCEDURE

7.1 Weigh 5.0 g of air-dry soil into a 500-mL fleaker. If a trace of gypsum is present, a 20-g sample size may be used. If the EC reading is >0.85 mmhos cm^{-1}, repeat the procedure using a smaller sample size (1.0, 0.50. 0.25, or 0.125 g). For sample sizes <1 g, use 80-mesh sample to obtain representative subsample.

7.2 Use a dispenser to add 100 mL of distilled water to sample.

7.3 Cap the fleaker and shake for 30 min at 100 epm on the shaker.

7.4 Filter the suspension. The first few mL of filtrate is usually cloudy and should be discarded. Collect the clear filtrate in a 125-mL flask.

7.5 Pipet 5 mL of filtrate into 15-mL conical centrifuge tube.

7.6 Use a solvent dispenser to add 5 mL acetone.

7.7 Cap tube with a polyethylene stopper and mix.

7.8 Carefully release pressure within tube by loosening the stopper.

7.9 Let stand for at least 10 min to allow the precipitate to flocculate.

7.10 Use acetone (1 or 2 mL) to rinse stopper and inside rim of tube to prevent gypsum loss.

7.11 Remove stopper and centrifuge at 2200 rpm for 5 min.

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(<20-mm Basis) (6F4)

7.12 Decant and discard supernatant. Invert and drain the tube on filter paper or on towel for 5 min.

7.13 Add 5 mL of acetone to the tube. Replace stopper. Use Vortexer to shake sample until the precipitate dissolves.

7.14 Carefully remove stopper and rinse it and the inside rim of tube with acetone (1 or 2 mL).

7.15 Centrifuge the sample tube at 2200 rpm for 5 min.

7.16 Discard supernatant. Drain tube upside down for 5 min.

7.17 Use a dispenser to add 10 mL of distilled water to tube.

7.18 Stopper and shake with Vortexer until the precipitate dissolves.

7.19 Calibrate the EC meter and cell by drawing the 0.010 *N* KCl solution into the cell.

7.20 Flush the cell and fill with distilled water. Digital reading should be 0.00.

7.21 Read the EC of dissolved precipitate by drawing up solution into cell and flush at least once.

7.22 If the EC reading is >0.85 mmhos cm^{-1}, repeat the procedure using a smaller sample weight.

8. CALCULATIONS

8.1 % Gypsum (uncorrected) =

$$\frac{\text{Gypsum x Water x 0.08609 x AD/OD}}{\text{Sample Weight (g) x 5}}$$

where:
Gypsum   = Gypsum (meq 100 g^{-1}). Refer to Table 1.
Water   = Volume distilled water (mL) to dissolve gypsum
AD/OD   = Air-dry/oven-dry ratio, (procedure 4B5)

8.2 % Gypsum (corrected) =

$$\frac{\text{\% Gypsum (uncorrected)}}{\text{1 + [0.001942 x \% Gypsum (uncorrected)]}}$$

8.3 Use the percent gypsum (corrected) to recalculate the AD/OD (procedure 4B5). The corrected AD/OD (procedure 6F3) uses the correction for the crystal water of gypsum.

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(<20-mm Basis) (6F4)

8.4 Refer to Table 1 to convert EC (mmhos cm^{-1}) to gypsum (meq 100 g^{-1}) for the above calculations. Enter Table 1 using both the x and y axis for the EC reading to determine gypsum content (meq 100 g^{-1}).

8.5 Calculate gypsum on <20-mm basis (procedure 6F4) as follows:

$$(\%) \text{ Gypsum} = A \times B + [C \times (1 - B)]$$

where:
A = Gypsum (%) in <2-mm fraction
B = Weight of the <20-mm fraction minus the 20- to 2-mm fraction divided by the weight of the <20-mm fraction
C = Gypsum (%) in the 20- to 2-mm fraction

Table 1. Convert EC reading (mmhos/cm) to gypsum content (meq/100).

EC	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0						0.40				
0.1	0.80	0.89	0.98	1.10	1.22	1.31	1.40	1.50	1.60	1.70
0.2	1.80	1.90	2.00	2.10	2.20	2.30	2.40	2.50	2.60	2.70
0.3	2.80	2.90	3.00	3.10	3.20	3.30	3.40	3.50	3.60	3.72
0.4	3.85	3.98	4.10	4.22	4.35	4.48	4.60	4.70	4.80	4.90
0.5	5.00	5.12	5.25	5.38	5.50	5.62	5.75	5.88	6.00	6.12
0.6	6.25	6.35	6.45	6.58	6.70	6.92	6.95	7.05	7.15	7.28
0.7	7.40	7.52	7.65	7.78	7.90	8.04	8.18	8.32	8.45	8.58
0.8	8.70	8.82	8.95	9.05	9.15	9.28	9.40	9.55	9.70	9.85
0.9	10.00	10.12	10.25	10.38	10.50	10.62	10.75	10.88	11.00	11.15
1.0	11.30									

9. REPORT
Report gypsum as a percent to the nearest whole unit.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is run with every batch of samples. With 25 observations of the quality control check sample, the mean, standard deviation, and C.V. for gypsum are 12.2, 0.29, and 2.4%, respectively.

11. REFERENCES
Nelson, R.E. 1982. Carbonate and gypsum. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:181-197.

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA-SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

CHEMICAL ANALYSES
EXTRACTABLE ACIDITY (6H)
BaCl$_2$-TRIETHANOLAMINE IV, AUTOMATIC EXTRACTOR (6H5)
BACK-TITRATION WITH HCl, AUTOMATIC TITRATOR
METROHM 686 TITROPROCESSOR (6H5a)

1. APPLICATION

The extractable acidity is the acidity released from the soil by a barium chloride-triethanolamine (BaCl$_2$-TEA) solution buffered at pH 8.2 and includes all the acidity generated by replacement of the H and Al from permanent and pH dependent exchange sites. Extractable acidity may be measured at any pH, and a variety of methods have been used to measure it. The Soil Conservation Service adopted a pH of 8.2 because it approximates the calculated pH of a soil containing free CaCO$_3$ in equilibrium with the normal CO$_2$ content (0.03%) of the atmosphere. A pH of 8.2 also closely corresponds to the pH of complete neutralization of soil hydroxy-Al compounds. This pH is conveniently maintained by Mehlich's BaCl$_2$-TEA buffered extraction technique. Although other pH values are valid for some types of soils, and the BaCl$_2$-TEA, pH 8.2 method may not always accurately reflect the nature of soils as they occur in the environment, this method has become a standard reference to which other methods are compared.

2. SUMMARY OF METHOD

A soil sample is leached with a BaCl$_2$-TEA solution buffered at pH 8.2 using a mechanical vacuum extractor (Holmgren et al., 1977). The extract is back-titrated with HCl. The difference between a blank and the extract is the extractable acidity. Extractable acidity is reported in meq 100 g^{-1} oven-dry soil.

3. INTERFERENCES

No significant interferences are known to exist with this method. However, for some very acid soils, the buffer capacity of the BaCl$_2$-TEA solution may be exceeded. More study of this phenomenon is needed.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. EQUIPMENT

5.1 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE

5.2 Mechanical vacuum extractor, Mavco Sampletex, 5300 N. 57th St., Lincoln, NE

5.3 Pipettors or dispenser, adjustable volume to 20 mL

5.4 Titration beakers, polyethylene, 250 mL

5.5 Automatic titrator, Metrohm 686 Titroprocessor Series 04 or 670 Titroprocessor Series 11, 664 Control Unit, 674 Sample Changer Series 5, and 665 Dosimat Series 14, Metrohm Ltd., Brinkmann Instruments, Inc.

5.6 Syringes, polypropylene, disposable, 60 mL, for extraction vessel, extractant reservoir, and extraction syringe

5.7 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm, (1/8 ID x 1/4 OD x 1 in) for connecting syringe barrels

5.8 Analytical filter pulp, ash-free, Schleicher and Schuell, No. 289

5.9 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.

5.10 Electronic balance, ±1-mg sensitivity

6. REAF TDaˊlubi0 -1.2048 TDɪˊ-0.002 Tcıˊ(5.1)Tjıˊ/F7 1 Tfıˊ1.3855bastto neudeber0.0d 3.DDI goge aneicher and Sc **5.2**

CHEMICAL ANALYSES
EXTRACTABLE ACIDITY (6H)
BaCl$_2$-TRIETHANOLAMINE IV, AUTOMATIC EXTRACTOR (6H5)
BACK-TITRATION WITH HCl, AUTOMATIC TITRATOR
METROHM 686 TITROPROCESSOR (6H5a)

6.3 Buffer solution (0.5 *N* BaCl$_2$, 0.2 *N* Triethanolamine (TEA), pH 8.2). Dissolve 977 g of
BaCl$_2$ · 2H$_2$O in 8 L of DDI water. Dissolve 477 g of TEA in 4 L of DDI water. Mix two solutions
and bring to nearly 16-L volume with DDI water. Adjust to pH 8.2 with ~ 33 mL of
concentrated HCl or barium hydroxide. Bring to 16-L volume with DDI water.

6.4 Replacement solution. Dissolve 500 g of BaCl$_2$·2H$_2$O in 4 L of DDI water. Add 40 mL of buffer
solution and dilute to 8-L volume with DDI water.

6.5 HCL, 0.13 *N*, standardized. Dilute 193 mL of concentrated HCl to 16-L volume with DDI water.
Refer to Appendix VIII, Standardization of Acids.

7. PROCEDURE

Extraction of Acidity

7.1 Prepare extraction vessel by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe
barrel with a modified plunger.

7.2 Weigh 2.00 g of <2-mm, air-dry soil and place in an extraction vessel. Prepare at least one reagent
blank (no sample in syringe) and one quality control check sample per 24 samples. Place the extraction
vessel on the upper disk of the extractor and connect an extraction syringe. Use 25.4-mm (1 in) length
rubber tubing to insert the plunger handle in the slot of the stationary extractor disk.

7.3 Use a dispenser to add 10.00 mL of BaCl$_2$-TEA solution to the extraction vessel. During the
addition, wash the sides of the tube and wet the sample. For organic soils, shaking, swirling, or stirring
may be required to wet the sample. Allow the sample to stand for 30 min.

7.4 Set the extractor for a 30-min extraction rate. Refer to Appendix III and IV for operation of
mechanical vacuum extractor. Extract solution to a 0.5- to 1.0-cm height above the sample. Turn off the
extractor. Do not allow the sample to become dry.

7.5 Add a second 10.00-mL aliquot of BaCl$_2$-TEA solution to the sample. Extract at the 30-min rate until
nearly all the solution has been pulled through the sample.

7.6 Use a dispenser to add 20.00 mL of replacement solution. Extract the sample at 30-min rate, pulling
the solution almost completely through the sample. Refer to Appendix III and IV for operation of
mechanical vacuum extractors.

7.7 Add a second 20.00-mL aliquot of replacement solution. Extract at 30-min rate until all the solution
has been drawn through the sample.

Titration of BaCl$_2$-TEA Extract

7.8 Transfer the BaCl$_2$-TEA extract from the syringe to a 250-mL polyethylene titration beaker.

7.9 Add 100 mL of DDI water to the beaker. The solution is ready to be titrated.

7.10 Refer to the Appendix XV for operation of the automatic titrator. Calibrate the titrator meter with
7.00 and 4.00 pH buffers. Set the titration endpoint of the BaCl$_2$-TEA to pH 4.60.

7.11 Record the titer to the nearest 0.01 mL. Record the normality of the HCl solution. Average the titer
of the reagent blanks and record.

8. CALCULATIONS

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Extractable acidity (meq 100 g⁻¹) =
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$$\text{Extractable acidity (meq 100 g}^{-1}) = \frac{[\text{Blank} - \text{Titer}] \times N \times 100 \times \text{AD/OD}}{\text{Sample Weight (g)}}$$

where:
Blank   = Average reagent blank titer (mL)
Titer   = Sample titer (mL)
N = Normality of HCl
100   = Conversion factor (100-g basis)
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)

9. REPORT

Report extractable acidity in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq   100 g^{-1}.

10. PRECISION

Precision data are not available for this procedure. A quality control check sample is run with every batch of 24 samples. For 76 observations of the quality control check sample, the mean, standard deviation, and C.V. for extractable acidity are 3.9, 0.39, 10.2%, respectively.

11. REFERENCES

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled
variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.

CHEMICAL ANALYSES
CARBONATE AND BICARBONATE (6I and 6J)
SATURATION EXTRACT (6I1 and 6J1)
ACID TITRATION, AUTOMATIC EXTRACTOR
METROHM TITROPROCESSOR 686 (6I1b and 6J1b)

1. APPLICATION
         The water soluble anions that usually are determined in saturation extracts are carbonate, bicarbonate, sulfate, chloride, nitrate, nitrite, fluoride, phosphate, silicate, and borate. Carbonate and bicarbonate are analyzed by titration. In saturation extracts, carbonate is measurable if the pH >9 (U.S. Salinity Laboratory Staff, 1954). The bicarbonate concentration is seldom >10 meq L^{-1} in the absence of carbonate anions (U.S. Salinity Laboratory Staff, 1954). The bicarbonate concentration at pH $\leq$7 seldom exceeds 3 or 4 meq L^{-1} (U.S. Salinity Laboratory Staff, 1954).
         The total dissolved ion amounts generally increase with increasing soil moisture content. While some ions increase, some ions may decrease. The carbonate and bicarbonate anions are among those ions which are most dependent upon soil moisture. Therefore, in making interpretations about carbonate and bicarbonate in soil solution, there must be careful consideration about the chemistry of the soil and the soil solution.

2. SUMMARY OF METHOD
         An aliquot of the saturation extract (procedure 8A3) is titrated on an automatic titrator to pH 8.25 and pH 4.60 end points. The carbonate and bicarbonate are calculated from the titers, aliquot volume, blank titer, and acid normality. Carbonate and bicarbonate are reported in meq L^{-1}.

3. INTERFERENCES
         Clean the electrode by rinsing with distilled water and patting it dry with tissue. Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization.
         Slow electrode response time may cause over shooting the end point. A combination of slowing the buret speed and increasing the time delay may help. Cleaning the electrode with detergent may decrease the response time. If all else fails, changing the electrode generally solves the problem. Blanks may not titrate properly because some sources of distilled water have a low pH.

4. SAFETY
         Wear protective clothing and eye protection. When preparing reagents, exercise care. Thoroughly wash hands after handling reagents. Restrict the use of concentrated H_2SO_4 to the fume hood. Use showers and eyewash stations to dilute spilled acids. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Follow the manufacturer's safety precautions when operating the automatic titrator.

5. EQUIPMENT
5.1 Automatic titrator, Metrohm 686 Titroprocessor Series 04, or 670 Titroprocessor Series 11, 664 Control Unit, 674 Sample Changer Series 5, and 665 Dosimat Series 14, Metrohm Ltd., Brinkmann Instruments, Inc.
5.2 Combination pH-reference electrode, Metros part no. 6.0210.100, Metrohm Ltd., Brinkmann Instruments, Inc.
5.3 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 μL and 10 mL

6. REAGENTS
6.1 Distilled water
6.2 Sulfuric acid (H_2SO_4), concentrated, 18 *N*
6.3 H_2SO_4, 0.0240 *N* standardized. Carefully dilute 2.67 mL of concentrated H_2SO_4 in 4 L of distilled degassed water. Restandardize the acid at regular intervals. Refer to Appendix VIII, Standardization of Acids.

CHEMICAL ANALYSES
CARBONATE AND BICARBONATE (6I and 6J)
SATURATION EXTRACT (6I1 and 6J1)
ACID TITRATION, AUTOMATIC EXTRACTOR
METROHM TITROPROCESSOR 686 (6I1b and 6J1b)

7. PROCEDURE

7.1 Pipet 3 mL of the fresh saturation extract (procedure 8A3) into a 250-mL titration beaker.

7.2 Add 72 mL of distilled water into a titration beaker. Final volume is 75 mL. Run 8 to 12 blanks of distilled water through the titration procedure.

7.3 Refer to Appendix XV, Automatic Titrator, and manufacturer's manual for operation of the automatic titrator.

7.4 Set-up the automatic titrator to set end point titration mode. The "Set" pH parameters are listed as follows:

Parameter	Value
Ep_1	pH 8.25
Dyn change pH	1.5 units
Drift	0.4 mV s^{-1}
Time delay	10 s
Ep_2	pH 4.60
Dyn change pH	1.5 units
Drift	0.4 mV s^{-1}
Temp	25°C
Stop Volume	35 mL
Buret speed setting	2.5

7.5 Place the 250-mL titration beakers in the sample changer.

where:

T_1	=	Titer of CO_3^{2-} (mL)
T_2	=	Titer of HCO_3^- (mL)
N	=	Normality of H_2SO_4
Blank	=	Average titer of blank solutions (mL)
Aliquot	=	Volume of saturation extract titrated (mL)

9. REPORT

Report saturation extract CO_3^{2-} and HCO_3^- in units of meq L^{-1} to the nearest 0.1 meq L^{-1}.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH, ANION SUPPRESSOR
DIONEX 2110i ION CHROMATOGRAPH
(6K1d, 6L1d, 6M1d, 6U1b, and 6W1b)

1. APPLICATION

The soluble anions that are commonly determined in saline and alkali soils are carbonate, bicarbonate, sulfate, chloride, nitrate, nitrite, fluoride, phosphate, silicate, and borate (Khym, 1974; U.S. Salinity Laboratory Staff, 1954). Carbonate and bicarbonate are determined by titration. Phosphate, silicate, and borate usually are not determined because they are found only occasionally in measurable amounts in soils. Chloride, sulfate, nitrate, fluoride, and nitrite are measured in solution by chromatography. In saline and alkali soils, carbonate, bicarbonate, sulfate, and chloride are the anions that are found in the greatest abundance. In general, soluble sulfate is usually more abundant than soluble chloride.

2. SUMMARY OF METHOD

The saturation extract is diluted according to its electrical conductivity (EC_s). The diluted sample is injected into the ion chromatograph, and the anions are separated. A conductivity detector is used to measure the anion. A chart recording is made of the chromatograph. Standard anions are used to calibrate the system. A calibration curve is determined, and the anion concentrations are calculated. A computer program automates these actions. The saturated extract anions, Cl^-, SO_4^{2-}, NO_3^-, F^-, and NO_2^- are reported in meq L^{-1} in procedures 6K1d, 6L1d, 6M1d, 6U1b, and 6W1b, respectively.

3. INTERFERENCES

Some saturation extracts contain suspended solids. Filtering after dilution removes the particles. Saturation extracts of acid soils that contain Fe and/or Al may precipitate and clog the separator column. Saturation extracts of very high pH may contain organic material which may clog or poison the column. Low molecular weight organic anions will co-elute with inorganic anions from the column.

4. SAFETY

Wear protective clothing and safety glasses. When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Follow the manufacturer's safety precautions when using the chromatograph.

5. EQUIPMENT
5.1 Ion chromatograph, Series 2110i, dual-channel system
5.2 Analytical column, AS4A 4mm P/N 37041, Dionex Corp., 1228 Titan Way, Sunnyvale, CA
5.3 Guard column, AG4A 4mm P/N 37042, Dionex Corp., 1228 Titan Way, Sunnyvale, CA
5.4 Analytical pumps, Dionex Corp., 1228 Titan Way, Sunnyvale, CA
5.5 Automated sampler, Dionex Corp., 1228 Titan Way, Sunnyvale, CA
5.6 Conductivity detectors, Dionex Corp., 1228 Titan Way, Sunnyvale, CA
5.7 Anion self-regenerating suppressor (ASRS-1) with controller (SRC-1), Dionex Corp., 1228 Titan Way, Sunnyvale, CA
5.8 Computer interfaces, Dionex Corp., 1228 Titan Way, Sunnyvale, CA
5.9 Computer software, A1-450 Chromatography Software Program Release 3.32, Microsoft Windows Operating Environment; Dionex Corp., 1228 Titan Way, Sunnyvale, CA
5.10 Computer, DFI.
5.11 Printer, Epson, Fx-850
5.12 Poly-vials, 5 mL, P/N 038008, Dionex Corp., 1228 Titan Way, Sunnyvale, CA
5.13 Poly-vials, filtercaps, 5 mL, P/N 038009, Dionex Corp., 1228 Titan Way, Sunnyvale, CA
5.14 Digital diluter/dispenser, MicroLab 500, Hamilton C., P.O. Box 10030, Reno, NV
5.15 Syringes, gas tight, Hamilton 1001 DX and 1010-TEF LL, Hamilton Co., P.O. Box 10030, Reno, NV

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH, ANION SUPPRESSOR
DIONEX 2110i ION CHROMATOGRAPH
(6K1d, 6L1d, 6M1d, 6U1b, and 6W1b)

5.16 Disposable 0.2-μm pore size, 25-mm filter assembly, Gelman Sciences, Inc., 674 South Wagner Road, Ann Arbor, MI 48106. Use for saturation extracts and standards.

5.17 Disposable 0.2-µm pore size, Ultipor N_{66} DFA3001NAEY, Pall Trinity Micro Corp., Cortland, NY. Use for filtering distilled deionized (DDI) water.

6. REAGENTS

6.1 Distilled deionized (DDI) filtered water

6.2 Sulfuric acid (H_2SO_4), concentrated, reagent

6.3 Toluene

6.4 Isopropanol to de-gas column

6.5 Stock $NaHCO_3$ solution, 0.480 *M*. Mix 40.34 g of dried $NaHCO_3$ with filtered DDI water and dilute to 1-L volume.

6.6 Stock Na_2CO_3 solution, 0.5040 *M*. Mix 53.42 g of dried Na_2CO_3 with filtered DDI water and dilute to 1-L volume.

6.7 Working eluent solution. Mix 100 mL of 0.5040 *M* $NaHCO_3$ and 100 mL of 0.4800 *M* Na_2CO_3 with filtered DDI water and dilute to 20-L volume. Add 8 drops of toluene to retard microbial growth.

6.8 Primary SO_4^{2-} standard, 0.5 *M* (1.0 *N*). Mix 17.7560 g of Na_2SO_4 with filtered DDI water and dilute to 250-mL volume.

6.9 Primary Cl^- standard, 1.0 *M* (1.0 *N*). Add 18.6392 g of KCl with filtered DDI water and dilute to 250-mL volume.

6.10 Primary F^- standard, 0.125 *M* (0.125 *N*). Add 1.3122 g of NaF with filtered DDI water and dilute to 250-mL volume.

6.11 Primary NO_3^- standard, 1.0 *M* (1.0 *N*). Add 25.2770 g of KNO_3 with filtered DDI water and dilute to 250-mL volume.

6.12 Primary mixed standard. Prepare 1 primary mixed standard by taking aliquots of each of the proceeding primary standards and diluting the combined aliquots to a 1-L volume with working eluent as follows:

Primary Standards	Aliquot	Final Volume w/Eluent	Concentration
	mL	mL	meq L^{-1}
Na_2SO_4	50	1000	50
KCl	10	1000	10
NaF	100	1000	12.5
KNO_3	30	1000	30

Add eight drops of toluene to primary mixed standard to retard microbial growth and store in a glass container.

6.13 Mixed calibration standards. Prepare 4 mixed calibration standards (0.5, 1.0, 3.0, and 7.0 readings) by taking aliquots of primary mixed standard and diluting each aliquot to 100-mL volume with working eluent as follows:

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH, ANION SUPPRESSOR
DIONEX 2110i ION CHROMATOGRAPH
(6K1d, 6L1d, 6M1d, 6U1b, and 6W1b)

Primary Mixed Standards	Final Volume w/Eluent	Concentration			
		SO_4^{2-}	Cl^-	F^-	NO_3^-
mL	mL	$meq\ L^{-1}$			
0.5	100	0.25	0.05	0.0625	0.15
1.0	100	0.50	0.10	0.125	0.30
3.0	100	1.5	0.30	0.375	0.90
7.0	100	3.5	0.70	0.875	2.1

6.14 $NaNO_2$, Baker reagent grade, 99.5% purity

6.15 Primary NO_2^- standard, 1 *N* (1000 meq L^{-1}). Mix 69.3568 g of reagent grade $NaNO_2$ with filtered DDI water and dilute to 1-L volume. Take 5 mL aliquot of primary NO_2^- standard and dilute with 500 mL of filtered DDI water (10 meq L^{-1}). Add eight drops of toluene to primary NO_2^- standard to retard microbial growth and store in a glass container.

6.16 NO_2^- calibration standards. Prepare 4 NO_2^- calibration standards (0.5, 1.0, 3.0, and 7.0 readings) by taking aliquots of primary NO_2^- standard (10 meq L^{-1}) and diluting each aliquot to 100-mL volume with working eluent as follows:

Primary Standard meq L^{-1}	Final Volume w/Eluent	NO_{2-} Concentration
mL	mL	$meq\ L^{-1}$
0.5	100	0.5
1.0	100	1.0
3.0	100	3.0

7. PROCEDURE
Dilution of extracts
7.1 To estimate the total soluble anion concentration (meq L^{-1}), multiply the EC_s (procedure 8A3a) by 10. Subtract the CO_3^{2-} and HCO_3^- concentrations (procedures 6I1b and 6J1b) from the total anion concentration. The remainder is the $\approx$ concentration (meq L^{-1}) of anions to be separated by ion chromatography.

Anion concentration (meq L^{-1}) = EC_s x 10 - (HCO_3^- + CO_3^{2-})

7.2 Dilute the saturation extract with the working eluent as follows:

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH, ANION SUPPRESSOR
DIONEX 2110i ION CHROMATOGRAPH
(6K1d, 6L1d, 6M1d, 6U1b, and 6W1b)

EC_s (mmhos cm^{-1})	Dilution Factor
0.00 to 0.55	4
0.56 to 0.65	5
0.66 to 0.75	6
0.76 to 0.85	7
0.86 to 0.95	8
0.96 to 1.05	9
1.06 to 1.20	10
1.21 to 1.40	15
1.41 to 1.50	25
1.51 to 1.60	30
1.61 to 1.80	40
1.81 to 2.00	50
2.01 to 2.30	60
2.31 to 2.60	70
2.61 to 3.10	80
3.11 to 3.55	90
3.56 to 4.05	100
4.06 to 4.60	120
4.61 to 5.20	140
5.21 to 5.85	150
5.86 to 6.55	160
6.56 to 7.30	180
7.31 to 8.00	200
8.01 to 9.00	225
9.01 to 10.00	240
10.01 to 11.50	270
11.51 to 13.00	280
13.01 to 14.50	300
14.51 to 16.00	320
16.01 to 17.00	360
17.01 to 18.00	400
18.01 to 20.00	450
20.01 to 21.00	480
21.01 to 23.00	500
23.01 to 24.00	540
24.01 to 25.00	560
25.01 to 27.00	600
27.01 to 28.00	640
28.01 to 30.00	680
30.01 to 32.00	700
32.01 to 33.00	720
33.01 to 36.00	800
36.01 to 40.00	900
40.01 to 44.00	1000

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH, ANION SUPPRESSOR
DIONEX 2110i ION CHROMATOGRAPH
(6K1d, 6L1d, 6M1d, 6U1b, and 6W1b)

7.3 Place the diluted samples in the Poly-vials and cap with filtercaps.

7.4 Place the mixed calibration standards in the Poly-vials.

Set-up and Operation of Ion Chromatograph (IC)
7.5 Because any number of factors may cause a change in IC operating conditions, only a general set-up of the Dionex 2110i ion chromatograph is presented. Individual analysts may modify some or all of the operating conditions to achieve satisfactory results. Typical operation parameters are as follows:

Parameter	Range
Conductivity cell range	3 uS cm^{-1} full scale to 100 uS cm^{-1}
Auto offset	"On"
Analytical pump flow rate	2.0 to 2.5 mL min^{-1}
Low pressure limit	100 psi
High pressure limit	1200 psi
Regenerant flow rate	3 to 4 mL min^{-1}
Injector loop	0.50 mL
Air pressure	3 to 8 psi

7.6 Load the sample holder cassettes with the capped samples, standards, and check samples.

7.7 Refer to the Appendix XVI, Chromatograph, and manufacturer's manual for the operation of chromatograph.

8. CALCULATIONS

Calibration Calculations
8.1 Use the peak height of each anion standard to either construct a calibrated curve to plot anion concentration or use a least squares analysis to calculate anion concentration. The analytes are reported in meq L^{-1}.

8.2 *Calibration Curve*: Plot the peak height against the meq L^{-1} of each anion standard on graph paper. Construct the calibration curve by finding the "best" line that fits the plotted standards.

8.3 *Linear Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. An example for the anion Cl$^-$ is as follows:

```
Cl⁻ concentration (meq L⁻¹)  =  Y =  0.1     1.5     4.0
Peak height                  =  X =  8.43   170.0   441.5
Number of standards          =  n =  3
```

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH, ANION SUPPRESSOR
DIONEX 2110i ION CHROMATOGRAPH
(6K1d, 6L1d, 6M1d, 6U1b, and 6W1b)

$$\sum Y_i = 5.6 \qquad\qquad \sum X_i = 619.93$$

$$\sum Y_i/n = Y = 1.866 \qquad \sum X_i/n = X = 206.6433$$
$$\sum X_i Y_i = 2021.843 \qquad \sum X_i^2 = 223893.31$$
$$\sum X_i \sum Y_i = 3471.608$$

$$b = \frac{\sum X_i Y_i - \sum X_i \sum Y_i/n}{\sum X_i^2 - (\sum X_i)^2/n} = \frac{2021.843 - 1157.2027}{223893.31 - 128104.4} = 0.0090265$$

b = slope of the line, i.e., the amount that Y changes when X changes by 1 unit.

The equation is as follows:

$$Y = Y + b (X - X)$$

$$Y = 1.866 + 0.0090265 (X) - 1.8653$$

Analyte Calculation

8.4 *Calibration curve*: Read the analyte concentration (meq L^{-1}) directly from the calibration curve.

8.5 *Linear regression*: Put the peak height in the preceding equation and solve for analyte concentration (meq L^{-1}). Thus, if sample extract has 204 peak height, the preceding equation is as follows:

$Y = 1.866 + 0.0090265 (204) - 1.8653 = 1.84$ meq L^{-1}

8.6 Repeat the calibration set and analyte calculation for each anion.

8.7 The chromatograph software automatically calculates the analyte concentrations and prints a report of the results.

9. REPORT

Report the saturation extract anions in units of meq L^{-1} to the nearest 0.1 meq L^{-1}.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

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CHEMICAL ANALYSES
NITRATE (6M)
1 M KCl EXTRACTION (6M2)
FLOW INJECTION, AUTOMATED ION ANALYZER
LACHAT, QUIKCHEM AE (6M2a)

1. APPLICATION

The inorganic combined N in soils is predominantly NH_4^+ and NO_3^- (Keeney and Nelson, 1982). Nitrogen in the form of ammonium ions and nitrate are of particular concern because they are very mobile forms of nitrogen and are most likely to be lost to the environment (National Research Council, 1993). All forms of nitrogen, however, are subject to transformation to ammonium ions and nitrate as part of the nitrogen cycle in agroecosystems and all can contribute to residual nitrogen and nitrogen losses to the environment (National Research Council, 1993).

2. SUMMARY OF METHOD

A 2.5-g sample of <2-mm, air-dry soil is mechanically shaken for 30 min in 25-mL of 1 *M* KCl. The sample is then filtered through Whatman No. 42 filter paper. A flow injection automated ion analyzer is used to measure the soluble inorganic nitrate (NO_3^-). The nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-1-naphthylethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Absorbance is proportional to the concentration of NO_3^- in the sample. Concentration of extract NO_3^- is reported as mg N L^{-1}. These extract data are then converted to mg N kg^{-1} (ppm) in the soil.

3. INTERFERENCES

Low results can be obtained for samples that contain high concentration of Fe, Cu, or other metals. In this method, EDTA is added to the buffer to reduce this interference (LACHAT, 1993).

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of NH_4OH and concentrated HCl to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Cadmium is toxic and carcinogenic. Wear gloves and follow the precautions described on the Material Safety Data Sheet. If repacking the cadmium-copper reduction column, do all transfers over a special tray or beaker dedicated to this purpose. Preferably, send the cadmium-copper column to LACHAT for repacking.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity
5.2 Centrifuge tubes, polypropylene, round bottom, 25-mL
5.3 Centrifuge tubes, polypropylene, round bottom, 13-mL, 16.0 mm x 98.3 mm
5.4 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 oscillations min^{-1}, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI
5.5 Centrifuge, high-speed, International Equipment Co., IECB-22M
5.6 Filter paper, Whatman No. 42
5.7 Funnel, 60° angle, long stem, 50-mm diameter
5.8 Erlenmeyer flasks, 50-mL, acid-washed
5.9 Volumetric flasks, 1-L and 250-mL
5.10 Bottles, plastic, dark, 1-L
5.11 Flow Injection Automated Ion Analyzer, QuikChem AE, LACHAT Instruments, Milwaukee, WI
5.12 XYZ Sampler, LACHAT Instruments, Milwaukee, WI
5.13 Reagent Pump, LACHAT Instruments, Milwaukee, WI
5.14 Automated Dilution Station, LACHAT Instruments, Milwaukee, WI

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5.15 Sample Processing Module (SPM) or channel, QuikChem Method (12-107-04-1-B, nitrate in 2 M (1 M) KCl 0.02 to 20.0 mg N L^{-1}), LACHAT Instruments, Milwaukee, WI

5.16 IBM computer PS/2 Model 20/286, 1024 kB Ram, 640 kB user memory

5.17 Okidata ML 182 printer

5.18 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 μL and 10 mL

5.19 Vials, plastic, 25-mL (standards)

5.20 Culture tubes, glass, 10-mL (samples)

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 15 M NaOH. In a 500-mL container, add 250 ml DDI H2$_0$. Slowly add 150 g NaOH. (CAUTION: The solution will get very hot!) Swirl until dissolved. Cool and store in a plastic bottle.

6.3 Ammonium chloride buffer, pH 8.5. In a hood, add 500 mL DDI to a 1-L volumetric flask. Add 105 mL concentrated HCl, 95 mL ammonium hydroxide (NH$_4$OH) and 1.0 g disodium EDTA. Dissolve and dilute to mark. Invert to mix.

6.4 Sulfanilamide color reagent. To a 1-L volumetric flask, add 600 mL DDI H$_2$O followed by 100 mL 85 percent phosphoric acid (H$_3$PO$_4$), 40.0 g sulfanilamide, and 1.0 g N-1-naphthylethylenediamine dihydrochloride (NED). Shake to wet and stir to dissolve 20 min. Dilute to mark, invert to mix. Store in dark bottle and discard when pink.

6.5 1 M KCl Extracting Solution, Carrier and Standards Diluent. Dissolve 74.5 g potassium chloride (KCl) in 800 mL DDI H$_2$O. Dilute to mark and invert to mix. The extracting solution is used also as the carrier and a component of the N standards.

6.6 Stock Standard N Solution (SSNS), 200.0 mg N L^{-1} (ppm) as NO$_3^-$ in 1 M KCl. In a 1-L volumetric flask, dissolve 1.444 g potassium nitrate (KNO$_3$) and 74.5 g KCl in 600 mL DDI H$_2$O. Add 1 mL chloroform. Dilute to mark with DDI H$_2$O and invert to mix.

6.7 Working Stock Standard N Solution (WSSNS), 20.0 mg N L^{-1} (ppm) as NO$_3^-$ in 1 M KCl. To a 1-L volumetric flask, add 100 ml SSNS. Dilute to mark with 1 M KCl and invert to mix. Make fresh weekly.

6.8 Standard N calibration standards (SNCS) or working standards, 10.00, 2.00, 0.80, 0.08, and 0.00 mg N L^{-1} (ppm) as NO$_3^-$ in 1 M KCl. To five 250-mL volumetric flasks add as follows:

a. 10.00 mg N L^{-1} = 125.0 mL WSSNS
b. 2.00 mg N L^{-1} = 25.0 mL WSSNS
c. 0.80 mg N L^{-1} = 10.0 mL WSSNS
d. 0.08 mg N L^{-1} = 1.00 mL WSSNS
e. 0.00 mg N L^{-1} = 0.0 mL WSSNS

Dilute each SNCS to the mark with 1 M KCl and invert three times. Do not degas.

7. PROCEDURE

7.1 Weigh 2.5 g of <2-mm, air-dry soil to nearest 0.01 g on an electronic balance and place into a 50-mL Erlenmeyer flask.

7.2 Add ~ 25 mL of 1 M KCl to sample. Place the sample in a horizontal shaker set at 120 oscillations min^{-1} and shake for 30 min.

7.3 Remove the sample from the shaker. Decant and filter solution. Collect extract in 10-mL culture tubes.

7.4 Centrifuging or repeated filtering may be necessary to obtain clear extracts. Decant into 13-mL centrifuge tube and centrifuge at 10000 RPM for 10 min. Refer to Appendix XVIII for operation of the high-speed centrifuge.

7.5 Transfer sample extracts into culture tubes and place in XYZ sample trays marked "Samples". If extracts are not to be determined immediately after collection, then store samples at 4°C. If samples are to be stored for long periods, then freeze extracts.

7.6 Transfer WNCS standards into plastic vials and place in descending order in XYZ sample trays marked "Standards".

7.7 Refer to the operating and software reference manuals for LACHAT for set-up and operation. Also refer to Appendix XVII for a more detailed discussion on the routine operation and maintenance of the flow injection system, automated ion analyzer.

7.8 Turn main power switch "ON".

7.9 Before inserting cadmium-copper reduction column, pump all reagents (6.3, 6.4, and 6.5) into manifold. Turn pump off. On the column, disconnect the center tubing from one of the union connectors and immediately connect to the outlet tubing of the buffer mixing coil. Connect the open tubing on the column to the tee fitting where the color reagent is added. Do not let air enter the column. Return the pump to normal speed. If air is introduced accidentally, connect the column into the manifold, turn the pump on maximum, and tap firmly with a screwdriver handle, working up the column until all air is removed. Average life of column is approximately 600 samples. Upon degradation, the column needs to be repacked.

7.10 On computer main menu, select "Methods" and then "Analysis Select and Download". On method list, select 1 *M* KCl N method. System unit receives the downloaded method and initializes it.   On computer main menu, select "Samples", "Tray Definition and Submit", and then "Edit" to create new sample tray followed by "Submit" to run new sample tray.

7.11 Upon connection of cadmium column and downloading of 1 *M* KCl Method, continue to pump reagents into manifold. Continue this step and observe baseline. A good baseline needs to be smooth and at zero absorbance. Scatter is indicative of air bubbles and irregular reagent flow. Also observe for any back-pressure in manifold tubing. Refer to Appendix XVII for a more detailed discussion of the operation of the LACHAT.

7.12 Method parameters specific to 1 *M* KCl N are defined within the "Method Definition" menu. Some of these parameters have been modified from the QuikChem Method 12-107-04-1-B, nitrate in 2 *M* (1 *M*) KCl soil extracts (U.S. Environmental Protection Agency, 1983; U.S. Department of Interior, Geological Survey; LACHAT Instruments, 1993).

7.13 Some of the method parameters as they relate to calibration standards are as follows:

a. There are 5 calibration standards (20.0, 2.00, 0.80, 0.08, and 0.00 mg N L^{-1}) with a data format of ####.###, i.e., data rounded to 3 places.

b. The segments/boundaries for the calibration standards are A - C (20.0 to 0.80 mg N L^{-1}) and C - E (0.80 to 0.00 mg N L^{-1}).

c. The protocol (replications) for the calibration standards is as follows: AA BB CCC DDD EE.

d. The check standard is 20.0 mg P L^{-1}. Maximum number of consecutive trays between check standard is one; maximum number of consecutive samples between check standard is 60; and maximum elapse time between check standards is 2 h.

e. Calibration strategy for segments A - C and C - E are normal and very low. The normal strategy requires a minimum correlation coefficient of 0.95. The very low strategy requires a minimum correlation coefficient of 0.90. Both require a maximum standard deviation in slope of 50%. A calibration passes only when both criteria are met. Strategies are user designated. In addition, calibration strategies are based on the full chord. Chord 0 is full chord, and chord 1 - 5 are sections of peak from start of peak to end of peak.

7.14 Method parameters in relation to timing are as follows:

a. Cycle period: 40 s

b. Inject to start of peak period: 27 s. To see if peaks are being timed correctly, scan across correlation coefficients for all chords 1 - 5. The most peak area is supposed to be in chords 2 - 4 with the most signal-to-noise ratio in chords 1 and 5.

c. Inject to end of peak period: 63 s

d. Automatic timing, where standard assumptions are in effect; no manual timing.

7.15 Method parameters in relation to data presentation are as follows:

a. Top Scale Response: 0.50 abs

b. Bottom Scale Response: 0.00 abs

7.16 Refer to the "Method Definition" for 1 *M* KCl nitrate for other method parameters not discussed here.

7.17 Upon completion of run, place the transmission lines into DDI H_2O and pump for approximately 20 min and proceed with the normal "Shut-down" procedure. Refer to Appendix XVII.

7.18 The accumulation of 1 *M* KCl in the manifold tubing and the fittings may cause clogs over time. Upon completion of analysis, the valves and fittings need to be washed with DDI H_2O. Some fittings may need to be soaked overnight or placed in a sonic bath for 10 to 15 min to remove any KCl accumulations.

8. CALCULATIONS

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., $T = P/P_o$ and is often expressed as a percentage, i.e., $\%T = P/P_o \times 100$. The absorbance of a solution is directly proportional to concentration and is defined by the equation, $A = -\log_{10} T$. These relationships are derived from Beer's law.

8.2 Absorbance data are converted to extract concentration of NO_3^- and are reported as mg L^{-1} or ppm. These extract data are converted to soil NO_3^- (ppm or lbs/A) as follows:

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Soil N (ppm) = Extract N (ppm) x 10

Soil N (lbs/A) = Extract N (ppm) x 20

9. REPORT

Report soil nitrate in units of mg N kg^{-1} (ppm) to the nearest 0.001 mg N kg^{-1}.

10. PRECISION

Precision data are not available for this procedure. Example calibration statistics are as follows:

Correlation Coefficients

```
        Segmented Standards
             A-C   C-E
Full Chord   0.9998       0.9862
Chord 1      0.9772       0.9522
Chord 2      0.9799       0.9844
Chord 3      0.9993       0.9501
Chord 4      0.9911       0.9723
Chord 5      0.9533       0.8678
```

The percent relative standard deviation in slope for Full Chord for A-C and C-E Segmented Standards are 0.9 and 6.7 percent, respectively. The correlation coefficient (CC) for each segment line is for the full chord. The CC is the "r-squared" statistic, which is ideally 1.0000 for a perfect correlation between dependent variable, absorbance, and the independent variable, concentration. The CC does not distinguish between accuracy of fit and precision and is, at best, a general indicator of error. Good CC's generally vary between 0.9000 to 1.0000. Percent relative standard deviation (RSD) for the slope of each segment line is calculated. If the line is a good fit to the data points, the size of this statistic generally gives the user an idea of the precision of the concentrations of both calibration standards and subsequent samples.

The AE QuikChem LACHAT calibration statistics are based on linear regressions (straight line, $y = a + bx$), i.e., there is no curve fitting ($y = a + bx + cx^2$) with the present QuikChem software. In addition, the calculated statistics may have multiple calculated linear regressions, depending on the number of user-designated segments. This calibration strategy may or may not always be the best approach to the natural dynamic range for nitrate ions as well as other ions that could be measured with the flow injection system, automated ion analyzer. Therefore, as an alternative, a curve-fit can be determined independently by hand-calculator or other software. Several curve-fits have been run on these calibration standards data with a CC of 0.9999.

11. REFERENCES

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National Research Council. 1993. Soil and water quality. An agenda for agriculture. Committee on long-range soil and water conservation. Natl. Acad. Press, Washington, DC.

U.S. Environmental Protection Agency. 1983. Methods for chemical analysis of water and wastes. EPA-600/4-79-020. Revised March, 1983, Method 353.2.

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CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM
(6N, 6O, 6P, and 6Q)

1. INTRODUCTION

The extractable bases of Ca^{2+}, Mg^{2+}, Na^+, and K^+ (meq 100 g^{-1} oven-dry soil) are generally assumed to be those major exchangeable bases on the cation exchange sites of the soil. The term extractable rather than exchangeable bases is used because any additional source of soluble bases influences the results. The extractable bases of Ca^{2+}, Mg^{2+}, Na^+, and K^+ are extracted with NH_4OAc, buffered at pH 7.0 in procedure 5A8c and measured by atomic absorption in procedures 6N2, 6O2, 6P2, and 6Q2, respectively.

In soils with carbonates or soluble salts, the soluble cations (meq L^{-1} solution) are measured separately, and the results are subtracted from the extractable bases for determination of exchangeable bases, i.e., exchangeable bases minus extractable bases equal soluble bases. The water-soluble cations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ in the saturated paste extraction in procedure 8A3 are determined by atomic absorption in procedures 6N1, 6O1, 6P1, and 6Q1, respectively.

Exchangeable Na^+ is computed with acceptable accuracy unless salt contents >20 mmhos cm^{-1} at 25°C. Exchangeable Na^+ equals extractable Na^+ minus saturation extract Na^+ multiplied by saturation percentage. Saturation percentage is the water percentage in the saturated paste divided by 1000. Exchangeable Na^+ can be determined with greater accuracy than the other cations in the presence of gypsum or carbonates. If exchangeable K^+ is negligible compared to exchangeable Ca^{2+} and Mg^{2+}, then exchangeable Ca^{2+} plus Mg^{2+} equals CEC (NH_4OAc, pH 7.0) minus exchangeable Na^+. This approximation is suitably reproducible for comparison between soils and for soil classification. Exchangeable Mg^{2+} can be computed in the same manner as exchangeable Na^+. Results are not so satisfactory for exchangeable Ca^{2+} when computed in the presence of carbonates or large amounts of gypsum. To prevent misuse of the Ca^{2+} values, NH_4OAc extractable Ca^{2+} is omitted from the data sheet when the carbonates are thought to significantly influence the results.

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(6N, 6O, 6P, and 6Q)
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(6N1, 6O1, 6P1, and 6Q1)
ATOMIC ABSORPTION
PERKIN-ELMER AA 5000
(6N1b, 6O1b, 6P1b, and 6Q1b)

1. APPLICATION

The commonly determined soluble cations are Ca^{2+}, Mg^{2+}, Na^+, and K^+. In soils with a low saturation pH, measurable amounts of Fe and Al may be present. Determination of soluble cations is used to obtain the relations between total cation concentration and other properties of saline solutions such as electrical conductivity and osmotic pressure (U.S. Salinity Laboratory Staff, 1954). The relative concentrations of the various cations in the soil-water extracts also provide information on the composition of the exchangeable cations in the soil. Complete analyses of the soluble ions provide a means to determine total salt content of the soils and salt content at field moisture conditions.

2. SUMMARY OF METHOD

The saturation extract from procedure 8A3a is diluted with an ionization suppressant ($LaCl_3$). The analytes are measured by an atomic absorption spectrophotometer (AA). The data are automatically recorded by a microcomputer and printer. The saturation extracted cations, Ca^{2+}, Mg^{2+}, Na^+, and K^+, are reported in meq L^{-1} in procedures 6N1b, 6O1b, 6P1b, and 6Q1b, respectively.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the analysis of these cations. These interferences vary in importance, depending upon the particular analyte selected. See the Appendix X, Atomic Absorption Spectroscopy, for an explanation of these interferences.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity

5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell

5.3 Atomic absorption spectrophotometer (AA), model 5000, Perkin-Elmer Corp., Norwalk, CT

5.4 Automatic burner control, model 5000, Perkin-Elmer Corp., Norwalk, CT

5.5 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

5.6 Dot matrix printer, P-132, Interdigital Data Systems,Inc.

5.7 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.8 Digital diluter/dispenser, MicroLab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.9 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.10 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.11 Containers, polypropylene

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CALCIUM, MAGNESIUM, SODIUM AND POTASSIUM
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PERKIN-ELMER AA 5000
(6N1b, 6O1b, 6P1b, and 6Q1b)

6. REAGENTS
6.1 Distilled deionized (DDI) water
6.2 Hydrochloric acid (HCl), concentrated 12 *N*
6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.
6.4 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.
6.5 NH_4OH, reagent grade, sp gr 0.90
6.6 Glacial acetic acid, 99.5%
6.7 Primary stock mixed standards solution (PSMSS). Dissolve 0.8759 g of oven-dry reagent grade calcium carbonate ($CaCO_3$) in a minimum of volume of 1:1 HCl:DDI. Add 0.2127 g of clean Mg ribbon dissolved in 1:1 HCl. Add 1.0956 g of dry reagent grade sodium chloride (NaCl) and 0.1864 g of dry reagent grade KCl. Transfer to a 250-mL volumetric and bring to volume with 1% HCl solution. Resulting solution contains 70 meq L^{-1} (1403 ppm) Ca; 70 meq L^{-1} (851 ppm) Mg; 75 meq L^{-1} (1724 ppm) Na; 10 meq L^{-1} (391 ppm) K. Store in a polypropylene container.
6.8 NH_4OAc solution, 1.0 *N*, pH 7.0, reagent blank. Mix 57 mL of glacial acetic acid in 600 mL DDI water. While stirring, carefully add 68 mL concentrated of NH_4OH. Cool and adjust pH to 7.0 using NH_4OH or acetic acid. Dilute to 1 L with DDI water. The NH_4OAc solution is used for extraction of cations (procedure 5A8c).
6.9 Working stock mixed standards solution (WSMSS).   Dilute 20 mL of the PSMSS with 80 mL DDI water (1:5). Resulting solution contains 14 meq L^{-1} (281 ppm) Ca; 14 meq L^{-1} (170 ppm) Mg; 15 meq L^{-1} (345 ppm Na); 2 meq L^{-1} (78 ppm) K. Store in a polypropylene container.
6.10 Stock lanthanum ionization suppressant solution, 65,000 ppm. Wet 152.4 g of lanthanum oxide (La_2O_3) with 100 mL DDI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La_2O_3. Cooling the solution is necessary. Dilute to 2 L with DDI water. Filter solution. Store in polypropylene container.
6.11 Lanthanum ionization suppressant solution, 6500 ppm. Dilute 200 mL of stock lanthanum ionization suppressant solution with 1800 mL of DDI water (1:10). Store in polypropylene container.
6.12 Dilute calibration mixed standards solution (DCMSS). Dilute 1 part of the WSMSS with 39 parts of the lanthanum solution (1:40). Resulting solution contains 0.35 meq L^{-1} (7 ppm) Ca; 0.35 meq L^{-1} (4 ppm) Mg; 0.375 meq L^{-1} (9 ppm) Na; 0.05 meq L^{-1} (2 ppm) K. Store in polypropylene container.
6.13 Dilute calibration reagent blank solution (DCRBS). Dilute 1 part of DDI water with 39 parts of the lanthanum solution (1:40). Store in polypropylene container.
6.14 Compressed air with water and oil traps.
6.16 Acetylene gas, purity 99.6%.

7. PROCEDURE

Dilution of Sample Extracts and Standards
7.1 The 10-mL syringe is for diluent (lanthanum ionization suppressant solution). The 1-mL syringe is for   saturation sample extracts (procedure 8A3a), calibration reagent blanks, and calibration standards. Set the digital diluter at 1:40 dilution for saturation sample extracts, reagent blanks, and calibration standards as follows:

7.2 Dilute 1 part saturation sample extract with 39 parts of lanthanum ionization suppressant solution (1:40 dilution).

7.3 Dilute 1 part WSMSS with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This dilution is the DCMSS. Refer to reagents section.

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CALCIUM, MAGNESIUM, SODIUM AND POTASSIUM
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PERKIN-ELMER AA 5000
(6N1b, 6O1b, 6P1b, and 6Q1b)

7.4 Dilute 1 part DDI water with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This dilution is the DCRBS. Refer to reagents section.

7.5 Dispense the diluted solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration

7.6 Use the DCRBS and the DCMSS to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

AA Set-up and Operation

7.7 Refer to the Appendix XI, Atomic Absorption, and manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc. (meq L^{-1})	Burner & angle	Wavelength (nm)	Slit (mm)	Fuel/Oxidant (C_2H_2/Air)
Ca	14.00	50 cm @ 0°	422.7	0.7	10/25
Mg	14.00	50 cm @ 30°	285.2	0.7	10/25
K	2.00	50 cm @ 0°	766.5	1.4	10/25
Na	15.00	50 cm @ 30°	589.0	0.4	10/25

7.8 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.9 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with the lanthanum ionization suppressant solution (1:40 dilution).

7.10 Analyze one quality control check sample for every 48 samples.

7.11 The instrument readings are usually programmed in meq L^{-1}. Record analyte readings to 0.01 meq L^{-1}.

8. CALCULATIONS

8.1 The instrument readings are the analyte concentration (meq L^{-1} cation) in undiluted extract. Use these values and dilution ratio (if any) and calculate the analyte concentration in meq L^{-1} cation.

Analyte Concentration in Soil (meq L^{-1}) = Analyte AA reading (meq L^{-1}) x Dilution ratio (if any)

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9. REPORT

Report the saturation extraction cations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ in units of meq L^{-1} to the nearest 0.1 meq L^{-1}.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM AND POTASSIUM
(6N, 6O, 6P, and 6Q)
SATURATION EXTRACTION
(6N1, 6O1, 6P1, and 6Q1)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE AA 4000
(6N1c, 6O1c, 6P1c, and 6Q1c)

1. APPLICATION

The commonly determined soluble cations are Ca^{2+}, Mg^{2+}, Na^+, and K^+. In soils with a low saturation pH, measurable amounts of Fe and Al may be present. Determination of soluble cations is used to obtain the relations between total cation concentration and other properties of saline solutions such as electrical conductivity and osmotic pressure (U.S. Salinity Laboratory Staff, 1954). The relative concentrations of the various cations in the soil-water extracts also provide information on the composition of the exchangeable cations in the soil. Complete analyses of the soluble ions provide a means to determine total salt content of the soils and salt content at field moisture conditions.

2. SUMMARY OF METHOD

The saturation extract from procedure 8A3a is diluted with an ionization suppressant ($LaC1_3$). The analytes are measured by an atomic absorption spectrophotometer (AA). The data are automatically recorded by a microcomputer and printer. The saturation extracted cations, Ca^{2+}, Mg^{2+}, Na^+, and K^+, are reported in meq L^{-1} in procedures 6N1c, 6O1c, 6P1c, and 6Q1c, respectively.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the analysis of these cations. These interferences vary in importance, depending upon the particular analyte selected. See the Appendix X, Atomic Absorption Spectroscopy, for an explanation of these interferences.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity

5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell

5.3 Atomic absorption spectrophotometer (AA), Smith-Hieftje Model 4000, Thermo Jarrell Ash Corp., Franklin, MA

5.4 Autosampler, Model 150, Thermo Jarrell Ash Corp., Franklin, MA

5.5 ThermoSpec software, Version 3.01, Enable 4.0, DOS 5.0, Thermo Jarrell Ash Corp., Franklin, MA

5.6 Computer, CUi Advantage 486, Thermo Jarrell Ash Corp., Franklin, MA

5.7 Printer, NEC Pinwriter P3200

5.8 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.9 Digital diluter/dispenser, MicroLab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.10 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM AND POTASSIUM
(6N, 6O, 6P, and 6Q)
SATURATION EXTRACTION
(6N1, 6O1, 6P1, and 6Q1)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE AA 4000
(6N1c, 6O1c, 6P1c, and 6Q1c)

5.11 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.12 Containers, polypropylene

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.5 NH_4OH, reagent grade, sp gr 0.90

6.6 Glacial acetic acid, 99.5%

6.7 Primary stock mixed standards solution (PSMSS). Dissolve 0.8759 g of oven-dry reagent grade calcium carbonate ($CaCO_3$) in a minimum of volume of 1:1 HCl:DDI. Add 0.2127 g of clean Mg ribbon dissolved in 1:1 HCl. Add 1.0956 g of dry reagent grade sodium chloride (NaCl) and 0.1864 g of dry reagent grade KCl. Transfer to a 250-mL volumetric and bring to volume with 1% HCl solution. Resulting solution contains 70 meq L^{-1} (1403 ppm) Ca; 70 meq L^{-1} (851 ppm) Mg; 75 meq L^{-1} (1724 ppm) Na; 10 meq L^{-1} (391 ppm) K. Store in a polypropylene container.

6.8 NH_4OAc solution, 1.0 *N*, pH 7.0, reagent blank. Mix 57 mL of glacial acetic acid in 600 mL DDI water. While stirring, carefully add 68 mL concentrated of NH_4OH. Cool and adjust pH to 7.0 using NH_4OH or acetic acid. Dilute to 1 L with DDI water. The NH_4OAc solution is used for extraction of cations (procedure 5A8c).

6.9 Working stock mixed standards solution (WSMSS). Dilute 20 mL of the PSMSS with 80 mL DDI water (1:5). Resulting solution contains 14 meq L^{-1} (281 ppm) Ca; 14 meq L^{-1} (170 ppm) Mg; 15 meq L^{-1} (345 ppm Na); 2 meq L^{-1} (78 ppm) K. Store in a polypropylene container.

6.10 Stock lanthanum ionization suppressant solution, 65,000 ppm. Wet 152.4 g of lanthanum oxide (La_2O_3) with 100 mL DDI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La_2O_3. Cooling the solution is necessary. Dilute to 2 L with DDI water. Filter solution. Store in polypropylene container.

6.11 Lanthanum ionization suppressant solution, 6500 ppm. Dilute 200 mL of stock lanthanum ionization suppressant solution with 1800 mL of DDI water (1:10). Store in polypropylene container.

6.12 Dilute calibration mixed standards solution (DCMSS). Dilute 1 part of the WSMSS with 39 parts of the lanthanum solution (1:40). Resulting solution contains 0.35 meq L^{-1} (7 ppm) Ca; 0.35 meq L^{-1} (4 ppm) Mg; 0.375 meq L^{-1} (9 ppm) Na; 0.05 meq L^{-1} (2 ppm) K. Store in polypropylene container.

6.13 Dilute calibration reagent blank solution (DCRBS). Dilute 1 part of DDI water with 39 parts of the lanthanum solution (1:40). Store in polypropylene container.

6.14 Compressed air with water and oil traps.

6.16 Acetylene gas, purity 99.6%.

7. PROCEDURE

Dilution of Sample Extracts and Standards

7.1 The 10-mL syringe is for diluent (lanthanum ionization suppressant solution). The 1-mL syringe is for saturation sample extracts (procedure 8A3a), calibration reagent blanks, and calibration standards. Set the digital diluter at 1:40 dilution for saturation sample extracts, reagent blanks, and calibration standards as follows:

CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM AND POTASSIUM
(6N, 6O, 6P, and 6Q)
SATURATION EXTRACTION
(6N1, 6O1, 6P1, and 6Q1)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE AA 4000
(6N1c, 6O1c, 6P1c, and 6Q1c)

7.2 Dilute 1 part saturation sample extract with 39 parts of lanthanum ionization suppressant solution (1:40 dilution).

7.3 Dilute 1 part WSMSS with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This dilution is the DCMSS. Refer to reagents section.

7.4 Dilute 1 part DDI water with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This dilution is the DCRBS. Refer to reagents section.

7.5 Dispense the diluted solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration

7.6 Use the DCRBS and the DCMSS to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

AA Set-up and Operation

7.7 Refer to the Appendix XII, Atomic Absorption, and manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc. (meq L^{-1})	Burner & angle	Wavelength (nm)	Slit (mm)	Fuel/Oxidant (C_2H_2/Air)
Ca	14.00	50 cm @ 0°	422.7	0.7	4/16
Mg	14.00	50 cm @ 30°	285.2	0.7	4/16
K	2.00	50 cm @ 0°	766.5	1.4	4/16
Na	15.00	50 cm @ 30°	589.0	0.4	4/16

7.8 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.9 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with the lanthanum ionization suppressant solution (1:40 dilution).

7.10 Analyze one quality control check sample for every 48 samples.

7.11 The instrument readings are usually programmed in meq L^{-1}. Record analyte readings to 0.01 meq L^{-1}.

**CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM AND POTASSIUM
(6N, 6O, 6P, and 6Q)
SATURATION EXTRACTION
(6N1, 6O1, 6P1, and 6Q1)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE AA 4000
(6N1c, 6O1c, 6P1c, and 6Q1c)**

8. CALCULATIONS

8.1 The instrument readings are the analyte concentration (meq L^{-1} cation) in undiluted extract. Use these values and dilution ratio (if any) and calculate the analyte concentration in meq L^{-1} cation.

Analyte Concentration in Soil (meq L^{-1}) = Analyte AA reading (meq L^{-1}) x Dilution ratio (if any)

9. REPORT
Report the saturation extraction cations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ in units of meq L^{-1} to the nearest 0.1 meq L^{-1}.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM
(6N, 6O, 6P, and 6Q)
NH$_4$OAC EXTRACTION
(6N2, 6O2, 6P2, and 6Q2)
ATOMIC ABSORPTION
PERKIN-ELMER AA 5000
(6N2e, 6O2d, 6P2b, and 6Q2b)

1. APPLICATION

The extractable bases (Ca^{2+}, Mg^{2+}, Na$^+$, and K$^+$) from the NH$_4$OAC extraction (procedure 5A8c) are generally assumed to be those exchangeable bases on the cation exchange sites of the soil. The abundance of these cations usually occurs in the sequence of Ca^{2+} > Mg^{2+} > K$^+$ > Na$^+$. Deviation from this usual order signals that some factor or factors, e.g., free CaCO$_3$ or gypsum, serpentine (high Mg^{2+}), or natric material (high Na$^+$), have altered the soil chemistry. The most doubtful cation extractions with this method are Ca^{2+} in the presence of free CaCO$_3$ or gypsum and K$^+$ in soils that are dominated by mica or vermiculite (Thomas, 1982).

2. SUMMARY OF METHOD

The NH$_4$OAc extract from procedure 5A8c is diluted with an ionization suppressant (LaC1$_3$). The analytes are measured by an atomic absorption spectrophotometer (AA). The analyte is measured by absorption of the light from a hollow cathode lamp. An automatic sample changer is used to aspirate a series of samples. The AA converts absorption to analyte concentration. The data are automatically recorded by a microcomputer and printer. The NH$_4$OAc extracted cations, Ca^{2+}, Mg^{2+}, Na$^+$, and K$^+$, are reported in meq 100 g^{-1} oven-dry soil in procedures 6N2e, 6O2d, 6P2b, and 6Q2b, respectively.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the analyses of these cations. These interferences vary in importance, depending upon the particular analyte selectedtheı˝-0dCp depex X, An atomAs absorptiSn specscopy.g.oularOAcplar orption of s The

2. AFETYCES

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CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM
(6N, 6O, 6P, and 6Q)
NH$_4$OAC EXTRACTION
(6N2, 6O2, 6P2, and 6Q2)
ATOMIC ABSORPTION
PERKIN-ELMER AA 5000
(6N2e, 6O2d, 6P2b, and 6Q2b)

5.10 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.11 Containers, polypropylene

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.5 NH$_4$OH, reagent-grade, sp gr 0.90

6.6 Glacial acetic acid, 99.5%

6.7 Primary stock mixed standards solution (PSMSS). Dissolve 0.8759 g of ovendry reagent grade calcium carbonate (CaCO$_3$) in a minimum of volume of 1:1 concentrated HCl:DDI water. Add 0.2127 g of clean Mg ribbon dissolved in 1:1 HCl. Add 1.0956 g of dry reagent grade sodium chloride (NaCl) and 0.1864 g of dry reagent grade KCl. Transfer to a 250-mL volumetric and bring to volume with 1% HCl solution. Resulting solution contains 70 meq L^{-1} (1403 ppm) Ca; 70 meq L^{-1} (851 ppm) Mg; 75 meq L^{-1} (1724 ppm) Na; 10 meq L^{-1} (391 ppm) K. Store in a polypropylene container.

6.8 NH$_4$OAc solution, 1.0 *N*, pH 7.0, reagent blank. Mix 57 mL of glacial acetic acid in 600 mL of DDI water. While stirring, carefully add 68 mL of concentrated NH$_4$OH. Cool and adjust pH to 7.0 using NH$_4$OH or acetic acid. Dilute to 1 L with DDI water. The NH$_4$OAc solution is used for extraction of cations (procedure 5A8c).

6.9 Working stock mixed standards solution (WSMSS). Dilute 20 mL of the PSMSS with 80 mL DDI water (1:5). Resulting solution contains 14 meq L^{-1} (281 ppm) Ca; 14 meq L^{-1} (170 ppm) Mg; 15 meq L^{-1} (345 ppm Na); 2 meq L^{-1} (78 ppm) K. Store in a polypropylene container.

6.10 Stock lanthanum ionization suppressant solution, 65,000 ppm. Wet 152.4 g lanthanum oxide (La$_2$O$_3$) with 100 mL DDI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La$_2$O$_3$. Cooling the solution is necessary. Dilute to 2 L with DDI water. Filter solution. Store in polypropylene container.

6.11 Lanthanum ionization suppressant solution, 6500 ppm. Dilute 200 mL of stock lanthanum ionization suppressant solution with 1800 mL of DDI water (1:10). Store in polypropylene container.

6.12 Dilute calibration mixed standards solution (DCMSS). Dilute 1 part of the WSMSS with 39 parts of the lanthanum solution (1:40). Resulting solution contains 0.35 meq L^{-1} (7 ppm) Ca; 0.35 meq L^{-1} (4 ppm) Mg; 0.375 meq L^{-1} (9 ppm) Na; 0.05 meq L^{-1} (2 ppm) K. Store in polypropylene container.

6.13 Dilute calibration reagent blank solution (DCRBS). Dilute 1 part of DDI water with 39 parts of the lanthanum solution (1:40). Store in polypropylene container.

6.14 Compressed air with water and oil traps.

6.15 Acetylene gas, purity 99.6%.

7. PROCEDURE

Dilution of Sample Extracts and Standards

7.1 The 10-mL syringe is for diluent (lanthanum ionization suppressant solution). The 1-mL syringe is for NH$_4$OAc sample extracts (procedure 5A8c), calibration reagent blanks, and calibration standards. Set the digital diluter at a 1:40 dilution for the NH$_4$OAc sample extracts, reagent blanks, and calibration standards as follows:

CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM
(6N, 6O, 6P, and 6Q)
NH₄OAC EXTRACTION
(6N2, 6O2, 6P2, and 6Q2)
ATOMIC ABSORPTION
PERKIN-ELMER AA 5000
(6N2e, 6O2d, 6P2b, and 6Q2b)

7.2 Dilute 1 part NH₄OAc sample extract with 39 parts of lanthanum ionization suppressant solution (1:40 dilution).

7.3 Dilute 1 part WSMSS with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This is the DCMSS. Refer to reagents section.

7.4 Dilute 1 part DDI water with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This is the DCRBS. Refer to reagents section.

7.5 Dispense the diluted solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration
7.6 Use the DCRBS and the DCMSS to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

AA Set-up and Operation
7.7 Refer to the Appendix XI, Atomic Absorption, and manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc. (meq L^{-1})	Burner & angle	Wavelength (nm)	Slit (mm)	Fuel/Oxidant (C_2H_2/Air)
Ca	14.00	50 cm @ 0°	422.7	0.7	10/25
Mg	14.00	50 cm @ 30°	285.2	0.7	10/25
K	2.00	50 cm @ 0°	766.5	1.4	10/25
Na	15.00	50 cm @ 30°	589.0	0.4	10/25

7.8 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.9 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with the lanthanum ionization suppressant solution (1:40 dilution).

7.10 Analyze one quality control check sample for every 48 samples.

7.11 The instrument readings are usually programmed in meq L^{-1}. Record analyte readings to 0.01 meq L^{-1}.

CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM
(6N, 6O, 6P, and 6Q)
NH$_4$OAC EXTRACTION
(6N2, 6O2, 6P2, and 6Q2)
ATOMIC ABSORPTION
PERKIN-ELMER AA 5000
(6N2e, 6O2d, 6P2b, and 6Q2b)

8. CALCULATIONS

8.1 The instrument readings are the analyte concentration (meq L^{-1} cation) in undiluted extract. Use these values and calculate the analyte concentration on an ovendry soil basis (meq 100 g^{-1}).

$$\text{Analyte Concentration in Soil (meq 100 g}^{-1}) = \frac{A \times B \times C \times E}{10 \times D}$$

where:

A = Analyte concentration in extract (meq L^{-1})

B = Extract volume (mL). Refer to procedure 5A8c.

$$= \frac{\text{Weight of extract in syringe (g)}}{\text{Density of 1 } N \text{ NH}_4\text{OAc (1.0124 g cm}^{-3})}$$

C = Dilution ratio, if needed

D = Soil sample weight (g)

E = AD/OD ratio (procedure 4B5)

9. REPORT
Report the extractable Ca^{2+}, Mg^{2+}, Na$^+$, and K$^+$ in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq 100 g^{-1}.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples. The number of observations, mean, standard deviation, and C.V. for the quality control check sample are as follows:

Cation	n	Mean	Std. Dev.	C.V.
Ca	85	18.4	0.95	5.1%
Mg	84	7.5	0.23	3.1%
K	81	2.04	0.10	4.8%

11. REFERENCES
Thomas, G.W. 1982. Exchangeable cations. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:159-165.

CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM
(6N, 6O, 6P, and 6Q)
NH$_4$OAC EXTRACTION
(6N2, 6O2, 6P2, and 6Q2)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE 4000
(6N2f, 6O2e, 6P2c, and 6Q2c)

1. APPLICATION

The extractable bases (Ca^{2+}, Mg^{2+}, Na$^+$, and K$^+$) from the NH$_4$OAC extraction (procedure 5A8c) are generally assumed to be those exchangeable bases on the cation exchange sites of the soil. The abundance of these cations usually occurs in the sequence of Ca^{2+} > Mg^{2+} > K$^+$ > Na$^+$. Deviation from this usual order signals that some factor or factors, e.g., free CaCO$_3$ or gypsum, serpentine (high Mg^{2+}), or natric material (high Na$^+$), have altered the soil chemistry. The most doubtful cation extractions with this method are Ca^{2+} in the presence of free CaCO$_3$ or gypsum and K$^+$ in soils that are dominated by mica or vermiculite (Thomas, 1982).

2. SUMMARY OF METHOD

The NH$_4$OAc extract from procedure 5A8c is diluted with an ionization suppressant (LaC1$_3$). The analytes are measured by an atomic absorption spectrophotometer (AA). The data are automatically recorded by a microcomputer and printer. The NH$_4$OAc extracted cations, Ca^{2+}, Mg^{2+}, Na$^+$, and K$^+$, are reported in meq 100 g^{-1} oven-dry soil in procedures 6N2f, 6O2e, 6P2c, and 6Q2c, respectively.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected. See the Appendix X, Atomic Absorption Spectroscopy, for an explanation of these interferences.

4. SAFETY

Wear protective clothing and safety glasses. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts.

Follow standard laboratory procedures when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity

5.2 Filter paper, pre-pleated, 185-mm diameter, Schleicher and Schuell

5.3 Atomic absorption spectrophotometer (AA), Smith-Hieftje Model 4000, Thermo Jarrell Ash Corp., Franklin, MA

5.4 Autosampler, Model 150, Thermo Jarrell Ash Corp., Franklin, MA

5.5 ThermoSpec software, Version 3.01, Enable 4.0, DOS 5.0, Thermo Jarrell Ash Corp., Franklin, MA

5.6 Computer, CUi Advantage 486, Thermo Jarrell Ash Corp., Franklin, MA

5.7 Printer, NEC Pinwriter P3200

5.8 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA

5.9 Digital diluter/dispenser, MicroLab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.10 Syringes, 10000 and 1000 µL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM
(6N, 6O, 6P, and 6Q)
NH$_4$OAC EXTRACTION
(6N2, 6O2, 6P2, and 6Q2)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE 4000
(6N2f, 6O2e, 6P2c, and 6Q2c)

5.11 Test tubes, 15-mL, 16 mm x 100, for sample dilution and sample changer, Curtin Matheson Scientific, Inc., Houston, TX

5.12 Containers, polypropylene

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of concentrated HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of concentrated HCl to 1 L with DDI water.

6.5 NH$_4$OH, reagent-grade, sp gr 0.90

6.6 Glacial acetic acid, 99.5%

6.7 Primary stock mixed standards solution (PSMSS). Dissolve 0.8759 g of ovendry reagent grade calcium carbonate (CaCO$_3$) in a minimum of volume of 1:1 concentrated HCl:DDI water. Add 0.2127 g of clean Mg ribbon dissolved in 1:1 HCl. Add 1.0956 g of dry reagent grade sodium chloride (NaCl) and 0.1864 g of dry reagent grade KCl. Transfer to a 250-mL volumetric and bring to volume with 1% HCl solution. Resulting solution contains 70 meq L^{-1} (1403 ppm) Ca; 70 meq L^{-1} (851 ppm) Mg; 75 meq L^{-1} (1724 ppm) Na; 10 meq L^{-1} (391 ppm) K. Store in a polypropylene container.

6.8 NH$_4$OAc solution, 1.0 *N*, pH 7.0, reagent blank. Mix 57 mL of glacial acetic acid in 600 mL of DDI water. While stirring, carefully add 68 mL of concentrated NH$_4$OH. Cool and adjust pH to 7.0 using NH$_4$OH or acetic acid. Dilute to 1 L with DDI water. The NH$_4$OAc solution is used for extraction of cations (procedure 5A8c).

6.9 Working stock mixed standards solution (WSMSS). Dilute 20 mL of the PSMSS with 80 mL DDI water (1:5). Resulting solution contains 14 meq L^{-1} (281 ppm) Ca; 14 meq L^{-1} (170 ppm) Mg; 15 meq L^{-1} (345 ppm Na); 2 meq L^{-1} (78 ppm) K. Store in a polypropylene container.

6.10 Stock lanthanum ionization suppressant solution, 65,000 ppm. Wet 152.4 g lanthanum oxide (La$_2$O$_3$) with 100 mL DDI water. Slowly and cautiously add 500 mL of 6 *N* HCl to dissolve the La$_2$O$_3$. Cooling the solution is necessary. Dilute to 2 L with DDI water. Filter solution. Store in polypropylene container.

6.11 Lanthanum ionization suppressant solution, 6500 ppm. Dilute 200 mL of stock lanthanum ionization suppressant solution with 1800 mL of DDI water (1:10). Store in polypropylene container.

6.12 Dilute calibration mixed standards solution (DCMSS). Dilute 1 part of the WSMSS with 39 parts of the lanthanum solution (1:40). Resulting solution contains 0.35 meq L^{-1} (7 ppm) Ca; 0.35 meq L^{-1} (4 ppm) Mg; 0.375 meq L^{-1} (9 ppm) Na; 0.05 meq L^{-1} (2 ppm) K. Store in polypropylene container.

6.13 Dilute calibration reagent blank solution (DCRBS). Dilute 1 part of DDI water with 39 parts of the lanthanum solution (1:40). Store in polypropylene container.

6.14 Compressed air with water and oil traps.

6.15 Acetylene gas, purity 99.6%.

7. PROCEDURE

Dilution of Sample Extracts and Standards

7.1 The 10-mL syringe is for diluent (lanthanum ionization suppressant solution). The 1-mL syringe is for NH$_4$OAc sample extracts (procedure 5A8c), calibration reagent blanks, and calibration standards. Set the digital diluter at a 1:40 dilution for the NH$_4$OAc sample extracts, reagent blanks, and calibration standards as follows:

CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM
(6N, 6O, 6P, and 6Q)
NH₄OAC EXTRACTION
(6N2, 6O2, 6P2, and 6Q2)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE 4000
(6N2f, 6O2e, 6P2c, and 6Q2c)

7.2 Dilute 1 part NH₄OAc sample extract with 39 parts of lanthanum ionization suppressant solution (1:40 dilution).

7.3 Dilute 1 part WSMSS with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This is the DCMSS. Refer to reagents section.

7.4 Dilute 1 part DDI water with 39 parts of lanthanum ionization suppressant solution (1:40 dilution). This is the DCRBS. Refer to reagents section.

7.5 Dispense the diluted solutions into test tubes which have been placed in the sample holders of the sample changer.

AA Calibration
7.6 Use the DCRBS and the DCMSS to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. Perform one calibration, i.e., blank plus standard, for every 12 samples.

AA Set-up and Operation
7.7 Refer to the Appendix XII, Atomic Absorption, and manufacturer's manual for operation of the AA. The following are only very general guidelines for instrument conditions for the various analytes.

Analyte	Conc. (meq L^{-1})	Burner & angle	Wavelength (nm)	Slit (mm)	Fuel/Oxidant (C₂H₂/Air)
Ca	14.00	50 cm @ 0°	422.7	0.7	10/25
Mg	14.00	50 cm @ 30°	285.2	0.7	10/25
K	2.00	50 cm @ 0°	766.5	1.4	10/25
Na	15.00	50 cm @ 30°	589.0	0.4	10/25

7.8 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.9 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with the lanthanum ionization suppressant solution (1:40 dilution).

7.10 Analyze one quality control check sample for every 48 samples.

7.11 The instrument readings are usually programmed in meq L^{-1}. Record analyte readings to 0.01 meq L^{-1}.

CHEMICAL ANALYSES
CALCIUM, MAGNESIUM, SODIUM, AND POTASSIUM
(6N, 6O, 6P, and 6Q)
NH$_4$OAC EXTRACTION
(6N2, 6O2, 6P2, and 6Q2)
ATOMIC ABSORPTION
THERMO JARRELL ASH, SMITH-HIEFTJE 4000
(6N2f, 6O2e, 6P2c, and 6Q2c)

8. CALCULATIONS

8.1 The instrument readings are the analyte concentration (meq L^{-1} cation) in undiluted extract. Use these values and calculate the analyte concentration on an ovendry soil basis (meq 100 g^{-1}).

```
Analyte Concentration in Soil (meq 100 g⁻¹) = A x B x C x E
                                              _____
                                                   10 x D
```

where:
A = Analyte concentration in extract (meq L^{-1})
B = Extract volume (mL). Refer to procedure 5A8c.

```
      Weight of extract in syringe (g)
=  _____
   Density of 1 N NH₄OAc (1.0124 g cm⁻³)
```

C = Dilution ratio, if needed
D = Soil sample weight (g)
E = AD/OD ratio (procedure 4B5)

9. REPORT
Report the extractable Ca^{2+}, Mg^{2+}, Na$^+$, and K$^+$ in units of meq 100 g^{-1} of oven-dry soil to the nearest 0.1 meq 100 g^{-1}.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples.

11. REFERENCES
Thomas, G.W. 1982. Exchangeable cations. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:159-165.

CHEMICAL ANALYSES
TOTAL SULFUR (6R)
SO$_2$ EVOLUTION, INFRARED (6R3)
LECO SC-444 SULFUR ANALYZER (6R3c)

1. APPLICATION

Organic and inorganic S forms are found in soils, with the organic S fraction accounting for >95% of the total S in most soils from humid and semi-humid (Tabatabai, 1982). Mineralization of organic S and its conversion to sulfate by chemical and biological activity may serve as a source of plant available S. Total S typically ranges from 0.01 to 0.05% in most mineral soils. In organic soils, total S may be >0.05%.

In well-drained, well-aerated soils, most of the inorganic S normally occurs as sulfate. In marine tidal flats, other anaerobic marine sediments, and mine spoils, there are usually large amounts of reduced S compounds which oxidize to sulfuric acid upon exposure to the air. In arid regions, significant amounts of inorganic S are found as sulfates such gypsum and barite.

The typical use of total S is as an index of the total reserves of this element, which may be converted to plant available S. The SSL uses the combustion technique (LECO sulfur analyzer) for analysis of total S (procedure 6R3b). Extractable sulfate S (SO$_4^2$-S) is an index of readily plant-available S. Reagents that have been used for measuring SO$_4^2$-S include water, hot water, ammonium acetate, sodium carbonate and other carbonates, ammonium chloride and other chlorides, potassium phosphate and other phosphates, and ammonium fluoride (Bray-1). Extractable SO$_4^2$-S does not include the labile fraction of soil organic S that is mineralized during the growing season (Tabatabai, 1982). Extraction reagents for organic S include hydrogen peroxide, sodium bicarbonate, sodium hydroxide, sodium oxalate, sodium peroxide, and sodium pyrophosphate. There other methods available for determination of soil S, especially for total S and SO$_4^2$-S. The investigator may refer to the review by Beaton et al. (1968).

2. SUMMARY OF METHOD

A fine-ground (<80-mesh) soil sample is oxidized at high temperature. The gases released are scrubbed, and the SO$_2$ in the combustion gases are measured using an infrared detector. Percent S is reported on an oven-dry soil basis.

3. INTERFERENCES

No significant interferences are known to affect the oxidizable S measurement.

4. SAFETY

Wear protective clothing and safety glasses. Magnesium perchlorate may form explosive mixtures. Magnesium perchlorate may contain traces of perchloric acid, which remain from manufacturer's operations. This acid is anhydrous because of the strong desiccating capability of the salt. Avoid prolonged contact with oxidizable material or material capable of forming unstable perchlorate esters or salts. Remove magnesium perchlorate by using an excess of water to thoroughly dilute the material.

The use of high temperatures in the oxidation of samples requires that extreme caution be used to prevent burns and fires. Follow standard laboratory procedures when handling compressed gases. Oxygen is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the sulfur analyzer.

5. EQUIPMENT

5.1 Sulfur analyzer, Leco Model SC-444, Sulfur and Carbon Analyzers, Leco Corp., St. Joseph, MI
5.2 Combustion boats, part no. 529-203, Leco Corp., St. Joseph, MI
5.3 Single-stage regulator, Oxygen Service, Part No. E11-W-N115BOX, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105
5.4 Electronic balance, ±1-mg sensitivity

CHEMICAL ANALYSES
TOTAL SULFUR (6R)
SO$_2$ EVOLUTION, INFRARED (6R3)
LECO SC-444 SULFUR ANALYZER (6R3c)

6. REAGENTS

6.1 Anhydrone, anhydrous magnesium perchlorate, granular

6.2 Glass wool

6.3 Compressed oxygen, >99.5% @ 30 psi

6.4 Calcium carbonate, $CaCO_3$, reagent grade.

6.5 Solid/Powder Combustion Controller, part no. 501-426, Leco Corp., St. Joseph, MI

6.6 Soil Calibration Sample, part no. 502-062, Leco Corp., St. Joseph, MI

6.7 Sulfur Calibration Sample, part no. 502-648, Leco Corp., St. Joseph, MI

7. PROCEDURE

7.1 Use a fine-ground 80-mesh, air-dry soil

7.2 Prepare instrument as outlined in the operator's instruction manual (Leco, 1994; Leco, 1993) and Appendix V.

7.3 Methods are created with the method menu and stored in the instrument memory. System parameters are set as follows:

Furnace operating temperature: 1450°C
Lance delay: 20 s
Analysis time settings: 120 to 300 s
Comparator level settings: 0.3%

7.3 Condition instrument by analyzing a few soil samples, until readings are stable.

7.4 Calibrate instrument by analyzing at least three replicates of each calibration standard. Use the soil calibration standard for samples with less than 0.01 percent TS and the sulfur standard for samples with more than 0.01 percent TS. Weigh standards in a range from 0.2 to 0.5 g.

7.5 Load samples on autoload rack, place in the analyzer, and press analyze key.

7.6 Weigh 0.2 to 0.5 g sample in a tared combustion boat. Add approximately 1 g of solid/powder combustion controller to sample.

7.7 Load samples on autoload rack, place in the analyzer, and press analyze key.

7.9 Repack the reagent (anhydrous magnesium perchlorate) tubes whenever the reagent becomes caked or moist or the warning alarm displays.

8. CALCULATIONS

S (%) = S$_i$ x AD/OD

where:
S (%)   = S (%) on oven-dry basis
S$_i$ = S (%) instrument
AD/OD   = air-dry/oven-dry ratio (procedure 4B5)

9. REPORT

Report total S as a percentage of oven-dry weight to the nearest 0.1%.

10. PRECISION

Precision data are not available for this procedure. A quality control check sample is run in every batch of 12 samples. A blank (crucible only) and a rerun of one of the 12 samples (unknowns) also are run in every batch. For 27 observations of the quality control check sample, the mean, standard deviation, and C.V. for total S are 0.57, 0.02, and 4.3%, respectively.

11. REFERENCES

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Tabatabai, M.A. 1982. Sulfur. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:501-538.

CHEMICAL ANALYSES
PHOSPHORUS (6S)

INTRODUCTION

Methods for determining soil P, i.e., the various plant available forms, have been essential to the development of knowledge about the nature and behavior of soil P. To characterize the P in the soil system requires the selection of an appropriate method of determination. This selection is influenced by many factors, e.g., objectives of study; soil properties; sample condition or environment; accuracy; and reproducibility (Olsen and Sommers, 1982).

Most soil P determinations have two phases, i.e., the preparation of a solution that contains the soil P or fraction thereof and the quantitative determination of P in the solution. The selected colorimetric method for P determination depends on the concentration of solution P; concentration of interfering substances in the solution to be analyzed; and the particular acid system involved in the analytical procedure (Sommers and Olsen, 1982).

The SSL determines Bray P-1 absorbed P (procedure 6S3); New Zealand P retention (procedure 6S4); and citrate extractable P (procedure 6S5). The Bray P-1 procedure is widely adopted as an index of available soil P. In *Soil Taxonomy*, the New Zealand P retention of soil material and the citrate extractable soil P are used as criterion for andic soil properties and for distinguishing between mollic and anthrophic epipedons, respectively (Soil Survey Staff, 1994).

REFERENCES

Olsen, S.R., and L.E. Sommers. 1982. In A.L. Page, R.H. Miller, and D.R. Kenney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy9:403-430.
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CHEMICAL ANALYSES
BRAY P-1 ABSORBED PHOSPHORUS (6S)
BAUSH AND LAUMB, SPECTROPHOTOMETER 20 (6S3)

1. APPLICATION

The Bray P-1 procedure is widely used as an index of available P in the soil. The selectivity of the Bray extractant is designed to remove the easily acid-soluble P, largely calcium phosphates, and a portion of the phosphates of Al and Fe (Bray and Kurtz, 1945; Olsen and Sommers, 1982). In general, this method has been most successful on acid soils (Bray and Kurtz, 1945; Olsen and Sommers, 1982).

2. SUMMARY OF METHOD

A 1-g soil sample is shaken with 10 mL of extracting solution for 15 min at 100 oscillations per min^{-1}. The solution is filtered. A 2-mL aliquot is transferred to a colorimetric tube to which 8-mL of ascorbic acid molybdate solution are added. The percent transmittance of the solution is read using a spectrophotometer. The Bray P-1 is reported in mg kg^{-1} (ppm) P.

3. INTERFERENCES

Many procedures may be used to determine P. Studies have shown that incomplete or excessive extraction of P to be the most significant contributor to interlaboratory variation. The Bray P-1 procedure is sensitive to the soil/extractant ratio, shaking rate, and time. This extraction uses the ascorbic acid-potassium antimonyl-tartrate-molybdate method. The Fiske-Subbarrow method is less sensitive but has a wider range before dilution is required (North Central Regional Publication No. 221, 1988). For calcareous soils, the Olsen method is preferred. An alternative procedure for calcareous soils is to use the Bray P-1 extracting solution at a 1:50 soil:solution ratio. This procedure has been shown to be satisfactory for some calcareous soils (North Central Regional Publication No. 221, 1988; Smith et al., 1957).

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of concentrated H_2SO_4 and HCl to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity
5.2 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 oscillations min^{-1}, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI
5.3 Spectrophotometer 20, Baush and Laumb
5.4 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 μL and 10 mL
5.5 Cuvettes, glass, 10 mL, 1-cm light path
5.5 Funnel, 60° angle, long stem, 50-mm diameter
5.7 Filter paper, quantitative, Whatman grade 2, 9-cm diameter
5.8 Erlenmeyer flasks, 50 mL
5.9 Centrifuge, high-speed, International Equipment Co., IECB-22M

6. REAGENTS

6.1 Distilled deionized (DDI) water
6.2 Hydrochloric acid (HCl), concentrated, 12 *N*
6.3 HCl, 1 *N*. Carefully add 83.33 mL of concentrated HCl to DDI water and dilute to 1-L volume.
6.4 Sulfuric acid (H_2SO_4), concentrated, 36 *N*
6.5 Bray No. 1 Extracting solution, 0.025 *N* HCl and 0.03 *N* NH_4F. Dissolve 8.88 g of NH_4F in 4 L DDI H_2O. Add 200 mL of 1.0 *N* HCl and dilute to 8 L with DDI water. The solution pH should be 2.6 ± 0.5. Store in a polyethylene bottle.

6.6 Stock standard P solution (SSPS), 100 ppm P. Add 0.2197 g of KH_2PO_4 in 25 mL of DDI water. Dilute to a final volume of 500 mL with extracting solution. Store in a refrigerator. Solution is stable to 1 yr.

6.7 Sulfuric-tartrate-molybdate solution (STMS). Dissolve 60 g of ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in 200 mL of boiling DDI water. Allow to cool to room temperature. Dissolve 1.455 g of antimony potassium tartrate (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6 \cdot 1/2H_2O)$ in the ammonium molybdate solution. Slowly and carefully add 700 mL of concentrated H_2SO_4. Cool and dilute to 1 L with DDI water. Store in the dark in the refrigerator.

6.8 Ascorbic acid solution. Dissolve 33.0 g of ascorbic acid in DDI water and dilute to 250 mL with DDI water. Store in the dark in the refrigerator.

6.9 Working ascorbic acid molybdate solution (WAMS). Prepare fresh each day. Mix 25 mL of STMS solution with 800 mL of DDI water. Add 10 mL of ascorbic acid solution and dilute to 1 L with DDI water.

6.10 Standard P calibration solutions (SPCS), 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0, 7.0, and 8.0 ppm. Dilute the SSPS with the extracting solution as follows: 0.2 ppm = 0.5:250; 0.5 ppm = 0.5:100; 1.0 ppm = 1:100; 2.0 ppm = 2:100; 3.0 ppm = 3:100; 4.0 ppm = 4:100; 5.0 ppm = 5:100; 6.0 ppm = 6:100; 7:0 ppm = 7:100; 8.0 ppm = 8:100.

7. PROCEDURE

7.1 Weigh 1.00 g of air-dry soil into a 50-mL Erlenmeyer flask.

7.2 Dispense 10.0 mL of extracting solution to flask.

7.3 Securely place the flask in the shaker. Shake for 15 min at 100 oscillations min^{-1} at room temperature (20°C).

7.4 Remove the sample from the shaker. Decant, filter, and collect extract.

7.5 Centrifuging or repeated filtering may be necessary to obtain clear extracts. Decant into 13-mL centrifuge tube and centrifuge at 10000 RPM for 10 min. Refer to Appendix XVIII for operation of the high-speed centrifuge.

7.6 Use the pipettor to transfer a 2-mL aliquot of the sample to a cuvette. Also transfer a 2-mL aliquot of each SPCS to a cuvette. Use a clean pipette tip for each sample and SPCS.

7.7 Dispense 8 mL of the WAMS to sample aliquot and to each SPCS (1:5 dilution).

7.8 The color reaction requires a minimum of 20 min before analyst records readings.

7.9 Set the spectrophotometer (red bulb) to read at 882 nm.

7.10 Set the 100% transmittance against the blank which has 8 mL of the WAMS solution and 2 mL of extracting solution.

8. CALCULATIONS

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., $T = P/P_o$ and is often expressed as a percentage, i.e., $\%T = P/P_o \times 100$. The absorbance of a solution is directly proportional to concentration and is defined by the equation, $A = -log_{10} T$. These relationships are derived from Beer's law.

Calibration Calculations

8.2 Use transmission of each SPCS to either construct a calibrated curve to plot P or use a least squares analysis to calculate P. The P is reported in ppm.

8.3 *Calibration Curve*: Plot the transmittance against the ppm P of each SPCS on semilog graph paper or convert to absorbances and plot on linear graph paper. Construct the calibration curve by finding the "best" line that fits the plotted SPCS.

8.4 *Linear Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. To facilitate data manipulation in a least squares analysis, the following standard curve is developed using the concentration of SPCS as a $f[\ln(\%T)]$. Final calculated analyte concentration with either $\log_{10}$ or ln base would be the same. Using the following example, calculate analyte concentration with P (ppm) in extract = Y variable and percent transmittance (% T) = the X variable. The X variable is the natural logarithm of T.

P (ppm)	T (%)
0	100
2	77
4	59
6	45
8	33
10	24

Number of standards = n = 6

$\sum Y_i = 30$ $\qquad\qquad$ $\sum X_i = 23.5077$

$\sum Y_i/n = Y = 5$ $\qquad$ $\sum X_i/n = X = 3.9180$
$\sum X_i Y_i = 107.5902$ $\qquad$ $\sum X_i^2 = 93.5185$
$\sum X_i \sum Y_i = 705.231$

$$b = \frac{\sum X_i Y_i - \sum X_i \sum Y_i/n}{\sum X_i^2 - (\sum X_i)^2/n} = \frac{107.5902 - 117.5385}{93.5185 - 92.102} = -7.023$$

b = slope of the line, i.e., the amount that Y changes when X changes by 1 unit.

The equation is as follows:

Y = Y + b (X - X)

Y = 5 -7.023 (ln(X) - 3.9180)

Analyte Calculation

8.5 *Calibration Curve*: Read the P (ppm) directly from the calibration curve.

8.6 *Least Squares Analysis*: Put the ln(%T) in the preceding equation and solve for ppm P. Thus, if sample extract has 84% transmission, the preceding equation is as follows:

$$Y = 5 - 7.023 \ln(84) + 27.516 = 1.40 \text{ ppm}$$

8.7 Convert the extract P (ppm) to soil P (ppm or lbs/A) as follows:

Soil P (ppm) = Extract P (ppm) x 10

Soil P (lbs/A) = Extract P (ppm) x 20

9. REPORT

Report the soil Bray P-1 mg kg^{-1} (ppm) to the nearest whole number.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

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CHEMICAL ANALYSES
BRAY P-1 ABSORBED PHOSPHORUS (6S)
FLOW INJECTION, AUTOMATED ION ANALYZER (6S3)
LACHAT, QUIKCHEM AE (6S3B)

1. APPLICATION

The Bray P-1 procedure is widely used as an index of available P in the soil. The selectivity of the Bray extractant is designed to remove the easily acid-soluble P, largely calcium phosphates, and a portion of the phosphates of Al and Fe (Bray and Kurtz, 1945; Olsen and Sommers, 1982). In general, the method has been most successful on acid soils (Bray and Kurtz, 1945; Olsen and Sommers, 1982).

2. SUMMARY OF METHOD

A 1-g sample of <2-mm, air-dry soil is mechanically shaken for 15 min in 10-mL of Bray No. 1 extracting solution. The sample is then centrifuged until solution is free of soil mineral particles, and then filtered until clear extracts are obtained.

A flow injection automated ion analyzer is used to measure the orthophosphate ion (PO_4^{3-}). This ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. Absorbance is proportional to the concentration of PO_4^{3-} in the sample. Concentration of extract PO_4^{3-} is reported as mg P L^{-1}. These extract data are then converted to mg P kg^{-1} (ppm) in the soil.

3. INTERFERENCES

Silica forms a pale blue complex which also absorbs at 660 nm. This interference is generally insignificant as a silica concentration of approximately 4000 ppm would be required to produce a 1 ppm positive error in orthophosphate (LACHAT Instruments, 1989).

Concentrations of ferric iron greater than 50 mg L^{-1} will cause a negative error due to competition with the complex for the reducing agent ascorbic acid. Samples high in iron can be pretreated with sodium bisulfite to eliminate this interference. Treatment with bisulfite will also remove the interference due to arsenates (LACHAT Instruments, 1989).

The determination of phosphorus is sensitive to variations in acid concentrations in the sample since there is no buffer. With increasing acidity, the sensitivity of the method is reduced. Samples, standards, and blanks should be prepared in a similar matrix (LACHAT, Instruments, 1989).

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of concentrated HCl, NH_4F, and H_2SO_4 to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity
5.2 Erlenmeyer flasks, 50-mL, acid-washed
5.3 Centrifuge tubes, polypropylene, round bottom, 13-mL, 16.0 mm x 98.3 mm
5.4 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 oscillations min^{-1}, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI
5.5 Centrifuge, high-speed, International Equipment Co., IECB-22M
5.6 Filter paper, Whatman No. 42, ashless
5.7 Funnel, 60° angle, long stem, 50-mm diameter
5.8 Volumetric flasks, 1-L and 250-mL
5.9 Bottles, plastic, dark, 1-L
5.10 Flow Injection Automated Ion Analyzer, QuikChem AE, LACHAT Instruments, Milwaukee, WI
5.11 XYZ Sampler, LACHAT Instruments, Milwaukee, WI
5.12 Reagent Pump, LACHAT Instruments, Milwaukee, WI
5.13 Automated Dilution Station, LACHAT Instruments, Milwaukee, WI

CHEMICAL ANALYSES
BRAY P-1 ABSORBED PHOSPHORUS (6S)
FLOW INJECTION, AUTOMATED ION ANALYZER (6S3)
LACHAT, QUIKCHEM AE (6S3B)

5.14 Sample Processing Module (SPM) or channel, QuikChem Method (12-115-01-1-A, orthophosphate in waters, 0.4 to 20 mg P L^{-1}), LACHAT Instruments, Milwaukee, WI

5.15 IBM computer PS/2 Model 20/286, 1024 kB Ram, 640 kB user memory

5.16 Okidata ML 182 printer

5.17 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 μL and 10 mL

5.18 Vials, plastic, 25-mL (standards)

5.19 Culture tubes, glass, 10-mL (samples)

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Bray No. 1 Extracting Solution. 0.025 M HCl, and 0.03 M NH$_4$F. Dissolve 8.88 g of NH$_4$F in 4 L DDI H$_2$O. Add 200 mL of 1.0 N HCl and dilute to 8 L with DDI water. The solution pH should be 2.6 ± 0.5. Store in a polyethylene bottle.

6.3 Stock ammonium molybdate solution. In 1-L volumetric flask dissolve 40.0 g ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in approximately 800 mL DDI H$_2$O. Dilute to the mark with DDI H$_2$O and invert three times. Stir for 4 h. Store in plastic and refrigerate.

6.4 Stock antimony potassium tartrate solution. In 1-L flask, dissolve 3.0 g antimony potassium tartrate (potassium antimonyl tartrate hemihydrate K(SbO)C$_4$H$_4$O$_6 \cdot$ 1/2H$_2$O) in approximately 800 mL DDI H$_2$O. Dilute to the mark and invert three times. Store in dark bottle and refrigerate.

6.5 Molybdate color reagent. In 1 L volumetric flask, add 72 mL stock antimony potassium tartrate solution (reagent 6.4) and 213 mL stock ammonium molybdate solution (reagent 6.3). Dilute to volume with DDI H$_2$O and invert three times. Degas by vacuum ~ 5 min.

6.6 Ascorbic acid reducing solution. In l-L volumetric flask, dissolve 60.0 g ascorbic acid in about 700 mL DDI. Dilute to volume with DDI H$_2$O and invert three times. Degas by vacuum ~ 5 min. After dilution to volume and degassing, dissolve 1.0 g dodecyl sulfate (CH$_3$(CH$_2$)$_{11}$OSO$_3$Na). Prepare fresh weekly.

6.7 0.8 M H$_2$SO$_4$ Carrier. To a 1.1-L container, add 1.0 L of DDI H$_2$O and 43.5 mL concentrated H$_2$SO$_4$. (CAUTION: The solution will get very hot!) Invert to mix.

6.8 Sodium hydroxide - EDTA rinse. Dissolve 65 g sodium hydroxide (NaOH) and 6 g tetrasodium ethylenediamine tetraacetic acid (Na$_4$EDTA) in 1.0 L DDI H$_2$O.

6.9 Stock standard P solution (SSPS), 1000 mg P L^{-1} (ppm) as PO$_4^{3-}$. In a 1-L volumetric flask, dissolve 4.394 g primary standard grade anhydrous potassium dihydrogen phosphate (KH$_2$PO$_4$) that has been dried for 2 h at 110°C in about 800 of the extracting solution. Dilute to volume with DDI H$_2$O and invert three times. Do not degas. Store in a refrigerator. Solution is stable to 1 yr.

6.10 Working Stock Standard P Solution (WSSPS), 80.0 mg P L^{-1} (ppm) as PO$_4^{3-}$. In a 1-L volumetric flask, dilute 80.0 mL SSPS to mark with extracting solution. Invert three times.

6.11 Standard P calibration solutions (SPCS) or working standards, 20.0, 12.00, 4.00, 2.00, 0.800, 0.400, and 0.000 mg P L^{-1} (ppm) as PO$_4^{3-}$. To seven 250-mL volumetric flasks add as follows:

a. 20.0 mg P L^{-1} = 62.5 mL WSSPS
b. 12.00 mg P L^{-1} = 37.5 mL WSSPS
c. 4.00 mg P L^{-1} = 12.5 ml WSSPS
d. 2.00 mg P L^{-1} = 6.25 mL WSSPS
e. 0.800 mg P L^{-1} = 2.5 mL WSSPS
f. 0.400 mg P L^{-1} = 1.25 mL WSSPS
g. 0.000 mg P L^{-1} = 0 mL WSSPS (blank)

Dilute each SPCS to the mark with extracting solution and invert three times. Do not degas.

CHEMICAL ANALYSES
BRAY P-1 ABSORBED PHOSPHORUS (6S)
FLOW INJECTION, AUTOMATED ION ANALYZER (6S3)
LACHAT, QUIKCHEM AE (6S3B)

7. PROCEDURE

7.1 Weigh 1 g of <2-mm, air-dry soil to nearest 0.01 g on an electronic balance and place into a 50-mL Erlenmeyer flask.

7.2 Dispense 10.0 mL of extracting solution to flask. Securely place the flask in the shaker. Shake for 15 min at 100 oscillations min^{-1} at room temperature (20°C).

7.3 Remove the sample from the shaker. Decant and filter. Collect extract in 10-mL culture tubes.

7.4 Centrifuging or repeated filtering may be necessary to obtain clear extracts. Decant into 13-mL centrifuge tube and centrifuge at 10000 RPM for 10 min. Refer to Appendix XVIII for operation of the high-speed centrifuge.

7.5 Transfer sample extracts into culture tubes and place in XYZ sample trays marked "Samples". If extracts are not to be determined immediately after collection, then store samples at 4°C. If samples are to be stored for long periods, then freeze extracts.

7.6 Transfer SPCS standards into plastic vials and place in descending order in XYZ sample trays marked "Standards".

7.7 Refer to the operating and software reference manuals for LACHAT set-up and operation. Also refer to Appendix XVII for a more detailed discussion on the routine operation and maintenance of the flow injection system, automated ion analyzer.

7.8 Turn main power switch "ON" and allow 15 min for heater module to warm up to 60°C.

7.9 On reagent pump, set speed to 35.

7.10 On computer main menu, select "Methods" and then "Analysis Select and Download". On method list, select Bray P-1 Method. System unit receives the downloaded method and initializes it.

7.11 Pump reagents (6.5, 6.6 and 6.7) into appropriate chambers of the manifold. Continue this step and observe baseline. A good baseline needs to be smooth and at zero absorbance. Scatter is indicative of air bubbles and irregular reagent flow. Also observe for any back-pressure in manifold tubing. Refer to Appendix XVII for a more detailed discussion of the operation of the LACHAT.

7.12 On computer main menu, select "Samples", "Tray Definition and Submit", and then "Edit" to create new sample tray followed by "Submit" to run new sample tray.

7.13 Method parameters specific to Bray P-1 are defined within the "Method Definition" menu. Some of these parameters have been modified from the QuikChem Method 12-115-01-1-A, orthophosphate in soils (U.S. Environmental Protection Agency, 1983; U.S. Department of Interior, Geological Survey; LACHAT Instruments, 1989). Modifications are primarily related to the criteria and strategies for calibration standards and to injection timing.

7.14 Some of the method parameters as they relate to calibration standards are as follows:

a. There are 7 calibration standards (20.0, 12.00, 4.00, 2.00, 0.800, 0.400, and 0.000 mg P L^{-1}) with a data format of ####.###, i.e., data rounded to 3 places.

b. The segments/boundaries for the calibration standards are A - C (20.0 to 4.00 mg P L^{-1}); C - E (4.00 to 0.800 mg P L^{-1}); and E - G (0.800 to 0.000 mg P L^{-1}).

c. The protocol (replications) for the calibration standards is as follows: AA BB CCC DDDD EEEE FFFF GG.

d. The check standard is 20.0 mg P L^{-1}. Maximum number of consecutive trays between check standard is one; maximum number of consecutive samples between check standard is 60; and maximum elapse time between check standards is 2 h.

e. Calibration strategy for segments A - C, C - E, and E - G are normal, normal, and very low. The normal strategy requires a minimum correlation coefficient of 0.95. The very low strategy requires a minimum correlation coefficient of 0.90. Both require a maximum standard deviation in slope of 50%. A calibration passes only when both criteria are met. Strategies are user designated. In addition, calibration strategies are based on the full chord. Chord 0 is full chord, and chord 1 - 5 are sections of peak from start of peak to end of peak.

7.15 Method parameters in relation to timing are as follows:

a. Cycle period: 40 s

b. Inject to start of peak period: 18 s. To see if peaks are being timed correctly, scan across correlation coefficients for all chords 1 - 5. The most peak area should be between chords 2 - 4 with the most signal-to-noise ratio in chords 1 and 5.

c. Inject to end of peak period: 46 s

d. Automatic timing, where standard assumptions are in effect. Manual timing may be helpful in this method.

7.16 Method parameters in relation to data presentation are as follows:

a. Top Scale Response: 0.50 abs

b. Bottom Scale Response: 0.00 abs

7.17 Refer to the "Method Definition" for Bray P-1 for other method parameters not discussed here.

7.18 Upon completion of run, place the transmission lines into the NaOH - EDTA solution. Pump the solution for approximately 5 min to remove any precipitated reaction products. Then place these lines in DDI H_2O and pump for an additional 5 min and proceed with the normal "Shut-down" procedure.

8. CALCULATIONS

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., $T = P/P_o$ and is often expressed as a percentage, i.e., $\%T = P/P_o \times 100$. The absorbance of a solution is directly proportional to concentration and is defined by the equation, $A = -\log_{10} T$. These relationships are derived from Beer's law.

8.2 Absorbance data are converted to extract concentration of PO_4^{3-} and are reported as mg L^{-1} or ppm. These extract data are converted to soil P (ppm or lbs/A) as follows:

Soil P (ppm)   = Extract P (ppm) x 10

Soil P (lbs/A) = Extract P (ppm) x 20

9. REPORT

Report water soluble orthophosphate in the soil in units of mg P kg^{-1} (ppm) to the nearest 0.001 mg kg^{-1}.

10. PRECISION

Precision data are not available for this procedure. The correlation coefficient (CC) for each segment line is for the full chord. The CC is the "r-squared" statistic, which is ideally 1.0000 for a perfect correlation between dependent variable, absorbance, and the independent variable, concentration. The CC does not distinguish between accuracy of fit and precision and is, at best, a general indicator of error. Good CC's generally vary between 0.9000 to 1.0000. Percent relative standard deviation (RSD) for the slope of each segment line is calculated. If the line is a good fit to the data points, the size of this statistic generally gives the user an idea of the precision of the concentrations of both calibration standards and subsequent samples.

The AE QuikChem LACHAT calibration statistics are based on linear regressions (straight line, $y = a + bx$), i.e., there is no curve fitting ($y = a + bx + cx^2$) with the present QuikChem software. In addition, the calculated statistics may have multiple calculated linear regressions, depending on the number of user-designated segments. This calibration strategy may or may not always be the best approach to the natural dynamic range for P ions as well as other ions that could be measured with the flow injection system, automated ion analyzer. Therefore, as an alternative, a curve-fit can be determined independently by hand-calculator or other software. Several curve-fits have been run on these calibration standards data with a CC of 0.9999.

11. REFERENCES

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CHEMICAL ANALYSES
NEW ZEALAND P RETENTION (6S)
UV-VISIBLE SPECTROPHOTOMETER(6S4)
BECKMANN DU-7 (6S4b)

1. APPLICATION

In *Soil Taxonomy*, the P retention of soil material is a criterion for andic soil properties (Soil Survey Staff, 1990). Andisols and other soils that contain large amounts of allophane and other amorphous minerals have capacities for binding P (Gebhardt and Coleman, 1984). The factors that affect soil P retention are not well understood. However, allophane and imogolite have been considered as major materials that contribute to P retention in Andisols (Wada, 1985). Phosphate retention is also called P absorption, sorption, or fixation.

2. SUMMARY OF METHOD

A 5-g soil sample is shaken in a 1000-ppm P solution for 24 h. The mixture is centrifuged at 2000 rpm for 15 min. An aliquot of the supernatant is transferred to a colorimetric tube to which nitric vanadomolybdate acid reagent (NVAR) is added. The percent transmittance of the solution is read using a spectrophotometer. The New Zealand P retention is reported as percent P retained.

3. INTERFERENCES

No significant problems are known to affect the P retention measurement.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of concentrated HNO_3 to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. EQUIPMENT

5.1 Electronic balance, $\pm$0.01-g sensitivity

5.2 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 epm, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI

5.3 Digital diluter/dispenser, Microlab 500, Hamilton Co., P.O. Box 10030, Reno, NV

5.4 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV

5.5 Diluter/dispenser, 25 mL

5.6 UV-Visible Spectrophotometer, DU-7, Beckmann Instruments Inc.

5.7 Cuvettes, Labcraft Brand, disposable, polystyrene, square-bottom, 4.5 mL, 12.5 mm x 12.5 mm x 46 mm, Curtin Matheson Scientific, Inc., Houston, TX

5.8 Centrifuge, International No. 2, Model V, with no. 250 A head, International Equip. Co., Boston, MA

5.9 Trunions, International no. 320, International Equip. Co., Boston, MA

5.10 Centrifuge tubes, 50 mL, Oak-Ridge, polyallomer, Nalgene 3119, Nalge Co., Box 20365, Rochester, NY

5.11 Plastic cups, 2 fl. oz.

5.12 Pipets, volumetric, class A, glass, various sizes of 1 to 20 mL

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Nitric acid (HNO_3), concentrated, 16 *N*

6.3 P retention solution, 1000 ppm P. Dissolve 35.2 g of KH_2PO_4 and 217.6 g of sodium acetate ($Na_2C_2H_3O_2 \cdot 3H_2O$) in DDI water. Add 92 mL of glacial acetic acid. Dilute to 8 L with DDI water in a volumetric flask. The solution pH should range between 4.55 and 4.65.

6.4 Molybdate solution. Dissolve 16 g of ammonium molybdate (VI) [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] in 50°C DDI water. Allow the solution to cool to room temperature and dilute to 1 L with DDI water.

6.5 Nitric acid solution. Carefully and slowly dilute 100 mL of concentrated HNO_3 to 1 L of DDI water. Add the acid to the water.

6.6 Nitric vanadomolybdate acid reagent (NVAR), vanadate solution. Dissolve 0.8 g of NH_4VO_3 in 500 mL of boiling DDI water. Allow the solution to cool to room temperature. Carefully and slowly add 6 mL of concentrated HNO_3. Dilute to 1 L with DDI water. Mix the nitric acid solution with the vanadate solution and then add the molybdate solution. Mix well.

6.7 Stock P standard solution (SPSS), 4000 ppm P. Dissolve 17.6 g KH_2PO_4 in DDI water. Dilute to 1 L with DDI water.

6.8 Standard P calibration P solutions (SPCS), 100, 80, 60, 40, 20, and 0% P retained. Dilute the SPSS with a solution that contains 32.8 g of sodium acetate (CH_3COONa) and 23 mL of glacial acetic acid diluted to 2 L with DDI water as follows: 100% = DDI water (0 ppm); 80% = 1:20 (200 ppm); 60% = 1:10 (400 ppm); 40% = 3:20 (600 ppm); 20% = 1:5 (800 ppm); and 0% = 1:4 (1000 ppm). The percent amount refers to percent P retention.

7. PROCEDURE

7.1 Weigh 5.00 g of air-dry soil into a 50-mL centrifuge tube.

7.2 Use the dispenser to add 25.0 mL of P-retention solution to centrifuge tube.

7.3 Cap centrifuge tube and place in shaker and shake for 24 h at room temperature (20°C).

7.4 Add 2 to 3 drops of Superfloc, 0.02% w/v to each tube.

7.5 Centrifuge sample at 2000 rpm for 15 min. Filter using a Milipore filter, if necessary.

7.6 Pour sample supernatant into plastic cup.

7.7 Use the digital diluter to add the nitric vanadomolybdate acid reagent (NVAR) to each sample supernatant and to each SPCS. To fill a 4.5-mL cuvette, use a dilution of 1:20 sample dilution.

7.8 The color reaction requires a minimum of 30 min before the analyst records readings.

7.9 Set the spectrophotometer to read at 466 nm. Auto zero using the DDI water (blank). A blank has all reagents contained in the sample extract except the soil. Refer to Appendix XIX for operation and calibration of UV-visible spectrophotometer.

7.10 Record the percent transmittance to the nearest 0.01 unit for the sample extract and each SPCS.

8. CALCULATIONS

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., $T = P/P_o$ and is often expressed as a percentage, i.e., $T = P/P_o \times 100$. The absorbance of a solution is directly proportional to concentration and is defined by the equation, $A = -\log_{10} T$. These relationships are derived from Beer's law.

Calibration Calculations

8.2 Use the transmittance of each SPCS to either construct a calibrated curve to plot P or use a least squares analysis to calculate P. The P is reported in percent retained.

8.3 *Calibration Curve*: Plot the transmittances against the ppm P of each SPCS on semilog graph paper or convert to absorbances and plot on linear graph paper. Construct the calibration curve by finding the "best" line that fits the plotted SPCS.

8.4 *Least Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. To facilitate data manipulation in a least squares analysis, the following standard curve is developed using the concentration of SPCS as a f[ln(%T)]. Final calculated analyte concentration with either $\log_{10}$ or ln base would be the same. Refer to procedure 6S3b for an example of least squares analysis.

Analyte Calculation

8.5 *Calibration Curve*: Read the percent P directly from the calibration curve.

8.6 *Least Squares Analysis*: Refer to procedure 6S3 for an example of least squares analysis.

9. REPORT

Report the percent New Zealand P retention to the nearest whole number.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

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CHEMICAL ANALYSES
CITRIC ACID EXTRACTABLE PHOSPHORUS (6S)
BECKMANN DU-7, UV-VISIBLE SPECTROPHOTOMETER (6S5)

1. APPLICATION

In *Soil Taxonomy*, citric acid soluble P_2O_5 is a criterion for distinguishing between mollic (<250 ppm P_2O_5) and anthropic epipedons (>250 ppm P_2O_5) (Soil Survey Staff, 1975). Additional data on anthropic epipedons from several parts of the world may permit improvements in this definition (Soil Survey Staff, 1994). The procedure 6S5 is used by N.A.A.S. (England and Wales) and is based on the method developed by Dyer (1894).

2. SUMMARY OF METHOD

A sample is checked for $CaCO_3$ equivalent. Sufficient citric acid is added to sample to neutralize the $CaCO_3$ plus bring the solution concentration of citric acid to 1%. A 1:10 soil:solution is maintained for all samples. The sample is shaken for 16 h and filtered. Ammonium molybdate and stannous chloride are added. The percent transmittance of the solution is read using a spectrophotometer. The 1% citric acid extractable P_2O_5 is reported in mg kg^{-1} (ppm).

3. INTERFERENCES

Unreacted carbonates interfere with the extraction of P_2O_5. Sufficient citric acid is added to sample to neutralize the $CaCO_3$. However, a high citrate level in sample may interfere with the molybdate blue test. If this occurs, the method can be modified by evaporating the extract and ashing in a muffle furnace to destroy the citric acid.

Positive interferences in the analytical determination of P_2O_5 are silica and arsenic, if the sample is heated. Negative interferences in the P_2O_5 determination are arsenate, fluoride, thorium, bismuth, sulfide, thiosulfate, thiocyanate, or excess molybdate. A concentration of Fe >1000 ppm interferes with P_2O_5 determination. Refer to Snell and Snell (1949) and Metson (1956) for additional information on interferences in the citric acid extraction of P_2O_5.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in fume hood. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Follow standard laboratory procedures.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity

5.2 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 oscillations min^{-1}, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI

5.3 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. Box 10030, Reno, NV

5.4 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV,

5.5 Centrifuge tubes, 50 mL, Oak-Ridge, polyallomer, Nalgene 3119, Nalge Co., Box 20365, Rochester, NY

5.6 Filter paper, quantitative, Whatman grade 2, 9-cm diameter

5.7 Funnel, 60° angle, long stem, 50-mm diameter

5.8 Erlenmeyer flasks, 50 ml

5.9 Bottles with gas release caps

5.10 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 μL and 10 mL Digital Pipet, 10-ml

5.11 UV-visible spectrophotometer, DU-7, Beckmann Instruments, Inc.

5.12 Cuvettes, Labcraft Brand, disposable, polystyrene, square-bottom, 4.5 mL, 12.5 mm x 12.5 mm x 46 mm, Curtin Matheson Scientific, Inc., Houston, TX

6. REAGENTS

6.1 Distilled, dionized (DDI) water

6.2 Hydrochloric acid (HCl), concentrated, 12 *N*

6.3 Citric acid solution, 10%. Dissolve 100 g of anhydrous citric acid ($C_6H_8O_7$) in 1-L volumetric flask.

6.4 Citric acid solution, 1%. Dilute 100.0 ml of 10% citric acid solution to 1-L with DDI water

6.5 Ammonium molybdate solution, 1.5%. Dissolve 15.0 g of ammonium molybdate 〔$(NH_4)_6MO_7O_{24} \cdot 4H_2O$〕 in 300 mL of distilled water. Transfer to a 1-L volumetric flask and carefully add 310 mL of concentrated HCl. Allow to cool. Make to 1-L volume with DDI water. Store in brown bottle in the dark. Solution is stable for ~ 3 months.

6.6 Stock stannous chloride solution (SSCS). Dissolve 10 g of stannous chloride ($SnCl2 \cdot 2H_2O$) in 100 mL of concentrated HCl.

6.7 Working stannous chloride solution (WSCS). Dilute 2 mL of SSCS with 100 mL of DDI water. Use immediately as solution is only stable for ~ 4 h.

6.8 Stock standard P_2O_5 solution (SSPS), 250 ppm P. Dissolve 1.099 g of potassium dihydrogen orthophosphate (KH_2PO_4) with DDI water in 1-L volumetric flask. Add 5 ml of 2 N HCL. Make to 1-L volume with DDI water.

6.9 Working stock standard P_2O_5 solution (WSSPS), 2.5 ppm P. Pipet 10.0 mL of SSPS and dilute to 1-L in a volumetric flask with DDI water.

6.10 Standard P_2O_5 calibration solutions (SPCS). Pipet 0, 1, 2, 3, 4, and 5 mL of WSSPS into 50-mL oakridge tubes. Add 1 ml of 1% citric acid solution. Continue color development as for samples. Distilled water may be used as a blank.

7. PROCEDURE

7.1 Weigh 3.00 g of <2-mm, air-dry soil into a bottle gas release tops. If the soil does not contain free carbonates, proceed to step 7.3.

7.2 If the soil contains free $CaCO_3$, refer to Table 1 to determine the amount of 10% citric acid solution required to neutralize the $CaCO_3$. Add required mls of 10% citric acid into a graduated cylinder and bring to a volume of 30-ml with DDI water. Add this solution to the soil. Swirl the bottle over a period of 6 h at 100 oscillations min^{-1} dissolve and neutralize the $CaCO_3$. Proceed to step 7.4.

CHEMICAL ANALYSES
CITRIC ACID EXTRACTABLE PHOSPHORUS (6S)
BECKMANN DU-7, UV-VISIBLE SPECTROPHOTOMETER (6S5)

Table 1. Volume of 10% citric acid (mL) required to decompose $CaCO_3$ (%) and to bring solution concentration to 1% in a final volume of 30 mL for 3-g sample.

%CC[1]	ml CA[2]	%CC	ml CA	%CC	ml CA	%CC	ml CA
0	3.0	16	9.7	32	16.4	48	23.2
1	3.4	17	10.2	33	17.3	49	23.6
2	3.8	18	10.6	34	17.3	50	24.0
3	4.3	19	11.0	35	17.7	51	24.4
4	4.7	20	11.4	36	18.1	52	24.8
5	5.1	21	11.8	37	18.6	53	25.3
6	5.5	22	12.2	38	19.0	54	25.7
7	6.0	23	12.7	39	19.4	55	26.1
8	6.4	24	13.1	40	19.8	56	26.5
9	6.8	25	13.5	41	20.2	57	27.0
10	7.2	26	14.0	42	20.6	58	27.4
11	7.6	27	14.4	43	21.0	59	27.8
12	8.0	28	14.8	44	21.5	60	28.2
13	8.5	29	15.2	45	21.9	61	28.6
14	8.9	30	15.6	46	22.4	62	29.0
15	9.3	31	16.0	47	22.8	63	29.5

[1]%CC = percent calcium carbonate in a sample
[2]CA = ml of 10% citric acid needed to be diluted to 30-ml volume with DDI water and added to sample

7.3 If the soil contains no free $CaCO_3$, add 30 mL of 1% citric acid solution to the sample.

7.4 Cap the bottles, place in a shaker and shake for 16 h at 100 oscillations min^{-1}.

7.5 Remove the sample from shaker and filter.

7.6 Pipet 1 mL of sample extract into a 50-ml oakridge tube. Add 4mL of ammonium molybdate solution to all samples and standards. Bring up to 25 ml mark with DDI water. Add 2 ml stannous chloride. Shake to mix and allow to stand 20 min for color development.

7.7 Set the spectrophotometer to read at 660 nm. Refer to Appendix XIX and manufacturer's instruction manual for operation of UV-visible spectrophotometer. Set the zero against distilled water (blank). A blank has all reagents contained in the sample extract except the soil.

7.8 Record the percent transmittance to the nearest 0.01 unit for the sample extract and each SPCS.

8. CALCULATIONS

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., $T = P/P_o$ and is often expressed as a percentage, i.e., $\%T = P/P_o \times 100$. The absorbance of a solution is directly proportional to concentration and is defined by the equation, $A = -\log_{10} T$. These relationships are derived from Beer's law.

Calibration Calculations

8.2 Use transmission of each SPCS to either construct a calibrated curve to plot P_2O_5 or use a least squares analysis to calculate P_2O_5. The P_2O_5 is reported in ppm.

8.3 *Calibration Curve*: Plot the transmittances against the ppm P_2O_5 of each SPCS on semilog graph paper or convert to absorbances and plot on linear graph paper. Construct the calibration curve by finding the "best" line that fits the plotted SPCS.

8.4 *Linear Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. To facilitate data manipulation in a least squares analysis, the following SPCS curve is developed using the concentration of SPCS as a f[ln(%T]. Final calculated analyte concentration with either $\log_{10}$ or ln base would be the same. Refer to procedure 6S3 for an example of least squares analysis.

Analyte Calculation

8.5 *Calibration Curve*: Read the P_2O_5 (ppm) directly from the calibration curve.

8.6 *Least Squares Analysis*: Refer to procedure 6S3 for an example of least squares analysis.

8.7 Convert the extract P_2O_5 (ppm) to soil P_2O_5 (ppm or lbs/A) as follows:

$$\text{Soil P2O5} = \frac{\text{Extract } P_2O_5 \times \text{D.R.} \times 100 \times \text{AD/OD}}{\text{Sample Weight (g)}}$$

where:
Soil P_2O = P_2O_5 in soil (ppm)
Extract P_2O_5 = P_2O_5 in extract (ppm)
D.R   = Dilution ratio, if necessary, otherwise 1
100   = Conversion factor
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)

9. REPORT

Report the 1% citrate acid extractable P_2O_5 in mg kg^{-1} (ppm) to nearest whole number.

10. PRECISION

Precision data are not available for this procedure.

CHEMICAL ANALYSES
CITRIC ACID EXTRACTABLE PHOSPHORUS (6S)
BECKMANN DU-7, UV-VISIBLE SPECTROPHOTOMETER (6S5)

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CHEMICAL ANALYSES
WATER SOLUBLE ORTHOPHOSPHATE (6S)
FLOW INJECTION, AUTOMATED ION ANALYZER (6S7)
LACHAT, QUIKCHEM AE (6S7a)

1. APPLICATION

Phosphorus occurs in soil in both the solution and solid phase. These forms are well documented but questions still remain concerning the exact nature of the constituents and ionic forms found in water, soils, and sediments (National Research Council, 1993). These forms influence P availability in relation to root absorption and plant growth; runoff and water quality problems; and P loadings.

Water soluble P has been defined as P measured in water, dilute salt extracts (e.g., O.01 *M* $CaCl_2$), displaced soil solutions, or saturation paste extracts (Olsen and Sommers, 1982). Even though the water soluble fraction principally consists of inorganic orthophosphate ions, there is evidence that some organic P is also included (Rigler, 1968).

The water or dilute salt extracts represent an attempt to approximate the soil solution P concentration. As an index of P availability, the objectives of this method are (1) to determine the P concentration level in the soil extract that limits plant growth (Olsen and Sommers, 1982) and (2) to determine the composition of the soil solution so that the chemical environment of the plant roots may be defined in quantitative terms (Adams, 1974). The sum of water soluble P and pH 3 extractable P has also been defined as the available P in runoff (Jackson, 1958).

2. SUMMARY OF METHOD

A 5-g sample of <2-mm, air-dry soil is mechanically shaken for 5 min in 50-mL of distilled deionized water. The sample is then centrifuged until solution is free of soil mineral particles, and then filtered until clear extracts are obtained.

A flow injection automated ion analyzer is used to measure the orthophosphate ion (PO_4^{3-}). This ion reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. Absorbance is proportional to the concentration of PO_4^{3-} in the sample. Concentration of extract PO_4^{3-} is reported as mg P L^{-1} (ppm). These extract data are then converted to mg P kg^{-1} (ppm) in the soil.

3. INTERFERENCES

Silica forms a pale blue complex which also absorbs at 880 nm. This interference is generally insignificant as a Si concentration of approximately 30 mg SiO_2 L^{-1} would be required to produce a 0.005 mg P L^{-1} positive error in orthophosphate (LACHAT, 1993).

Glassware contamination is a problem in low-level P determinations. Glassware should be washed with 1:1 HCl and rinsed with deionized water. Commercial detergents should rarely be needed but, if they are used, use P-free preparation for lab glassware (LACHAT, 1993).

Concentrations of ferric ion >50 mg L^{-1} will cause a negative error due to competition with the complex for the reducing agent ascorbic acid. Samples high in Fe can be pretreated with sodium bisulfite to eliminate this interference. Treatment with bisulfite will also remove the interference due to arsenates (LACHAT, 1993).

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of concentrated H_2SO_4 and HCl to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity

5.2 Centrifuge tubes, polypropylene, round bottom, 13-mL, 16.0 mm x 98.3 mm

5.3 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 oscillations min^{-1}, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI

5.4 Centrifuge, high-speed, International Equipment Co., IECB-22M

5.5 Filter paper, Whatman No. 42, ashless

5.6 Funnel, 60° angle, long stem, 50-mm diameter

5.7 Erlenmeyer flasks, 50-mL, acid-washed

5.8 Volumetric flasks, 1-L and 250-mL

5.9 Bottles, plastic, dark, 1-L

5.10 Flow Injection Automated Ion Analyzer, QuikChem AE, LACHAT Instruments, Milwaukee, WI

5.11 XYZ Sampler, LACHAT Instruments, Milwaukee, WI

5.12 Reagent Pump, LACHAT Instruments, Milwaukee, WI

5.13 Automated Dilution Station, LACHAT Instruments, Milwaukee, WI

5.14 Sample Processing Module (SPM) or channel, QuikChem Method (10-115-01-1-A, orthophosphate in waters, 0.01 to 2.0 mg P L^{-1}), LACHAT Instruments, Milwaukee, WI

5.15 IBM computer PS/2 Model 20/286, 1024 kB Ram, 640 kB user memory

5.16 Okidata ML 182 printer

5.17 Pipettors, electronic digital, Rainin Instrument Co., Woburn, MA, 2500 μL and 10 mL

5.18 Vials, plastic, 25-mL (standards)

5.19 Culture tubes, glass, 10-mL (samples)

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Stock ammonium molybdate solution. In 1-L volumetric flask dissolve 40.0 g ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in approximately 800 mL DDI water. Dilute to the mark with DDI H_2O and invert three times. Stir for 4 h. Store in plastic and refrigerate.

6.3 Stock antimony potassium tartrate solution. In 1-L flask, dissolve 3.0 g antimony potassium tartrate (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$) in approximately 800 mL DDI H_2O. Dilute to the mark and invert three times. Store in dark bottle and refrigerate.

6.4 Molybdate color reagent. In 1 L volumetric flask, add about 500 mL DDI H_2O, then add 35.0 mL concentrated sulfuric acid (CAUTION: The solution will get very hot!). Swirl to mix. When it can be comfortably handled, add 72 mL stock antimony potassium tartrate solution (reagent 6.3) and 213 mL stock ammonium molybdate solution (reagent 6.2). Dilute to volume with DDI H_2O and invert three times. Degas by vacuum ~ 5 min.

6.5 Ascorbic acid reducing solution. In l-L volumetric flask, dissolve 60.0 g ascorbic acid in about 700 mL DDI. Dilute to volume with DDI H_2O and invert three times. Degas by vacuum ~ 5 min. After dilution to volume and degassing, dissolve 1.0 g dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$). Prepare fresh weekly.

6.6 Sodium hydroxide - EDTA rinse. Dissolve 65 g sodium hydroxide (NaOH) and 6 g tetrasodium ethylenediamine tetraacetic acid (Na_4EDTA) in 1.0 L DDI H_2O.

6.7 Stock standard P solution (SSPS), 100.0 mg P L^{-1} (ppm). In a 1-L volumetric flask, dissolve 0.439 g primary standard grade anhydrous potassium dihydrogen phosphate (KH_2PO_4) that has been dried for 2 h at 110°C in about 800 mL DDI water. Dilute to volume and invert three times. Do not degas. Store in a refrigerator. Solution is stable to 1 yr.

6.8 Working Stock Standard P Solution (WSSPS), 10.0 mg P L^{-1} (ppm). In a 1-L volumetric flask, dilute 100.0 mL SSPS to mark with DDI H_2O. Invert three times.

6.9 Standard P calibration solutions (SPCS) or working standards, 2.0, 1.0, 0.5, 0.20, 0.05, 0.01, and 0.00 mg P L^{-1} (ppm). To seven 250-mL volumetric flasks add as follows:

a. 2.0 mg P L^{-1} = 50.0 mL WSSPS
b. 1.0 mg P L^{-1} = 25.0 mL WSSPS
c. 0.5 mg P L^{-1} = 12.5 ml WSSPS
d. 0.20 mg P L^{-1} = 5.0 mL WSSPS
e. 0.05 mg P L^{-1} = 1.25 mL WSSPS
f. 0.01 mg P L^{-1} = 0.25 mL WSSPS
g. 0.00 mg P L^{-1}= 0 mL WSSPS (blank)

Dilute each SPCS to the mark with DDI H$_2$O and invert three times. Do not degas.

7. PROCEDURE

7.1 Weigh 5 g of <2-mm, air-dry soil to nearest 0.01 g on an electronic balance and place into a 50-mL Erlenmeyer flask.

7.2 Add ~ 50 mL of DDI H$_2$O to sample. Place the sample in a horizontal shaker set at 120 oscillations min^{-1} and shake for 5 min.

7.3 Remove the sample from the shaker. Decant and filter solution. Collect extract in 10-mL culture tubes.

7.4 Centrifuging or repeated filtering may be necessary to obtain clear extracts. Decant into 13-mL centrifuge tube and centrifuge at 10000 RPM for 10 min. Refer to Appendix XVIII for operation of the high-speed centrifuge.

7.5 Transfer sample extracts into culture tubes and place in XYZ sample trays marked "Samples". If extracts are not to be determined immediately after collection, then store samples at 4°C. If samples are to be stored for long periods, then freeze extracts.

7.6 Transfer SPCS standards into plastic vials and place in descending order in XYZ sample trays marked "Standards".

7.7 Refer to the operating and software reference manuals for LACHAT set-up and operation. Also refer to Appendix XVII for a more detailed discussion on the routine operation and maintenance of the flow injection system, automated ion analyzer.

7.8 Turn main power switch "ON" and allow 15 min for heater module to warm up to 37°C.

7.9 On reagent pump, set speed to 35. Pump DDI H$_2$O through system for 20 min.

7.10 On computer main menu, select "Methods" and then "Analysis Select and Download". On method list, select water soluble P method. System unit receives the downloaded method and initializes it.

7.11 Pump reagents into manifold. Continue this step and observe baseline. A good baseline needs to be smooth and at zero absorbance. Scatter is indicative of air bubbles and irregular reagent flow. Also observe for any back-pressure in manifold tubing. Refer to Appendix XVII/F3 1 Tfı˝0 -2.4058 TDı˝-0.002 1es Refer to thr o

7.2   On computer main menu, marked , "01 yxtrfthod e operaSubmit , Methods" aEdit g. crmin needs to

CHEMICAL ANALYSES
WATER SOLUBLE ORTHOPHOSPHATE (6S)
FLOW INJECTION, AUTOMATED ION ANALYZER (6S7)
LACHAT, QUIKCHEM AE (6S7a)

7.13 Method parameters specific to water soluble P are defined within the "Method Definition" menu. Some of these parameters have been modified from the QuikChem Method 10-115-01-1-A, orthophosphate in waters (U.S. Environmental Protection Agency, 1983; U.S. Department of Interior, Geological Survey; LACHAT Instruments, 1993). Modifications are primarily related to the criteria and strategies for calibration standards and to injection timing.

7.14 Some of the method parameters as they relate to calibration standards are as follows:

a. There are 7 calibration standards (2.0, 1.0, 0.5, 0.20, 0.05, 0.01, and 0.00 mg P L^{-1}) with a data format of ####.###, i.e., data rounded to 3 places.

b. The segments/boundaries for the calibration standards are A - D (2.0 to 0.20 mg P L^{-1}) and D - G (0.20 to 0.00 mg P L^{-1}).

c. The protocol (replications) for the calibration standards is as follows: AA BB CCC DDDD EEEE FFFF GG

d. The check standard is 2.0 mg P L^{-1}. Maximum number of consecutive trays between check standard is one; maximum number of consecutive samples between check standard is 60; and maximum elapse time between check standards is 2 h.

e. Calibration strategy for segments A - D and D - G are normal and very low. The normal strategy requires a minimum correlation coefficient of 0.95. The very low strategy requires a minimum correlation coefficient of 0.90. Both require a maximum standard deviation in slope of 50%. A calibration passes only when both criteria are met. Strategies are user designated. In addition, calibration strategies are based on the full chord. Chord 0 is full chord, and chord 1 - 5 are sections of peak from start of peak to end of peak.

7.15 Method parameters in relation to timing are as follows:

a. Cycle period: 40 s

b. Inject to start of peak period: 28 s. To see if peaks are being timed correctly, scan across correlation coefficients for all chords 1 - 5. The most peak area should be between chords 2 - 4 with the most signal-to-noise ratio in chords 1 and 5.

c. Inject to end of peak period: 52 s

d. Automatic timing, where standard assumptions are in effect; no manual timing.

7.16 Method parameters in relation to data presentation are as follows:

a. Top Scale Response: 0.70 abs

b. Bottom Scale Response: 0.00 abs

7.17 Method parameters in relation to data results are as follows:

a. Set Default Chord to 3. This change must be made to both the sample and the calibration RDF's.

7.18 Refer to the "Method Definition" for water soluble P for other method parameters not discussed here.

7.19 Upon completion of run, place the transmission lines into the NaOH - EDTA solution. Pump the solution for approximately 5 min to remove any precipitated reaction products. Then place these lines in DDI H_2O and pump for an additional 5 min and proceed with the normal "Shut-down" procedure.

8. CALCULATIONS

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., T = P/P_o and is often expressed as a percentage, i.e., %T = P/P_o x 100. The absorbance of a solution is directly proportional to concentration and is defined by the equation, A = -$\log_{10}$ T. These relationships are derived from Beer's law.

8.2 Absorbance data are converted to extract concentration of PO_4^{3-} and are reported as mg L^{-1} or ppm. These extract data are converted to soil P (ppm or lbs/A) as follows:

Soil P (ppm)   = Extract P (ppm) x 10

Soil P (lbs/A) = Extract P (ppm) x 20

9. REPORT
        Report water soluble orthophosphate in the soil in units of mg P kg^{-1} (ppm) to the nearest 0.001 mg kg^{-1}.

10. PRECISION
        Precision data are not available for this procedure. Example calibration statistics are as follows:

Correlation Coefficients

```
        Segmented Standards
             A-D  D-G
Full Chord  0.9983 0.9671
Chord 1     0.9874 0.9165
Chord 2     0.9995 0.9686
Chord 3     0.9995 0.9603
Chord 4     0.9980 0.9817
Chord 5     0.9594 0.8576
```

        The percent relative standard deviation in slope for Chord 3 for A-D and D-G Segmented Standards are 0.8 and 5.4 percent, respectively.
        The correlation coefficient (CC) for each segment line is for the full chord. The CC is the "r-squared" statistic, which is ideally 1.0000 for a perfect correlation between dependent variable, absorbance, and the independent variable, concentration. The CC does not distinguish between accuracy of fit and precision and is, at best, a general indicator of error. Good CC's generally vary between 0.9000 to 1.0000. Percent relative standard deviation (RSD) for the slope of each segment line is calculated. If the line is a good fit to the data points, the size of this statistic generally gives the user an idea of the precision of the concentrations of both calibration standards and subsequent samples.
        The AE QuikChem LACHAT calibration statistics are based on linear regressions (straight line, y = a + bx), i.e., there is no curve fitting (y = a + bx + cx^2) with the present QuikChem software. In addition, the calculated statistics may have multiple calculated linear regressions, depending on the number of

user-designated segments. This calibration strategy may or may not always be the best approach to the natural dynamic range for P ions as well as other ions that could be measured with the flow injection system, automated ion analyzer. Therefore, as an alternative, a curve-fit can be determined independently by hand-calculator or other software. Several curve-fits have been run on these calibration standards data with a CC of 0.9999.

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MINERALOGY
INSTRUMENTAL ANALYSES (7A)

INTRODUCTION

The physical and chemical properties of a soil are controlled to a very large degree by the soil minerals, especially by those minerals constituting the clay fraction (Whittig and Allardice, 1986). Positive identification of mineral species and quantitative estimation of their proportions in soils usually require the application of several complementary qualitative and quantitative analyses (Whittig and Allardice, 1986). Some of the semiquantitative and quantitative procedures performed by the SSL include X-ray diffraction (procedure 7A2) and thermal analysis (procedures 7A3c, 7A4c, and 7A6b).

Many soil constituents undergo several thermal reactions upon heating, which serve as diagnostic properties for the qualitative and quantitative identification of these substances (Tan et al., 1986). Thermogravimetric analysis (TGA) is a technique for determining weight loss of a sample while it is heated at a constant rate. The TGA is an outgrowth of dehydration curves that were used in early studies of various phyllosilicate clay minerals (Jackson, 1956). The TGA differs from these earlier dehydration curves in that sample weight is monitored continuously rather than measured at discrete intervals after periods of heating at a constant temperature (Earnest, 1984). The TGA only measures reactions that involve a weight loss of the sample.

Differential scanning calorimetry (DSC) is a calorimetric technique that measures the amount of energy required to establish zero temperature difference between sample and reference material as the two are heated side by side at a controlled rate (Tan et al, 1986). The DSC is used for the same purposes as differential thermal analysis (DTA) but has the advantage of directly measuring the magnitude of an energy change (H, enthalpy or heat content) in a material undergoing an exothermic or endothermic reaction. In the DSC procedure, the sample and reference, usually an empty pan, are each heated independently from one another by separate heating elements. Samples are held isothermal with respect to one another by increasing or decreasing the power supplied to the sample heater in response to an isothermic or exothermic event in the sample. In order to maintain sample temperature equal to that of the reference material, thermal energy is added to the sample when an endothermic change occurs or subtracted from the sample when an exothermic transition occurs. The energy input is equivalent in magnitude to the energy absorbed or evolved in the particular transition (Tan et al., 1986). The amount of thermal energy required to balance temperature differences is recorded.

The DTA method (procedure 7A3c) is not described in this laboratory methods manual. In DTA, the sample and a thermally inert reference material, e.g., Al_2O_3 or ignited kaolinite, are heated at a constant rate by a common furnace or heating element. Thermocouples are in contact with two platinum pans or may reside within sample and inert reference material. One pan contains the sample, and the other pan contains the inert reference material of similar composition. If a reaction occurs, thermocouples measure the temperature differential between the sample and reference, i.e., the samples are not held isothermal to one another as in DSC. The magnitude of the temperature differential depends on the nature of the reaction and the amount of reacting substance in the sample. The temperature at which the reaction occurs identifies the substance, if enough is known about the sample to predict the possibilities.

The TGA, DSC and DTA are complementary methods available to the analyst. Many of the same clay mineral reactions, e.g., dehydroxylation, loss of surface adsorbed water, decomposition of carbonates, and oxidation, that are studied by DSC or DTA can also be studied by TGA. However, some transformation reactions, e.g., melting or structural reorganization (quartz alpha-beta transition), cannot be measured by TGA because no weight loss is involved. The DSC and DTA procedures provide information about energy relationships in the structures and reactions of the soil solid phase, whereas TGA provides quantitative information about quantities of substances gained or lost by the solid phase during certain thermally driven reactions. Liquid samples also can be analyzed by the above techniques but are not treated here.

The X-ray diffraction analysis is a useful method to identify and to make semiquantitative estimates of the crystalline mineral components of soil. Angles of diffraction, as affected by differentiating sample treatments, are distinctive for a particular mineral and help to identify that mineral. Intensities of diffraction maxima are related to the number of corresponding diffraction planes in a sample and provide a basis for the estimation of concentrations of the mineral species present (Whittig and Allardice, 1986). Diffraction can occur whenever Bragg's Law is satisfied. However, in X-ray

analysis of soils or clay samples, there are difficulties in evaluation of and compensation for variations in chemical composition, crystal perfection, amorphous substances, and particle-size (Whittig and Allardice, 1986). A more reliable and accurate estimation of mineral percentages is provided when X-ray diffraction analysis is used in conjunction with other methods, e.g., differential-thermal, surface-area, elemental analysis, and other species-specific chemical methods (Alexiades and Jackson, 1966).

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MINERALOGY
INSTRUMENTAL ANALYSES (7A)
X-RAY DIFFRACTION (7A2)
PHILLIPS XRG-300 X-RAY DIFFRACTOMETER
THIN FILM ON GLASS, RESIN PRETREATMENT II (7A2i)
(Mg Room Temp, Mg Glycerol Solvated, K 300°C, K 500°C)

1. APPLICATION

Clay fractions of soils are commonly composed of mixtures of one or more phyllosilicate minerals together with primary minerals inherited directly from the parent material (Whittig and Allardice, 1986). Positive identification of mineral species and quantitative estimation of their proportions in these polycomponent systems usually require the application of several complementary qualitative and quantitative analyses (Whittig and Allardice, 1986). One of the most useful methods to identify and to make semiquantitative estimates of the crystalline mineral components of soil is X-ray diffraction analysis.

The operational strategy at the SSL and the preceding Lincoln Soil Survey Laboratory has been to adjust instrumental parameters to keep peak intensity of a soil reference constant from 1964 to present through the evolution of instrumentation. The intent is to keep the same quantitative interpretations consistent from sample to sample.

2. SUMMARY OF METHOD

Soils are dispersed and separated into fractions of interest. Sands and silts are mounted on glass slides as slurries or on double sticky tape for analysis. Clay suspensions are placed on glass slides to dry and to preferentially orient the clay minerals. The soil clay minerals of greatest interest are phyllosilicates, e.g., kaolinite, mica (illite), smectite, vermiculite, hydroxy-interlayered vermiculite, and chlorite.

Generally, no two minerals have exactly the same interatomic distances in three dimensions and the angle at which diffraction occurs is distinctive for a particular mineral (Whittig and Allardice, 1986). These interatomic distances within a mineral crystal result in a unique array of diffraction maxima, which help to identify that mineral. When several minerals are present in a sample, species identification is usually accomplished most easily and positively by determining the interatomic spacings that give rise to the various maxima and by comparing these with known spacings of minerals (Whittig and Allardice, 1986).

X-ray diffraction produces peaks on a chart that correspond to 2θ angles on a goniometer. The angle of incidence of the goniometer is relative to the surface plane of the sample. Standard tables to convert θ or 2θ angles to crystal "d" spacings are published in the U.S. Geological Survey Circular 29 (Switzer et al., 1948) and in other publications (Brown, 1980). At the SSL, conversions are made by the analysis program on the Philips diffractometer, d-spacings are recorded on an IBM-compatible 486 DOS-based computer system, and hard copies are printed for interpretation and filing. The crystal "d" spacings of minerals, i.e., the interval between repeating planes of atoms, can be calculated by Bragg's Law as follows:

$$n\lambda = 2d \sin \theta$$

where:
n   = order of diffraction (integer)
λ = x-radiation wavelength (Angstroms, A)
d   = crystal "d" spacing (A)
θ = angle of incidence

When n = 1, diffraction is of the first order. The wavelength of radiation from an X-ray tube is constant and characteristic for the target metal in the tube. Copper radiation (CuKa) with a wavelength of 1.54 A (0.154 nm) is used at the SSL. Because of similar structures of layer silicates commonly present in soil clays, several treatments which characteristically affect the "d" spacings are necessary to identify

MINERALOGY
INSTRUMENTAL ANALYSES (7A)
X-RAY DIFFRACTION (7A2)
PHILLIPS XRG-300 X-RAY DIFFRACTOMETER
THIN FILM ON GLASS, RESIN PRETREATMENT II (7A2i)
(Mg Room Temp, Mg Glycerol Solvated, K 300°C, K 500°C)

components. At the SSL, four treatments are used, i.e., Mg^{2+} (room temperature); Mg^{2+}-glycerol (room temperature); K^+ (300°C); and K^+ (500°C).

3. INTERFERENCES

Intimate mixtures of similar phyllosilicate minerals on a fine scale cause problems in identification. The mixtures, differences in crystal size and purity, and background or matrix interferences affect quantification. No pretreatments other than dispersion with sodium hexametaphosphate are used for separation and isolation of the crystalline clay fraction. Impurities such as organic matter and iron oxides may act as matrix interferences causing peak attenuation during X-ray analysis or may interfere with clay dispersion and separation. The separation procedure to isolate the clay fraction from the other size fractions of the soil skews the <2-μm clay suspension toward the fine clay, but it minimizes the inclusion of fine silt in the fraction. Dried clay may peel from the XRD slide. One remedy is to rewet the peeled clay on the slide with 1 drop of glue-water mixture (1:7). Other remedies are as follows:

a. Place double sticky tape on the slide prior to adding the dried clay.

b. Dilute the suspension by half, if thick.

c. Crush with ethanol and dry, and then add water to make a slurry slide.

d. Roughen the slide surface with a fine grit sand paper.

Sufficient glycerol on the slides is required to solvate the clay, i.e., to expand smectites to 18 A. X-ray analysis should be performed 1 to 2 days after glycerol addition. If excess glycerol is applied to the slide and free glycerol remains on the surface, XRD peaks are attenuated. Some suggestions to dry the slides and achieve optimum glycerol solvation are as follows:

a. Use a desiccator to dry slide, usually when the clay is thin.

b. If the center of slide is whitish and dry, usually with thick clay, brush slide with glycerol or add an additional drop of glycerol.

4. SAFETY

Operate the centrifuge with caution. Keep the centrifuge lid closed when in operation. Ensure that all hangers and tubes are seated firmly in proper location. Use tongs and appropriate thermal protection when operating the muffle furnace. The diffraction unit presents an electrical and radiation hazard. Analysts must receive radiation safety training before operating the equipment. Employees must wear a radiation film badge while in the room when the diffraction unit is in operation.

5. EQUIPMENT
5.1 Teaspoon (5 g)
5.2 Dispenser, 5 mL, for sodium hexametaphosphate solution
5.3 Centrifuge, International No. 2, with No. 240 head and carriers for centrifuge tubes, International Equip. Co., Boston, MA
5.4 Centrifuge tubes, plastic, 100 mL, on which 10-cm solution depth is marked
5.5 Rubber stoppers, No. 6, for centrifuge tubes
5.6 Mechanical shaker, reciprocal, 120 oscillations min^{-1}

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5.7 Plastic cups, 60 mL (2 fl. oz.) with lids

5.8 Label machine

5.9 Hypodermic syringes, plastic, 12 mL, with tip caps

5.10 Screen, 80 mesh, copper

5.11 Dropper bottle, plastic, 30 mL (1 fl. oz.), for a 1:7 glycerol:water mixture

5.12 Muffle furnace

5.13 X-ray diffractometer, Philips XRG-300, with PW-1170 automated sample changer

5.14 PC-APD, Philips, software for Automatic Powder Diffraction (PW-1877), Version 3.5

5.15 Computer, IBM-compatible 486, Gateway 2000 4D X2-66V

5.16 Printer, Hewlett Packard LaserJet IV

5.17 Plotter, Hewlett Packard 7550 Plus

5.18 XRD slides, glass, 14 x 19 mm

5.19 XRD sample preparation board, wood, with 32 places for glass XRD slides

5.20 Slide holder. Accepts 14 x 19 mm XRD glass slides. Modified so slide surfaces rest flush with surface of holder.

5.21 Magazine for slide holder, 35 positions

5.22 Reference slides: quartz and clay from reference soil

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Sodium hexametaphosphate solution. Dissolve 35.7 g of sodium hexametaphosphate $(NaPO_3)_6$ and 7.94 g of sodium carbonate (Na_2CO_3) in 1 L DDI water.

6.3 Potassium chloride (KCl), 1.0 *N*. Dissolve 74.60 g KCl in 1 L DDI water or 671.40 g KCl in 9 L DDI water.

6.4 Magnesium chloride $(MgCl_2)$, 1.0 *N*. Dissolve 47.61 g $MgCl_2$ in 1 L DDI water or 428.49 g $MgCl_2$ in 9 L DDI water.

6.5 Glycerol:water mixture (1:7). Add 4 mL of glycerol to 28 mL DDI water plus 2 drops of toluene.

6.6 Exchange resin, Rexyn 101 (H), analytical grade. Pretreatment of resin as follows:

6.6.1 Divide equally Rexyn 101 (H), approximately 250-g portions, into two 600-mL beakers labelled K and Mg and add appropriate salt solution (1.0 *N* KCl or 1.0 *N* $MgCl_2$). Cover resin with salt solution.

6.6.2 Stir, let settle for 10 min, decant clear solution, and add salt solution. Repeat 3 times. Leave resin covered in salt solution for 8 to 12 h.

6.6.3 Repeat step 6.6.2 second day. Resin is ready for syringes. Saturated resin not used initially for syringes can be saved for future use.

6.7 White glue, diluted 1:7 with DDI water

7. PROCEDURE

Preparation (Recharge) of Resin-Loaded Syringes

7.1 Place a small circle of 80-mesh screen in a 12-mL syringe and add 4 cm^3 of exchange resin from which salt solution has been drained. Our procedure requires each sample to have 2 Mg and 2 K slides prepared, so we produce our syringes in sets of two.

7.2 Saturate the resin in each of the four syringes with 4 mL of the appropriate 1.0 *N* salt solution ($MgCl_2$ or KCl) and expel. Repeat saturation of resin.

7.3 Fill syringe completely with the salt solution and allow to equilibrate for 4 to 20 h.

7.4 Rinse syringe twice with 4 mL of DDI water and rinse tip cap.

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7.5 Completely fill syringe with DDI water and allow to equilibrate for 4 to 20 h.

7.6 Rinse syringe twice with DDI water.

7.7 Expel water, cap syringe, and store.

Preparation of Clay Suspension

7.8 Place ≈ 5 g (1 tsp) of air-dry <2-mm soil in a 100-mL plastic centrifuge tube. If the sample appears to be primarily sand, use 10 g (2 tsp) of <2-mm soil to obtain sufficient clay.

7.9 Add 5 mL of sodium hexametaphosphate solution. If the soil contains gypsum or is primarily calcium carbonate, use 10 mL of sodium hexametaphosphate dispersing agent.

7.10 Fill tube to 9.5-cm height with DDI water.

7.11 Place rubber stopper in tube and shake overnight in mechanical shaker.

7.12 Remove stopper from tube and rinse stopper and sides of tube with enough water to bring the volume to the 10-cm mark.

7.13 Balance the pairs of tubes and place in centrifuge. Centrifuge at 750 rpm for 3.0 min.

7.14 If the clay is dispersed, carefully decant 30 mL of suspension into a labelled, 60-mL, plastic cup. Place cap on cup.

7.15 If the clay did not disperse after being shaken overnight, remove the rubber stopper and carefully decant the clear supernatant liquid.

7.16 Add an additional 10 mL of sodium hexametaphosphate dispersing agent to sample and then add DDI water to 9.5-cm depth.

7.17 Stopper and shake overnight to disperse the clay. Rinse stopper and fill tube to 10-cm mark.

7.18 Centrifuge, decant, and store clay suspension.

7.19 Use the clay suspension for X-ray diffraction analysis and HF plus aqua regia dissolution analysis. Dry clay suspension for use in thermal analysis.

Thin Film on Glass, Resin Pretreatment

7.20 The SSL uses a sample board which holds 32 slides, i.e., 8 samples x 4 treatments. Prepare the sample board with glass XRD slides to receive the following 4 treatments per clay suspension sample.

Mg^{2+} -   room temperature
Mg^{2+} -   glycerol (room temperature)
K^+ -   300°C (heated for 2 h)
K^+ -   500°C (heated for 2 h)

7.21 Place one small drop of the glycerol:water mixture (1:7) on each Mg^{2+}-glycerol slide.

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7.22 Draw 1 mL of <2-μm clay suspension into the resin-loaded syringe and invert back and forth to facilitate cation exchange.

7.23 Dispense 3 drops to clear the tip.

7.24 Dispense ≈ 0.1 mL (6 to 10 drops) to cover the appropriate XRD slide. Draw DDI water into the syringe and expel 3 times to remove all of the clay suspension. Recharge the syringe after 10 times of use.

7.25 When the clay suspension has dried, transfer the slides with the K$^+$-saturated clays to transite plates and heat for a minimum of 2 h in a muffle furnace.

7.26 Heat the following sample slides on the XRD sample board.

K$^+$-300°C   -   slides 3, 7, 11, 15, 19, 23, 27, and 31

K$^+$-500°C   -   slides 4, 8, 12, 16, 20, 24, 28, and 32

7.27 After heating, remove the transite plate from the furnace, cool to air temperature, and return slides to XRD sample board.

X-ray Diffraction Operation
7.28 The X-ray analysis of the glycerol slide must be done within 1 to 2 days after the slide dries. If this is not possible, skip Step 7.21 when slide is prepared. Add one small drop of glycerol:water mixture (1:7) to dry slide 24 h prior to X-ray analysis.

7.29 Transfer the slides (1 to 32) from XRD sample board to slide holders (1 to 32) and place in slots (1 to 32) in a magazine for the automated sample changer.

7.30 Analyze one reference soil sample in each run. Place this sample in slot 33.

7.31 Analyze one quartz standard for 2θ and intensity calibrations in each run. Place this sample in slot 34. Intensity is measured at peak maximum at or near 26.66° 2θ for 10 s.

7.32 The 32 samples from one XRD board constitute one run on the diffraction unit. Prepare a run sheet for samples on each XRD sample board. Refer to example run instruction (7.33). Refer to Appendix XX and the manufacturer's manual for operation of the X-ray diffractometer.

7.33 Place the magazine in the automated sample changer. Confirm that the XRD shutter is off when changing magazines. Set the XRD unit parameters as follows:

CuKα radiation, λ: 1.54 A (0.154 nm)
Scan range: 2° to 34° 2θ
Generator settings: 40 kv, 20 ma
Divergence slit: 1°
Receiving slit: 0.2 mm
Monochrometer: Yes

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Step size and scan speed vary depending on intensity of X-rays generated from tube. Adjust settings to maintain same long-term peak intensities on standard reference clay and quartz standard regardless of tube intensities.

7.34 Enter run instruction from the keyboard. Create a batch file for the automated run. File names specified are of the sample number. An example run instruction is as follows:

Batch File Name: Project number (e.g., CP95LA022)

Raw Data File Name: Run number

First Sample: 1

Last Sample: 33
(reference soil clay)

7.35 Activate program. The run stores raw data on the hard disk under the subdirectory designated by project type and year, e.g., CP95. Refer to example run instruction (7.34).

7.36 Print a hard copy of the "Detected Peaks File" for each sample and perform level 1 smoothing on diffraction patterns.

7.37 Prepare and print a 4-color graphics chart. The 4 colors are blue (Mg^{2+}); green (Mg^{2+}-glycerol); pink (K^+ 300°C); and red (K^+ 500°C). Stamp chart with label; enter run parameter information, and complete soil information, e.g., soil name, horizon designation, and depth. File hard copies of detected peaks and graphics chart in pasteboard binders by state, county, and chronology.

7.38 Record "d" spacing and intensity of quartz standard in the logbook. Record the peak intensities for designated peaks for the reference soil clay.

7.39 File the detected peaks printout and graph for the reference soil in the reference soil-clay folder.

Interpretation of X-ray Diffraction Data
7.40 The angle in degrees two theta (2θ) measured in X-ray diffraction analyses is converted to angstroms (A) using tables complied according to Bragg's Law. Refer to summary of method. Angstroms convert to nanometers (nm) by a factor of 0.1, e.g., 14 A = 1.4 nm.

7.41 Use the following X-ray diffraction criteria to identify some common crystalline minerals. The reported "d" values are for 00*l* basal spacings. The Miller index (*hkl*) specifies a crystal face which has some orientation to the three crystallographic axes of a, b, and c. The Miller index (00*l*) indicates a crystal face that is parallel to the a and b axes, e.g., phyllosilicate minerals. The following X-ray diffraction criteria also has some questions (Q) that may aid the analyst in interpreting the diffraction patterns. These questions are a suggested procedural approach to help the analyst identify the relative locations of a few peaks and to confirm key criteria.

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X-Ray Diffraction Criteria

1. Kaolinite and Halloysite
a. Crystal structure missing at 500°C.
b. 7 A (7.2 to 7.5 A) with all other treatments
Q. Is there a 7 A peak? Is it destroyed at 500°C? Kaolinite or Halloysite.
Q. Is the peak sharp and at ~ 7.1 A? Kaolinite.
Q. Is the peak broad and at 7.2 to 7.5 A? Halloysite.

2. Mica (Illite)
a. 10 A with all treatments.
b. 10 A with Mg^{2+}-saturation
Q. Is there a 10 A peak with Mg^{2+}-saturation? Mica (Illite).

3. Chlorite
a. Crystal structure of Fe-chlorites destroyed at 650 to 700°C.
b. 14 A with all other treatments.
c. 14 A at 500°C.
d. Generally also has strong 7 A peak.
Q. Is there a 14 A peak when heated to 500°C? Chlorite.

4. Vermiculite
a. 14 A with Mg^{2+}-saturation.
b. 14 A with Mg^{2+}-glycerol solvation.
c. Nearly 10 A with K^+saturation.
d. 10 A when K^+-saturated and heated to 300°C.
Q. Is there an enhanced 10 A peak with K^+-saturation in comparison to Mg^{2+}saturation that cannot be attributed to smectitie? Vermiculite.

5. Smectite
a. 14 A with Mg^{2+}-saturation
b. 12 to 12.5 A with K^+- or Na^+-saturation.
c. 17 to 18 A with Mg^{2+}-glycerol solvation.
d. 10 A with K^+-saturation and heating to 300°C.
Q. Is there a 17 to 18 A peak upon solvation? Smectite.

6. Gibbsite
a. Peak at 4.83 A with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300°C.

7. Goethite
a. Peak at 4.18 A with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300°C.

8. Hydroxy-interlayed Vermiculite or Smectite
a. Incomplete collapse to 10 A of smectite or vermiculite when K^+-saturated and heated to 300°C.

9. Quartz
a. Peaks at 4.27 A and 3.34 A with all treatments (only 3.34 if small amounts).

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10. Lepidocrocite
a. Peak at 6.2 to 6.4 A with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300°C.

11. Potassium Feldspar
a. Peak at 3.24 A with all treatments.

12. Plagioclase Feldspar
a. Twin peaks between 3.16 and 3.21 with all treatments.

13. Calcite
a. Peak at 3.035 A with all treatments.

14. Dolomite
a. Peak at 2.88 to 2.89 A with all treatments.

15. Gypsum
a. Peak at 4.27 A with Mg^{2+} and Mg^{2+}-glycerol, but destroyed when heated to 300°C.

16. Mixed Layer Vermiculite-Mica
a. Peak at 11 to 13 A with Mg^{2+} that does not expand with Mg^{2+}-glycerol.
b. Peak collapses to 10 A with K^+-saturation and heating to 300°C.

17. Mixed Layer Smectite-Mica
a. Peak at 11 to 13 A with Mg^{2+} that expands to 14-16 A with Mg-glycerol.
b. Peak collapses to 10 A with K^+-saturation and heating to 300°C.

18. Mixed Layer Chlorite-Mica
a. Peak at 14 A with Mg^{2+} and Mg^{2+}-glycerol.
b. Peak collapses toward 10 A with K^+-saturation and heating to 300°C, and more completely with heating to 500°C, but never to 10 A.

19. Mixed Layer Chlorite-Smectite
a. Peak at 11 to 13 A with Mg^{2+}-saturation that expands to about 16 A with Mg^{2+}-glycerol.
b. Collapses to about 12 A with K^+-saturation and heating to 300°C and 500°C.

7.42 Use the X-ray diffraction criteria, i.e., diagnostic basal 00l spacings (A), in Table 1 for identification and ready reference of some common crystalline minerals as affected by differentiating sample treatments.

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Table 1. X-ray diffraction parameters of common soil clay minerals.

Mineral	Treatment						
	Na^+	Mg^{2+}	Mg^{2+} Gly	K^+	K^+ 300°C	K^+ 500°C	K^+ 700°C
	00l diffraction spacing in angstroms						
Kaolinite	7	7	7	7	7	**LD**[1]	LD
Halloysite	7B[2]	**7B**	7B	7B	7B	**LD**	LD
Mica (Illite)	10	10	**10**	10	10	10	10
Chlorite	14*[3]	14*	14*	14*	14*	**14***	T[4]
Vermiculite	14	14	**14**	**10**	10	10	10
Smectite	12.5	14	**18**	12.5	10	10	10
Gibbsite	4.85	**4.85**	4.85	4.85	**LD**	LD	LD
Goethite	4.18	**4.18**	4.18	4.18	**LD**	LD	LD
Interlayer	10-14	10-14	10-18	10-14	10-14	10-14	10-14
Quartz	**3.14** and **4.27** for all treatments						
Calcite	**3.035** for all treatments						
Dolomite	**2.88** for all treatments						

[1] LD = Lattice destroyed
[2] B = Broad peak is common
[3] * = Sometimes <14A
[4] T = Temperature of decomposition varies with chemical composition, particle-size, and heating conditions.

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7.43 Preferential orientation of clay mineral samples enhances diffraction from the basal (00*l*) spacing and tends to minimize the number and intensity of peaks from diffraction by other *hkl* planes. With preferential orientation, second, third, and fourth order peaks may be recorded in addition to the basal first order peaks. Groups of associated peaks that differ by order of diffraction are as follows:

Smectite (Mg^{2+}-glycerol):
a. 17 to 18 A.
b. 8.5 to 9 A (weak).

Chlorite, vermiculite, and smectite:
a. 14, 7, 4.7, and 3.5 A.
b. 7, 4.7, and 3.5 A weak for smectite.

Mica:
a. 10, 5 (weak in biotites and moderate in muscovites), and 3.3 A.

Kaolinite:
a. 7 and 3.5 A.

7.44 The differentiation of kaolinite and halloysite in a sample can be aided by the use of formamide (Churchman et al., 1984). The intercalation and expansion of halloysite to a d-spacing of $\approx$ 10.4 A is relatively rapid (20 to 30 min), whereas kaolinite expansion requires $\approx$ 4 h upon treatment. The procedure is as follows:

a. Lightly spray formamide as an aerosol on the dried Mg^{2+}-saturated slide.

b. Wait 15 min but not more than 1 h and X-ray approximately 7.6 to 13.5° 2θ (d = 11.6 to 6.55 A).

c. Halloysite will expand to $\approx$ 10.4 A, whereas kaolinite will remain unchanged.

d. Heating the sample to 110°C for 15 min will collapse the halloysite to $\approx$ 7 A.

e. The total amount of kaolinite and halloysite can be determined by thermal analysis. The intensity ratio of the 10.4 to 7.2 A peaks of the formamide-treated sample can be used to determine the relative percentage of halloysite and kaolinite.

8. CALCULATIONS
        X-ray diffraction produces peaks on a chart that corresponds to 2θ angle on a goniometer. Standard tables to convert θ or 2θ to crystal "d" spacings are published in the U.S. Geological Survey Circular 29 (Switzer et al., 1948) and in other publications (Brown, 1980). The crystal "d" spacings of minerals, i.e., the interval between repeating planes of atoms, can be calculated by Bragg's Law. Refer to summary of method.

9. REPORT
        From the "Detected Peaks File" and graphics chart, identify the minerals present according to the registered "d" spacings. As a first approximation, use the following peak intensities, i.e., peak

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heights above background in counts s^{-1}, to assign each layer silicate mineral to one of the 5 semiquantitative classes.

Class	Peak Height above Background (counts sec^{-1})
5 (Very Large)	>1.88 X 10^3
4 (Large)	1.12 to 1.88 X 10^3
3 (Medium)	0.36 to 1.12 X 10^3
2 (Small)	0.11 to 0.36 X 10^3
1 (Very Small)	<0.11 X 10^3

Adjust class placement to reflect area under the curve if peak is broad relative to peak height or if thermal, elemental, clay activity data, or other evidence warrant class adjustment. If there are no peaks or no evidence of crystalline components, place the sample in NX class (noncrystalline).

10. PRECISION

Precision data are not available for this procedure. Procedure 7A2i (X-ray diffraction) is semiquantitative.

11. REFERENCES

Brown, G. 1980. Appendix I (Tables for the determination of d in A from 2θ for the KA and KB radiations of copper, cobalt, and iron). *In* G.W. Brindley and G. Brown (eds.) Crystal structures of clay minerals and their x-ray identification. Mineralogical Soc. Monograph No. 5. Mineralogical Soc. Great Britain. pp 439-475.

Churchman, G.J., J.S. Whitton, G.G.C. Claridge, and B.K.G. Theng. 1984. Intercalation method using formamide for differentiating halloysite from kaolinite. Clays and Clay Minerals. 32:241-248.

Switzer, G., J.M. Axelrod, M.L. Lindberg, and E.S. Larsen 3d. 1948. U.S. Dept. Interior. Geological Survey. Circular 29. Washington, DC.

Whittig, L.D., and W.R. Allardice. 1986. X-ray diffraction techniques. *In* A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:331-362.

MINERALOGY
INSTRUMENTAL ANALYSES (7A)
THERM0GRAVIMETRIC ANALYSIS (7A4)
THERMAL ANALYZER, TGA 51 (7A4c)

1. APPLICATION

Thermal analysis defines a group of analyses that determine some physical parameter, e.g., energy, weight, or evolved substances, as a dynamic function of temperature (Tan et al., 1986; Karathanasis and Harris, 1994). Thermogravimetric analysis (TGA) is a technique for determining weight loss of a sample as it is being heated at a controlled rate. The weight changes are recorded as a function of temperature, i.e., a thermogravimetric curve, and provide quantitative information about substances under investigation, e.g., gibbsite ($Al(OH)_3$), kaolinite ($Al_2Si_2O_5(OH)_4$), and 2:1 expandable minerals (smectite and vermiculite).

2. SUMMARY OF METHOD

A 5- to 10-mg sample of soil clay is placed in a platinum sample pan, and the pan is placed in the TGA balance. The instrument records the initial sample weight. The sample is then heated from a temperature of 30 to 900°C at a rate of 20°C min^{-1} in a flowing N_2 atmosphere. The computer collects weight changes as a function of temperature and records a thermogravimetric curve. Gibbsite and kaolinite are quantified by calculating the weight loss between approximately 250 to 350°C and 450 to 550°C, respectively, and then relating these data to the theoretical weight loss of pure gibbsite or kaolinite. The weight loss is due to dehydroxylation, i.e., loss of crystal lattice water. Though not presently performed by the SSL, quantification of the 2:1 expandable minerals (smectite + vermiculite) is related to weight loss at <250°C, i.e., loss of adsorbed water (Karanthasis and Hajek, 1982; Tan et al., 1986). At this low temperature, adsorbed water is proportional to the specific area of the sample (Jackson, 1956; Karathanasis and Hajek, 1982; Mackenzie, 1970; Tan and Hajek, 1977).

3. INTERFERENCES

Organic matter is objectionable because it has a weight loss by dehydrogenation and by oxidation to CO_2 between 300 to 900°C (Tan, et al., 1986). Analysis in an inert N_2 atmosphere helps to alleviate this problem, but samples with significant organic matter should be pretreated with H_2O_2. Mineral salts that contain water of crystallization also may interfere. Samples should be washed free of any soluble salts. In some cases, weight loss from gibbsite and goethite overlap and prevent quantitative interpretation. These samples can be deferrated (procedure 6C2) to eliminate goethite.

A representative soil sample is important as sample size is small (<10 mg). Avoid large aggregates in sample, the presence of which may cause thermal interferences, i.e., differential kinetics of gas diffusion through the sample and physical movement of sample in a reaction.

In general, the same reactions that interfere with DSC/DTA also interfere with TGA determinations of kaolinite, gibbsite, and 2:1 expandable minerals. However, TGA is more sensitive to small water losses at slow rates, whereas DSC/DTA is more sensitive to large water losses at rapid rates (Tan, et al., 1986). This sensitivity difference may help to explain why kaolinite and gibbsite quantifications in TGA vs. DSC/DTA often are not equivalent, i.e., TGA estimates tend to be greater than the corresponding DSC/DTA estimates. In TGA, there is a greater probability of measuring water losses in specific temperature regimes that are not specifically associated with dehydroxylation reactions of interest. This problem is particularly apparent with illitic samples, which characteristically contain more "structural" water than ideal structural formulae would indicate (Rouston, et al., 1972; Weaver and Pollard, 1973).

Even though it is well established that various minerals lose the major portion of their crystal lattice water in different temperature ranges (Tan et al., 1986), there are overlaps in weight loss regions (WLR) of minerals which interfere in the identification and measurement of the minerals of interest. The goethite WLR (250 to 400°C) overlaps the gibbsite WLR (250 to 350°C) (Mackenzie and Berggen, 1970). The illite WLR (550 to 600°C) overlaps the high end of the kaolinite WLR (450 to 550°C) (Mackenzie and Caillere, 1975). The WLR of hydroxy-Al interlayers in hydroxy-Al interlayered vermiculite (HIV) (400 to 450°C) overlaps the low end of the kaolinite WLR (450 to 550°C), especially in

the poorly crystalline kaolinites (Mackenzie and Caillere, 1976). Similarly, the dehydroxylation of nontronites, Fe-rich dioctahedral smectites, (450 to 500°C) may interfere with kaolinite identification and measurement (Mackenzie and Caillere, 1975).

4. SAFETY

Secure high pressure N_2 tanks and handle with care. When changing the tanks, protect valves with covers. Do not program the analyzer for >950°C because it may present a safety hazard during sample analysis and cleaning cycles. Always use high quality purge gases with the TGA. Minimum purity of 99.9% is recommended. Handle hot furnace with care.

5. EQUIPMENT

5.1 Thermal analyzer, TGA 51, TA Instruments, New Castle, DE
5.2 Thermal analyzer operating system software, Thermal Analyst 2100, Version 8.10B, TA Instruments, New Castle, DE
5.3 Data analysis software, TGA Standard Data Analysis Version 5.1, TA Instruments, New Castle, DE
5.4 Computer, IBM-PC 368, MS-DOS Operating System, Version, 5.02
5.5 Thermal analyzer instrument controller (MIM), TA Instruments, New Castle, DE
5.5 Printer, Hewlett Packard, HP-7440, 8-pen plotter
5.6 N_2 gas, 99.99% purity
5.7 Two-stage gas regulators, 50 psi maximum outlet pressure
5.8 Forceps, flat-tipped
5.9 Weighing spatula
5.10 Desiccator, glass
5.11 Mortar and pestle
5.12 Sieve, 80 mesh
5.13cıʺ(5.12)Tjıʺ/F11 1 Tfıʺ12 0 9.1 -0 8.88 598.9226Tcıʺ(5.7)Tjıʺ/F7 1 Tfıʺ9.96 0 012.16-0 8.88 598.96Hssure Ncıʺ(5. 1 Tfı

5.

7.6 Turn on the N_2 purge gas and set to 100 cm^3 min^{-1} sample purge.

7.7 Place the empty platinum sample pan on quartz rod and slide into quartz furnace tube. Use the Auto Zero function in the TA 2100 software to zero the balance.

7.8 Remove the sample pan from the quartz rod. Weigh $\approx$ 10 mg of sample, i.e., <80-mesh fine-earth (<2 mm) soil fraction or derived <2-μm clay fraction, into tared sample pan. Refer to section on derived <2-μm clay fractions, Steps 7.1 to 7.4.

7.9 Use flat-tipped forceps to tap the sample pan against a hard surface several times to uniformly distribute the sample.

7.10 Carefully place sample pan on the quartz rod of the TGA microbalance.

7.11 The standard sample run heating program has a heating rate of 20°C min^{-1}, a starting temperature of 30°C, and an ending temperature of 900°C.

7.12 Immediately start the "Run" program.

7.13 At the end of sample run ($\approx$ 45 min), allow the TGA furnace to cool to 350°C.

7.14 Slide quartz furnace tube out of furnace. Pull furnace from main TGA unit and allow to cool on counter top. (Caution: Very Hot!).

7.15 Place spare furnace in TGA unit and prepare for next sample run.

7.16 To analyze data file for weight loss, enter Data Analysis menu of the Thermal Analysis 2100 System and select the TGA Standard Data Analysis software.

7.17 Display file and calculate weight loss in specific regions for selected minerals.

8. CALCULATIONS

The thermogravimetric curve is displayed on the computer monitor. The ordinate (Y) is expressed in a relative weight percentage, i.e., the initial sample weight is 100.0%. Use the computer to calculate the total change in sample weight (Δ Y), within the predetermined temperature range, as a δ sample weight percent.

$$\% \text{ Kaolinite} = \frac{(\Delta \text{ sample weight } \% \text{ } 450\text{-}550°\text{C})}{14} \times 100$$

where:
Δ sample weight = total change in sample weight expressed as relative percent
14 = percent weight of hydroxyl water lost from pure kaolinite during dehydoxylation

$$\% \text{ Gibbsite } = \frac{(\Delta \text{ sample weight } \%_{250-350^\circ C})}{34.6} \times 100$$

where:

Δ sample weight = total change in sample weight expressed as relative percent

34.6 = percent weight of hydroxyl water lost from pure gibbsite during dehydroxylation

If Fe oxides are removed prior to analysis to prevent the interference with gibbsite determination, the calculation is modified to account for weight loss due to deferration as follows:

% Gibbsite = {[Δ Sample weight x (Wt_2/Wt_1)]/34.6} x 100

where:

Wt_1 = Weight before deferration
Wt_2 = Weight after deferration

The percent weights of hydroxyl water lost from kaolinite and gibbsite are derived from the following assumed dehydroxylation reactions.

$Si_2Al_2O_5(OH)_4 \quad ---> \quad 2SiO_2 + Al_2O_3 + 2H_2O$
(kaolinite)

$2Al(OH)_3 \quad ---> \quad Al_2O_3 + 3H_2O$
(gibbsite)

Using kaolinite as an example, percent weight of hydroxyl water lost is calculated from the following formula weights.

$Si_2Al_2O_5(OH)_4 = 258$ g mol^{-1}
$2H_2O = 36$ g mol^{-1}

Percent weight of hydroxyl water lost = (36/258) x 100 = 14%

9. REPORT

Report percent gibbsite and/or kaolinite to nearest whole number.

10. PRECISION

Precision data are not available for this procedure.

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MINERALOGY
INSTRUMENTAL ANALYSES (7A)
DIFFERENTIAL SCANNING CALORIMETRY (7A6)
THERMAL ANALYZER, DSC 910S (7A6b)

1. APPLICATION

Calorimetry measures specific heat or thermal capacity of a substance. Differential scanning calorimetry (DSC) is a calorimetric technique in which the difference in the rate of heat flow between a sample and a reference material is measured as materials are held isothermal to one another. The DSC directly measures the magnitude of an energy change (H, enthalpy or heat content) in a material undergoing an exothermic or endothermic reaction. DSC is commonly used to quantify gibbsite ($Al(OH)_3$) and kaolinite ($Al_2Si_2O_5(OH)_4$) in soils and clays by measuring the magnitude of their dehydroxylation endotherms which are between approximately 250 to 350°C and 450 to 550°C, respectively (Karathanasis and Hajek, 1982; Jackson, 1956; Mackenzie and Berggen, 1970; Mackenzie, 1970).

2. SUMMARY OF METHOD

An 8 mg sample of soil clay is weighed into an aluminum sample pan and placed in the DSC sample holder. The sample and reference pans are heated under flowing N_2 atmosphere from a temperature of 30 to 600°C at a rate of 10°C min^{-1}. Data are collected by the computer and a thermograph is plotted. Gibbsite and kaolinite are quantified by measuring the peak area of any endothermic reactions between 250 to 350°C and 450 to 550°C, respectively, and by calculating the H of the reaction. These values are related to the measured enthalpies of standard mineral specimens (gibbsite and kaolinite).

3. INTERFERENCES

Organic matter is objectionable because it produces irregular exothermic peaks in air or O_2, commonly between 300 to 500°C, which may obscure important reactions from the inorganic components of interest (Schnitzer and Kodama, 1977). Analysis in an inert N_2 atmosphere helps to alleviate this problem. Pretreatment with H_2O_2 may be necessary for soils with significant amounts of organic matter. Mineral salts that contain water of crystallization also may be interferences. Samples should be washed free of any soluble salts.

Use a representative soil sample as sample size is small (<10 mg). Avoid large aggregates in sample, the presence of which may cause thermal interferences because of differential kinetics of gas diffusion through the sample and physical movement of sample in a reaction.

The dehydroxylation of goethite is between 250 to 400°C and may interfere with the identification and integration of the gibbsite endotherm (250 to 350°C) (Mackenzie and Berggen, 1970). The dehydroxylation of illite is between 550 to 600°C and partially overlaps the high end of the kaolinite endotherm (450 to 550°C), resulting in possible peak integrations (Mackenzie and Caillere, 1975). The dehydroxylation of hydroxy-Al interlayers in hydroxy-Al interlayered vermiculite (HIV) is between 400 to 450°C and may interfere with the low end of the kaolinite endotherm (450 to 550°C), especially in the poorly crystalline kaolinites (Mackenzie and Caillere, 1976). Similarly, the dehydroxylation of nontronites, Fe-rich dioctahedral smectites is between 450 to 500°C and may interfere with kaolinite identification and measurement (Mackenzie and Caillere, 1975).

4. SAFETY

Secure high pressure N_2 tanks and handle with care. When changing the tanks, valves should be protected with covers. Do not heat aluminum sample pans >600°C. Aluminum melts at 660°C, and the sample pans alloy with and destroy the DSC cell. Always use high quality purge gases with the DSC. Minimum purity of 99.9% is recommended.

5. EQUIPMENT

5.1 Thermal analyzer, DSC 910S, TA Instruments, New Castle, DE

5.2 Thermal analyzer operating system software, Thermal Analyst 2100, Version 8.10B, TA
Instruments, New Castle, DE
5.3 Data analysis software, TGA Standard Data Analysis Version 4.0, TA Instruments, New Castle, DE
5.4 Computer, IBM-PC 368, MS-DOS Operating System, Version, 5.02
5.5 Thermal analyzer instrument controller (MIM), TA Instruments, New Castle, DE
5.6 Autosampler, 920 Auto DSC, TA Instruments, New Castle, DE
5.7 Printer, Hewlett Packard, HP-7440, 8-pen plotter
5.8 Two-stage gas regulators, 50 psi maximum outlet pressure
5.9 Electronic balance, ±0.1-mg sensitivity, Mettler AE160
5.10 Forceps, flat-tipped
5.11 Weighing spatula
5.12 Desiccator
5.13 Mortar and pestle
5.14 Sieve, 80 mesh
5.15 N_2 gas, 99.99% purity
5.16 Kaolinite, standard, poorly crystalline, Georgia Kaolinite, Clay Minerals Society, Source Clay
Minerals Project, sample KGa-2.
5.17 Gibbsite, standard, Surinam Gibbsite, SSL, 67L022.

6. REAGENTS

6.1 Magnesium nitrate saturated solution $[Mg(NO_3)_2 \cdot 6H_2O]$
6.2 Ethanol

7. PROCEDURE

Derive <2μm Clay Fractions

7.1 Prepare Na-saturated clay as in procedure 7A2i, preparation of clay suspension, Steps 7.8 to 7.19.

7.2 Dry the clay suspension and transfer to mortar. Moisten sample with ethanol and grind with pestle
to make a homogeneous slurry.

7.3 Air-dry sample using flowing air in hood. Lightly grind sample with pestle to make a homogeneous
powder. Transfer to original container for storage until use.

7.4 Prior to analysis, sieve sample with 80-mesh screen. Equilibrate sample overnight over a saturated
magnesium nitrate solution (55% rh) in a glass desiccator.

DSC Operation

7.5 Set-up the instrument and calibrate. Refer to Appendix XXIII, Thermal Analyzers, and
manufacturer's manual for operation of the DSC. Samples can be analyzed singly or with the
autosampler for multiple samples.

7.6 Weigh ≈ 8 mg of sample, i.e., <80-mesh fine-earth (<2mm) soil fraction or derived <2-μm clay
fraction, into tared aluminum sample pan. Refer to section on derived <2-μm clay fractions, Steps 7.1 to
7.4.

7.7 Use flat-tipped forceps to remove aluminum sample pan from balance. Drop sample from a 4- to 5-
mm height to uniformly distribute sample in pan. Return the sample pan with sample to the balance and
record weight to nearest ±0.1 mg. This weight is entered into computer in appropriate menu.

7.8 Carefully place the aluminum sample pan in the center of DSC platinum sample side (front section) of sample holder.

7.9 Place empty aluminum sample pan in reference side (back section) of sample holder.

7.10 Cover the DSC cell.

7.11 The standard sample run heating program has a heating rate of 10°C min^{-1}, a starting temperature of 30°C, and an ending temperature of 600°C.

7.12 Start the "Run" program.

7.13 When the run is complete, data are analyzed by entering the Data Analysis 2100 System and selecting the DSC Standard Data Analysis Program.

7.14 Display file and calculate joules g^{-1} for the mineral endotherm.

8. CALCULATIONS

8.1 The area under a curve representing an endothermic dehydroxylation reaction is proportional to the enthalpy (H) of the reaction. The enthalpy is calculated with the DSC software per g of kaolinite or gibbsite (joules g^{-1}) as appropriate.

8.2 Analyze each of the standard clays on the DSC. Calculate the enthalpy per g for the endothermic reactions of the standard kaolinite and gibbsite (joules g^{-1}).

8.3 The purity of the standard clays are evaluated via TGA (7A4c). Adjust the DSC results of the standards using the purity measurements from TGA.

8.4 Determine the amount of kaolinite and gibbsite in soil samples by dividing the enthalpy of the sample (joules g^{-1}) by the enthalpy of the standard (joules g^{-1}). Multiply this result by 100 to express as a percentage.

9. REPORT
Report percent kaolinite and/or gibbsite to the nearest whole number.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
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MINERALOGY
OPTICAL ANALYSIS (7B)[1]
GRAIN STUDIES, ANALYSIS AND INTERPRETATION (7B1)

1. MINERALS

Identification criteria: Important properties in grain identification are listed below in approximate order of ease and convenience of determination. Estimates of several of these properties often allow identification of a grain so that detailed or extremely accurate measurements are seldom necessary. In the finer soil separates, grain identification may be impossible because the grains may be too small or not in the right position to permit measurement of some properties, e.g., optic angle or optic sign. A process to help practice estimating properties is to crush, sieve, and mount a set of known minerals and to compare these known standards to unknowns.

Refractive index can be estimated by relief or can be accurately determined by using calibrated immersion liquids. When relief is used to estimate refractive index, the grain shape, color, and surface texture must be considered, i.e., thin platy grains may be estimated low, whereas colored grains and grains with rough, hackly surface texture may be estimated to be high. Estimation is aided by comparing an unknown with known minerals.

Relief is an expression of the difference in refractive index between the grain and the mounting medium. The greater the difference, the greater the relief. The analogy is to topographic relief. When viewed through the microscope, grains with high relief are distinguished, whereas grains with low relief tend to fade into the background. The SSL selects a mounting medium with an index of refraction close to quartz, i.e., quartz has low relief. Most other minerals are distinguished by comparison.

Becke line is a bright halo of light that forms near the contact of the grain and the mounting medium because of the difference in refractive index of the two. As the plane of focus is moved upward through the grain, the Becke line appears to move into the component with the higher refractive index. In Petropoxy 154$_{TM}$, the Becke line moves away from potassium feldspar (index of refraction <1.54) but moves into mica (index of refraction >1.54).

Birefringence is the difference between the highest and lowest refractive index of the mineral. Accounting for grain thickness and orientation, the birefringence is estimated by interference color. Interference color is observed when an anisotropic mineral is viewed between crossed-polarized light. Several grains of the same species must be observed because the grains may not all lie in positions that show the extremes of refractive index. For example, mica has high birefringence but appears low when the platy mineral grain is perpendicular to the microscope axis because the refractive indices of the two crystallographic directions in the place of the plates are very close together. The carbonate minerals have extremely high birefringence (0.17 to 0.24). Most of the ferrogmagnesian minerals are intermediate (0.015 to 0.08). Orthoclase feldspar and apatite are low (0.008) and very low (0.005), respectively.

Color helps to discriminate among the heavy minerals. Pleochroism is the change in color or light absorption with stage rotation when the polarizer is inserted. Pleochroism is a good diagnostic characteristic for many colored minerals. Tourmaline, hypersthene,and staurolite are examples of pleochroic minerals.

Shape, cleavage, and crystal form are characteristic or unique for many minerals. Cleavage may be reflected in the external form of the grain or may appear as cracks within the grain that show as regularly repeated straight parallel lines or as sets of lines that intersect at definite repeated angles. The crystal shape may be different from the cleavage-fragment shape. Plagioclase feldspars, kyanite, and the pyroxenes have strong cleavage. Zircon and rutile usually appear in crystal forms.

Extinction angle and character of extinction observed between crossed-polarized light are important criteria for some groups of minerals. To measure extinction angles, the grain must show its cleavage or crystal form. These angles may be different along different crystallographic axes. Some minerals have sharp, quick total extinction, whereas other minerals have more gradual extinction. In some minerals with high light dispersion, the interference color dims and changes at the extinction position.

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[1] The discussion of identification and significance of minerals, microcrystalline aggregates, and amorphous substances in optical studies of grain mounts was modified by Warren C. Lynn, Research Soil Scientist, NSSC, NRCS, Lincoln, NE from material prepared by John G. Cady (1965).

MINERALOGY
OPTICAL ANALYSIS (7B)[1]
GRAIN STUDIES, ANALYSIS AND INTERPRETATION (7B1)

Optic sign, optic angle, and sign of elongation are useful, if not essential, determinations but are often difficult, unless grains are large or in favorable orientation. Determination of optic sign requires that the grains show dim, low-order interference colors or show no extinction. Grains with bright colors and with sharp, quick extinction rarely provide usable interference figures.

Particular mineral species: The following are the outstanding diagnostic characteristics of the most commonly occurring minerals and single-particle grains in the sand and silt fractions of soils. The refractive indices that are provided are the intermediate values.

Quartz has irregular shapes. The refractive index of quartz (1.54) approximates that of the epoxy (Petropoxy 154$_{TM}$) mounting medium. The Becke line may be split into yellow and blue components. The interference colors are low order but are bright and warm. There is sharp extinction with a small angle of rotation, i.e., "blink extinction". Crystal forms are sometimes observed and usually indicate derivation from limestone or other low-temperature secondary origin.

Potassium feldspars: Orthoclase may resemble quartz, but the refractive index (1.52) and birefringence are lower than that of quartz. In addition, orthoclase may show cleavage. *Microcline* has a refractive index of 1.53. The Becke line moves away from the grain with upward focus. A twinning intergrowth produces a plaid or grid effect between crossed-polarized light that is characteristic of microcline. *Sanidine* has the same refractive index and birefringence as other potassium feldspars. Grains are usually clear and twinning is not evident. In sanidine, the 2V angle is low (12°) and characteristic. The 2V angle is the acute angle between two optic axes, or more simply, the optical axial angle.

Plagioclase feldspars have refractive indices that increase with an increase in the proportion of calcium. The refractive index of the sodium end-member albite (1.53) is lower than that of quartz, but the refractive index of the calcium end-member anorthite (1.58) is noticeably higher than that of quartz. Some *oligoclase* has the same refractive index as quartz which prevents distinctions by the Becke line. Plagioclase feldspars usually show a type of twinning (defined as albite twinning) that appears as multiple alternating dark and light bands between crossed-polarized light. Cleavage is good in two directions parallel to (00$\bar{1}$) and (010), often producing lathlike or prismatic shapes.

Micas occur as platy grains that are often very thin. The plate view shows very low birefringence, whereas the edge view shows a very high birefringence. Plates are commonly equidimensional and may appear as hexagons or may have some 60° angles. *Biotite* is green to dark brown. Green grains may be confused with chlorite. Paler colors, a lowering of refractive index, and a distortion of the extinction and interference figure indicate weathering to *hydrobiotite* or *vermiculite*. *Muscovite* is colorless. Muscovite has a moderate refractive index (1.59) in the plate view and an interference figure that shows a characteristic 2V angle of 40° which can be used as a standard for comparing 2V angles of other materials.

Amphiboles are fibrous to platy or prismatic minerals with slightly inclined extinction, or occasionally with parallel extinction. Color and refractive index increase as the Fe content increases. Amphiboles have good cleavage at angles of ~ 56 and 124°. Refractive index of the group ranges from 1.61 to 1.73. *Hornblende* is the most common mineral of the amphiboles. Hornblende is slightly pleochroic; usually has a distinctive color close to olive-green; has inclined extinction; and is often used as an indicator of weathering.

Pyroxenes: Enstatite and hypersthene are prismatic and have parallel extinction. Hypersthene has unique and striking green-pink pleochroism. *Augite* and *diopside* have good cleavage at angles close to 90° and large extinction angles. Colors usually are shades of green. Refractive indices in the pyroxenes (1.65 to 1.79) are higher than in the amphiboles.

Olivine is colorless to very pale green and usually irregular in shape (weak cleavage). Olivine has vivid, warm interference colors. Olivine is an easily weathered mineral and may have cracks or seams filled with serpentine or goethite.

Staurolite is pleochroic yellow to pale brown and sometimes contains holes, i.e., the "Swiss cheese" effect. The refractive index is ~ 1.74. Grains may have a foggy or milky appearance which may be caused by colloidal inclusions.

Epidote is a common heavy mineral, but the forms that occur in soils may be difficult to identify positively. Typical epidote is unmistakable with its high refractive index (1.72 to 1.76), strong birefringence, and a pleochroism that includes the pistachio-green color. Commonly, grains show an optic axis interference figure with a 2V angle that is nearly 90°. However, epidote is modified by weathering or metamorphism to colorless forms with lower birefringence and refractive index. *Zoisite* and *clinozoisite* in the epidote group are more common than some of the literature indicates. These minerals of the epidote group commonly appear as colorless, pale-green, or bluish-green, irregularly shaped or roughly platy grains with high refractive index (1.70 to 1.73). Most of these minerals show anomalous interference colors (bright pale blue) and no complete extinction and can be confused with several other minerals, e.g., kyanite and diopside. Identification usually depends on determination of properties for many grains.

Kyanite is a common mineral but is seldom abundant. The pale blue color, the platy, angular cleavage flakes, the large cleavage angles, and the large extinction angles usually can be observed and make identification easy.

Sillimanite and *andalusite* resemble each other. These minerals are fibrous to prismatic with parallel extinction. However, their signs of elongation are different. In addition, sillimanite is colorless, and andalusite commonly has a pink color.

Garnet is found in irregularly shaped, equidimensional grains that are isotropic and have high refractive index (≥ 1.77). Garnet of the fine sand and silt size is often colorless. Pale pink colors are diagnostic in the larger grains.

Tourmaline has a refractive index of 1.62 to 1.66. Prismatic shape, strong pleochroism, and parallel extinction are characteristic. Some tourmaline is almost opaque when at right angles to the vibration plate of the polarizer.

Zircon occurs as tetragonal prisms with pyramidal ends. Zircon has very high refractive index (>1.9), parallel extinction, and bright, strong interference colors. Broken and rounded crystals frequently are found. Zircon crystals and grains are almost always clear and fresh appearing.

Sphene, in some forms, resembles zircon, but the crystal forms have oblique extinction. The common form of sphene, a rounded or subrounded grain, has a color change through ultrablue with crossed polarizers instead of extinction because of its high dispersion. Sphene is the only pale-colored or colorless high-index mineral that provides this effect. The refractive index of sphene is slightly lower than that of zircon, and the grains are often cloudy or rough-surfaced.

Rutile grains have prismatic shape. The refractive index and birefringence are extremely high (2.6 to 2.9). The interference colors usually are obscured by the brown, reddish-brown, or yellow colors of the mineral. Other TiO_2 minerals, *anatase* and *brookite*, also have very high refractive indices and brown colors and may be difficult to distinguish in small grains. The anatase and brookite usually occur as tabular or equidimensional grains.

Apatite is common in youthful soil materials. Apatite has a refractive index slightly <1.63 and a very low birefringence. Crystal shapes are common and may appear as prisms. Rounding by solution produces ovoid forms. Apatite is easily attacked by acid and may be lost in pretreatments.

Carbonates: Calcite, dolomite, and siderite, in their typical rhombohedral cleavage forms, are easily identified by their extremely high birefringence. In soils, these minerals have other forms, e.g., scales and chips; cements in aggregates; microcrystalline coatings or aggregates; and other fine-grained masses that are often mixed with clay and other minerals. The extreme birefringence is always the identification clue and is shown by the bright colors between crossed-polarized light and by the marked change in relief when the stage is rotated with one polarizer in. The microcrystalline aggregates produce a twinking effect when rotated between crossed-polarized light. These three minerals have differences in their refractive indices which may be used to distinguish them. Siderite is the only one with both indices >Petropoxy 154$_{TM}$. It is more difficult to distinguish calcite from dolomite, and additional techniques such as staining may be used.

Gypsum occurs in platy or prismatic flat grains with refractive index approximately equal to orthoclase.

MINERALOGY
OPTICAL ANALYSIS (7B)[1]
GRAIN STUDIES, ANALYSIS AND INTERPRETATION (7B1)

Opaque minerals, of which *magnetite* and *ilmenite* are the most common, are difficult to identify, especially when they are worn by transportation or otherwise affected by weathering. Observations of color and luster by reflected light, aided by crystal form if visible, are the best procedures. Magnetic separations help to confirm the presence of magnetite and ilmenite. Many grains that appear opaque by plain light can appear translucent if viewed between strong crossed-polarized light. Most grains that behave in this way are altered grains or aggregates and are not opaque minerals.

2. MICROCRYSTALLINE AGGREGATES AND AMORPHOUS SUBSTANCES

Identification criteria: Most microcrystalline aggregates have one striking characteristic feature, i.e., they show birefringence but do not have definite, sharp, complete extinction between crossed-polarized light. Extinction may occur as dark bands that sweep through the grain or parts of the grain when the stage is turned or may occur in patches of irregular size and shape. With a few exceptions, e.g., well-oriented mineral pseudomorphs and certain clay-skin fragments, some part of the grain is bright in all positions. Aggregates and altered grains should be examined with a variety of combinations of illumination and magnification in both plain and polarized lights. The principal properties that can be used to identify or at least characterize aggregates are discussed below.

Color, if brown to bright red, is usually related to Fe content and oxidation. Organic matter and Mn may contribute black and grayish-brown colors.

Refractive index is influenced by a number of factors, including elemental composition, atom packing, water content, porosity, and crystallinity. Amorphous (noncrystalline) substances have a single index of refraction, which may vary depending on chemical composition. For example, allophane has a refractive index of 1.47 to 1.49, but the apparent refractive index increases with increasing inclusion of ferrihydrite (noncrystalline Fe oxide) in the mineral.

Strength of birefringence is a clue to the identity of the minerals. Even though the individual units of the aggregate are small, birefringence can be estimated by interference color and brightness. Amorphous substances, having only a single index of refraction, exhibit no birefringence and are isotropic between crossed-polarized light.

Morphology may provide clues to the composition or origin of the aggregate. Some aggregates are pseudomorphs of primary mineral grains. Characteristics of the original minerals, i.e., cleavage traces, twining, or crystal form can still be observed. Morphology can sometimes be observed in completely altered grains, even in volcanic ash shards and basalt fragments. Other morphological characteristics may be observed in the individual units or in the overall structure, e.g., the units may be plates or needles, or there may be banding.

Particular species of microcrystalline aggregates and amorphous substances: For purposes of soil genesis studies, the aggregates that are present in sand or silt fractions are not of equal significance. Some are nuisances but must be accounted for, and others are particles with important diagnostic value. Useful differentiating criteria for some of the commonly occurring aggregate types are discussed below.

Rock fragments include chips of shale, schist, and fine-gained igneous rocks, e.g., rhyolite. Identification depends on the recognition of structure and individual components and the consideration of possible sources.

Clay aggregates may be present in a wide variety of forms. Silt and sand that are bound together into larger grains by a nearly isotropic brownish material usually indicate faulty dispersion. Clay skins may resist dispersion and consequently may appear as fragments in grain mounts. Such fragments are usually brown or red and translucent with wavy extinction bands. Care is required to distinguish these fragments from weathered biotite. Clay aggregates may be mineral pseudomorphs. Kaolin pseudomorphs of feldspar commonly are found. Montmorillonite aggregates, pseudomorphic of basic rock minerals, have been observed. In this form, montmorillonite shows high birefringence and an extinction that is mottled or patchy on a small scale. Coarse kaolinite flakes, books, and vermicular aggregates resist dispersion and may be abundant in sand and silt. These particles may resemble muscovite, but they are cloudy; show no definite extinction; and have very low birefringence. Many cases of anomalously high cation exchange

capacity (CEC) of sand and silt fractions that are calculated from whole soil CEC and from clay CEC and percent content, can be accounted for by the occurrence of these aggregates in the sand and silt fractions.

Volcanic glass is isotropic and has a low refractive index, lower than most of the silicate minerals. The refractive index ranges from 1.48 in the colorless siliceous glasses to as high as 1.56 in the green or brown glasses of basalt composition. Shapes vary, but the elongated, curved shard forms, often with bubbles, are common. This glassy material may adhere to or envelop other minerals. Particles may contain small crystals of feldspar or incipient crystals with needles and dendritic forms. The colorless siliceous types (acidic, pumiceous) are more common in soils as the basic glasses weather easily. Acidic glasses are more commonly part of "ash falls", as the magma usually is gaseous and explosive when pressure is released. Basic glasses are more commonly associated with volcanic flow rocks which are usually not gaseous.

Allophane is present in many soils that are derived from volcanic ash. Allophane seldom can be identified directly, but its presence can be inferred when sand and silt are cemented into aggregates by isotropic material with low refractive index, especially if volcanic ash shards are also present.

Opal, an isotropic material, occurs as a cementing material and in separate grains, some of which are of organic origin, i.e., plant opal, sponge spicules, and diatoms. The refractive index is very low (<1.45), which is lower than the value for volcanic ash. Identification may depend in part on form and occurrence.

Iron oxides may occur as separate grains or as coatings, cementing agents, and mixtures with other minerals. Iron oxides impart brown and red colors and raise the refractive index in the mixtures. *Goethite* is yellow to brown. Associated red areas may be hematite. These red varieties have a refractive index and birefringence that are higher and seem to be better crystallized, often having a prismatic or fibrous habit. Aggregates have parallel extinction. In oriented aggregates, the interference colors often have a greenish cast. *Hematite* has higher refractive index than goethite and is granular rather than prismatic. Large grains of hematite are nearly opaque.

Gibbsite often occurs as separate, pure, crystal aggregates, either alone or inside altered mineral grains. The grains may appear to be well-crystallized single crystals, but close inspection between crossed-fmic ferenc01 T shows patchy, banded extinction, indicating intergrown aggregates. Gibbsite is colorless. The refractive index (1.56 to 1.58) and the birefringence are higher for gibbsite than the corresponding values for quartz. The br01 T interference colors and aggregate extinction are characteristic of gibbsite.

Chalcedony is a microcrystalline form of quartz that was formerly considered a distinct species. Chalcedony occurs as minute quartz crystals and exhibits aggregate structure with patchy extinction between crossed-fmic ferenc01 T. It may occur in nodules of limestone deposits and may be a pseudomorphic replacement in calcareous fossils. The refractive index is sc01 Tly lower than that of quartz, and the birefringence is lower than that of gibbsite. *Chert* is a massive form of chalcedony.

Glauconite occurs in aggregates of small micaceous grains with high birefringence. When fresh, glauconite is dark green and almost opaque, but it weathers to brown and more translucent forms. Glauconite is difficult to identify on optical evidence alone.

Titanium oxide aggregates have been tentatively identified in the heavy mineral separates of many soils. These bodies have an extremely high refractive index and high birefringence similar to rutile. The yellow to gray colors are similar to those of anatase. The TiO_2 aggregates are granular and rough-surfaced. This growth habit with the little spurs and projections suggests that TiO_2 aggregates may be secondary.

MINERALOGY
OPTICAL ANALYSES (7B)
GRAIN STUDIES (7B1)
SEPARATION BY HEAVY LIQUIDS

APPLICATION

The sand and silt fractions of most soils are dominated by quartz or by quartz and feldspars (Cady, 1965). These minerals have a relatively low specific gravity (2.57 to 2.76). The large numbers of "heavy" mineral grains (specific gravity >2.8 or 2.9) with a wide range of weatherability and diagnostic significance may be only a small percentage of the grains (Cady, 1965). However, these "heavy" minerals are often indicative of provenance, weathering intensities, and parent material uniformity (Cady, Wilding, and Drees, 1986).

PROCEDURE

To study "heavy" minerals, a common practice is to concentrate these grains by specific-gravity separations in a heavy liquid. The procedure is rarely used at the SSL but is done on occasion for special studies.

Micas are difficult to separate because of their shape and because a little weathering, especially in biotite, significantly decreases the specific gravity. These differences in density in biotite may be used to concentrate weathered biotite in its various stages of alteration .

Separation of grains by heavy liquids is most effective when grains are clean. Organic matter may prevent wetting and cause grains to clump or raft together. Light coatings may cause heavy grains to float, and iron-oxide coatings may increase specific gravity. In some kinds of materials, an additional technique is to separate and weigh the magnetic fraction, either before or after the heavy-liquid separation.

Concentrate the "heavy" minerals, i.e., specific gravity >2.8 or 2.9, by specific-gravity separations in a heavy liquid. The reagent of choice is sodium polytungstate (density 2.8 g^{-1} mL). Dilute the sodium polytungstate with distilled water to obtain required densities <2.8 g^{-1} mL. Use a specific gravity $\approx$ 2.5, to concentrate volcanic glass, plant opal, or sponge spicules. When using this liquid, avoid contact with skin and work in a well-ventilated area.

Separation by specific gravity alone in separatory funnels, cylinders or various kinds of tubes is usually adequate for grains >0.10 mm. Separation by centrifuging is required for grains <0.10 mm. Use pointed, 15-ml centrifuge tubes for these separations.

Decant the light minerals after inserting a smooth bulb glass rod to stop off the tapered end of centrifuge tube. Alternatively, remove the heavy minerals by gravity flow using a lower stopcock or maintain the heavy minerals in place by freezing the lower part of tube.

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MINERALOGY
OPTICAL ANALYSES (7B)
GRAIN STUDIES (7B1)
GRAIN MOUNTS, EPOXY (7B1a)

1. APPLICATION

Grain counts are used to identify and quantify minerals in the coarse silt and sand fractions of soils. These data may be used to classify pedons in soil mineralogy families in *Soil Taxonomy* and to study lithology, soil weathering, or provenance.

2. SUMMARY OF METHOD

In particle-size analysis (procedures 3B1 or 3B2), soils are dispersed so that material <20 μm in diameter is separated by settling and decantation, and the sand and coarse silt fractions are separated by sieving. Refer to procedure 7B1 for the separation by heavy liquids of the less abundant minerals with a specific gravity >2.8 or 2.9.

Following sample selection, permanent mounts are prepared. The grains of the fraction(s) of interest are mounted in a thermo-setting epoxy cement with a refractive index of 1.54. The grains are then counted and identified under a petrographic microscope.

A mineralogical analysis of a sand or silt fraction may be entirely qualitative, or it may be quantitative to different degrees (Cady, 1965). The SSL performs a quantitative analysis. Data are reported as a list of minerals and an estimated quantity of each mineral as a percentage of the grains counted. The percentages of minerals are obtained by identifying and counting a minimum of 300 grains on regularly spaced line traverses that are 2 mm apart.

The identification procedures and reference data on minerals are described in references on sedimentary petrography (Deer et al., 1992; Durrell, 1948; Kerr, 1977; Krumbein and Pettijohn, 1938; Milner, 1962) and optical crystallography (Bloss, 1961).

3. INTERFERENCES

The sample must be thoroughly mixed because the subsample on the slide is small. If grains are coated with clay or if aggregates of finer material remain in the fraction that is counted, results may be skewed. Variations in the time or temperature of heating the epoxy may result in either matrix stress or variation in the refractive indexes of the epoxy. Do not use steel needles or spatulas because magnetic minerals may adhere to steel resulting in uneven distribution of grains on the slide.

4. SAFETY

Heat the epoxy in a fume hood. Use caution in handling hot glass slides. Use heat resistant gloves as needed. Immediately wash or remove any epoxy that comes in contact with the skin. Carefully handle slides and cover slips to avoid cuts.

5. EQUIPMENT
5.1 Petrographic microscope slides, precleaned, 27 x 46 mm
5.2 Cover slips, glass, 25 x 25 mm
5.3 Hot plate
5.4 Micro-spatula
5.5 Dissecting needle
5.6 Plywood covered with formica (6 x 8 x 1.25 cm)
5.7 Timer
5.8 Polarizing petrographic microscope
5.9 Tally counter

6. REAGENTS
6.1 Petropoxy 154$_{TM}$ Resin and Curing Agent, Palous Petro Products, Rt 1, Box 92, Palouse, WA
6.2 Index immersion oils

MINERALOGY
OPTICAL ANALYSES (7B)
GRAIN STUDIES (7B1)
GRAIN MOUNTS, EPOXY (7B1a)

7. PROCEDURE

Sample Selection and Grain Mount Preparation

7.1 Refer to the analysis request sheets. Record optical mineralogy requests in the "Request List for Optical Mineralogy" file. Note any special instructions by soil scientists. Sample selection depends on the purpose of analysis. In most work, e.g., checks on discontinuities or estimation of degree of weathering in different soil horizons, the study of those fractions that comprise a significant quantitative part of the soil is important.   The SSL convention is to count the most abundant fraction, i.e., coarse silt (CSI), very fine sand (VFS) or fine sand (FS), especially if the fraction is clearly larger. This procedure works well in the establishment of mineralogy families for *Soil Taxonomy*. This procedure may result in different size fractions being counted for different horizons within a single pedon. If fractions are rather equal in abundance, the VFS is selected as it provides the widest range of information. The SSL does not count multiple fractions for a single sample, or count combined fractions, or present the data as weighted averages. If it is appropriate to count the same size fraction for each horizon within a pedon or project such as for a study of soil lithology, this request must be specified by the project coordinator.

7.2 Refer to the "Request List for Optical Mineralogy" file for daily work or check the sand box lids to determine which sands have been fractionated. Sands are fractionated during particle-size analysis (PSA) (procedure 3B1 or 3B2). For CP and RP projects, the Grain Mount Index Program on the CMS Mainframe Computer generates a list as follows:

a. Sample numbers by project

b. Type of count requested (full grain count or glass count)

c. Percent of <2-mm fraction for CSI, VFS, or FS as determined by SSL PSA.

7.3 If the particle-size section does not provide a sand and coarse silt separate, derive these fractions by gravity sedimentations at 20 μm and sieving the 20-μm to 2.0-mm material as follows:

7.3.1 Disperse the sample in sodium hexametaphosphate as described in procedure 7A2i.

7.3.2 Pour the soil suspension into a 200-mL beaker that has a line marked 5 cm above the bottom.

7.3.3 Add DDI water to the beaker up to the 5-cm mark.

7.3.4 Stir the suspension and allow to settle 2.0 min. Use a stopwatch.

7.3.5 Decant and discard the suspension containing the clay and fine silt.

7.3.6 Repeat Steps 7.3.3 to 7.3.5 until the supernatant is clear or reasonably so.

7.3.7 Transfer the sediment to a drying dish and dry at 110°C.

7.3.8 Sieve the dried sample to isolate the individual fractions.

7.4 Review the PSA data and select samples. Make grain mounts from the one or two most abundant fractions, preferably from the CSI, VFS, or FS. Record sample numbers and respective PSA data.

7.5 Turn on hot plate and allow to equilibrate at 125°C for ≈ 1 h.

7.6 Mix a small amount of Petropoxy 154$_{TM}$ resin and curing agent (1:10 ratio resin to curing agent) in a clean graduated plastic beaker that is provided with the reagents.

7.7 To avoid the introduction of air bubbles, mix in slow, even figure-eights.

7.8 Heat for 4 min at 125°C.

7.9 Cool mixture to room temperature. If mixture is not to be used for a day or longer, store in refrigerator.

7.10 Remove mixture from refrigerator at least 40 min prior to use. If the petropoxy crystallizes, warm mixture until crystals dissolve.

7.11 At the base of the glass slides, record the grain size fraction (COSI, VFS, FS, etc.) and SSL sample number. An example is as follows:

VFS
88P1962

7.12 Obtain sand vials and/or silt dishes. Arrange in an orderly manner. Work with 6 slides and samples at a time.

7.13 Remove lids from sand vials and place upside down in front of respective vials. Remove capsule (VFS or FS) from vial. Rotate capsule to mix contents and place in lid. Stir with a micro-spatula to mix coarse silts.

7.14 Use a small, rounded glass rod to drop petropoxy mixture on the upper middle of each slide. Use one drop of petropoxy for COSI or VFS and two drops for FS.

7.15 Use a micro-spatula to add the mixed grains to petropoxy. Use larger amounts for smaller fractions. The analyst's technique of adding the appropriate amount of petropoxy and of making grain counts on prepared slides develops with experience. Use a dissecting needle to slowly and carefully stir the grains into the petropoxy. Avoid introduction of air bubbles.

7.16 Gently place one cover slip (check to be certain) on the petropoxy. Avoid fingerprints. Allow the petropoxy to spread under the cover slip. Center the cover slip at top center of glass microscope slide so that there is a parallel, equidimensional border around the top and sides of slide.

7.17 To ensure the uniform distribution of grains and the removal of air bubbles, use a dissecting needle to gently tap or press down cover slip. If necessary, the analyst may need to recenter the cover slip. Be careful not to crack cover slip.

7.18 Align a batch of 6 slides in two rows on center of hot plate.

7.19 Set timer and heat slides at 125°C for 10 min. Time can be adjusted by experience. As a rule, when epoxy is set, it has cured to yield a refractive index of 1.540. Longer heating may result in a distortion of the optical characteristics of the petropoxy and a refractive index of 1.540.

7.20 As one batch of slides heats, prepare the next batch. After heating for 10 min, slide the glass slides off the hot plate onto the formica block. Allow to cool.

MINERALOGY
OPTICAL ANALYSES (7B)
GRAIN STUDIES (7B1)
GRAIN MOUNTS, EPOXY (7B1a)

7.21 Examine the grain mount for quality. The epoxy medium should be isotropic. The presence of anisotropic stress lines around grains under X-Nicols may interfere with observation of optical properties. Remake any unsatisfactory grain mounts. Place satisfactory mounts in a microscope slide file box. Neatly record project number and grain mount positions on interior of box lid, and record box number(s) in the "Request List for Optical Mineralogy" and the "Location Index for Sand Grain Slides by States" files.

7.22 Return the petropoxy mixture to the refrigerator in order to extend shelf life of compound.

Observations of Grain Mount

7.23 Record raw grain count data in a logbook. Most grain counts are made with a 8X magnification ocular and either a 10X or 16X magnification objective lens.

7.24 The first step is to seat the grain mount in the mechanical stage of the microscope and to survey the slide with a low-power magnification power (10X) to become familiar with the grain assemblage and to make a rough estimate of the relative abundance of minerals and other grains.

7.25 Initially, identify the most abundant minerals as there are probably the easiest to identify, and their elimination decreases the number of possibilities to consider in identifying the more difficult minerals. Furthermore, there are certain likely and unlikely assemblages of minerals, and an awareness of the overall types that are present gives clues to the minor species that may be expected.

7.26 Note the observed minerals by a two-letter code, e.g., QZ for quartz. Refer to Appendix XXII, Mineralogy Codes.

7.27 Make grain counts in horizontal traverses across the grain mount. A 10X magnification objective is appropriate for FS and VFS. An 16X objective is appropriate for CSI.

7.28 To make a grain count, move the slide via the mechanical stage so that the left border of cover slip is in view and in the proximity of but not in the upper left corner. Place vertical scale on mechanical stage on an even number, e.g., 72 or 74 mm.

7.29 Set the rotating stage so that the horizontal movement of a grain, via the mechanical stage, parallels the horizontal cross-hair in the ocular.

7.30 List the most abundant grains and associated counter number in logbook. Mineral identification is facilitated by the familiarity with a few striking features and by the process of elimination.

7.31 Set counters to zero. Identify and tally all grains in the field of view that touch the horizontal cross-hair. Move the slide laterally one field width at a time. Identify and tally each grain that touches the horizontal cross-hair in each field of view until the right margin of cover slip is in view.

7.32 Translate the slide vertically a distance of 2 mm and run another traverse in the reverse direction.

7.33 Repeat process until the end of traverse in which 300 grains have been tallied. If there are only a few species, a counting of 300 grains provides a good indication of composition. As the number of species increases, the count should increase within limits of practicability. To count more than 1000 grains is seldom necessary.

MINERALOGY
OPTICAL ANALYSES (7B)
GRAIN STUDIES (7B1)
GRAIN MOUNTS, EPOXY (7B1a)

7.34 The counting of complete traverses minimizes the effects of non-random distribution of grains on the slide. This non-random distribution of grains is usually most pronounced near the edges of the cover slip. If the entire slide has been traversed, and the total grain count is <300, reverse the direction of vertical translation and count traverses on odd-numbered settings, e.g., 81 or 79 mm.

7.35 Counting isotropic grains only (e.g., volcanic glass) can be done more quickly as follows:

a. Positioning the polarizer slightly off "blackout" position.

b. Using crossed Nicols and a gypsum plate. The outline of the grains is visible with the color of the grain being the same as the epoxy background.

7.36 When the count is complete, enter the raw data (project, sample number, fraction(s), minerals, and counts) into the SSL data base.

8. CALCULATIONS

8.1 Calculations are made by a computer program written to facilitate data entry and manipulation. Required inputs are as follows: project number; sample number; grain-size fractions; mineral identification; and number of grains counted per mineral.

8.2 Percentage of minerals are calculated by the formula as follows:

$$\text{Mineral (\%)} = \frac{\text{Number of mineral grains}}{\text{Total number of counted grains}}$$

9. REPORT

Report mineral contents to the nearest whole percentage of grains counted. These data are accurate number percentages for the size-fraction analyzed but may need to be recomputed to convert to weight percentages. These data are reported on the mineralogy data page of the primary characterization data set. For each grain size counted, the mineral type and amount are recorded, i.e., quartz, 87% of fraction, is recorded as QZ87. Column 10 on mineralogy data page of the primary characterization data sheet reports the percentage of resistant minerals that is used in the siliceous mineralogy family determination.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

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MINERALOGY
OPTICAL ANALYSES (7B)
GRAIN STUDIES (7B1)
GRAIN MOUNTS, EPOXY (7B1a)

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MINERALOGY
TOTAL ANALYSIS (7C)
HF PLUS AQUA REGIA (HF + HNO$_3$ + HCl) DISSOLUTION (7C4a)

1. APPLICATION

Prior to the development of modern analytical techniques, e.g., X-ray diffraction and thermal analysis, identification of minerals was based on elemental analysis and optical properties (Washington, 1930; Bain and Smith, 1994). Chemical analysis is still essential to determine mineral structural formulas and to identify and quantify specific mineral species through elemental allocation to minerals. Many clay mineral groups are subdivided based on composition.

Analysis of the entire fine earth (<2-mm) fraction or specific particle-size separates provides information on parent material uniformity, pedon development, and mineral weathering within or between pedons. This interpretation is determined from differences between horizons or pedons in elemental concentrations, elemental ratios such as Si/Al, Si/Al+Fe, or Ti/Zr, or from differences in total elemental concentrations compared to concentrations determined by selective dissolution techniques.

The inherent fertility of a soil derived from its parent material can be examined by determination of the basic cations relative to the Si or Al content. Phosphorus fertility of a soil and potential water quality problems can be better understood by measurements of total P, especially when compared to other P measurements, such as water-soluble or Bray-extractable P.

Hydrofluoric acid (HF) is efficient in the digestion and dissolution of silicate minerals for elemental dissolution (Bernas, 1968; Sawhney and Stilwell, 1994). Aqua regia (HNO$_3$ and HCl) aids in digestion of soil components, especially the organic fraction. Procedure 7C4a is a digestion of 100 mg of dried clay suspension, the fine earth (<2-mm) fraction, or other particle size separate with HF and aqua regia. Closed digestion vessels (Parr Bombs) are heated in the oven at 110°C for at least six hours. Elemental concentration of the digestate is determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2. SUMMARY OF METHOD

A clay suspension (procedure 7A2i) containing approximately 100 mg of clay material is pipeted into a Teflon digestion container and dried at 110°C. A equal amount of suspension is pipeted into a tared aluminum-weighing dish and dried at 110°C to obtain a dried sample weight. An oven-dry 100-mg soil sample (<80 mesh) or a specific particle-size separate may be substituted for the clay suspension. The P and Na content of the clay fraction is not measurable when the soil is dispersed in sodium hexametaphosphate (procedure 7A2i). Total P and Na are measurable on the fine-earth fraction or other particle-size separates not dispersed in Na or P-containing reagents, and the analyses are included as a part of this procedure.

Following evaporation of the aqueous portion of the suspension, 0.75 mL HNO$_3$, 0.25 mL HCl, and 5 mL HF are added. The vessel is inserted into a stainless steel retainer vessel, heated, cooled, and 15 mL of 2.5 percent boric acid solution is added to neutralize the excess HF acid. The digestate is quantitatively transferred with boric acid solution, diluted to 100 mL, shaken, and allowed to stand overnight. Approximately 60 mL are saved for analysis. The concentration of Fe, Mn, Al, Ca, Mg, Na, K, P, Si, Zr, Cu, Zn, As, Ti, Se, Cd, and Pb are determined by ICP analysis in procedures 6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a, 8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a, respectively. Data are reported in procedure 7C4a.

3. INTERFERENCES

Insoluble fluorides of various metals may form. Formation of SiF$_4$ results in gaseous losses of Si, but additions of boric acid retards formation of this molecule as well as dissolves other metal fluorides.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated acids to the fume hood. Keep HF acid refrigerated and avoid contact with skin of all acids. Wash hands thoroughly after handling reagents. Filling the Teflon cup of the acid

MINERALOGY
TOTAL ANALYSIS (7C)
HF PLUS AQUA REGIA (HF + HNO$_3$ + HCl) DISSOLUTION (7C4a)

digestion bomb to greater than 25 percent of the free volume or adding organic reagents or oxidizing agents to the cup may result in explosion of the digestion bomb.

5. EQUIPMENT
5.1 Pipet(s) capable of delivering 5, 0.75, and 0.25 mL
5.2 Volumetric flasks, nalgene, 100 mL
5.3 Polypropylene bottles, 60 mL, with cap
5.4 Electronic balance, ±0.1 mg sensitivity
5.5 Acid digestion bombs: 25-mL Teflon containers with stainless steel retainer vessels
5.6 Oven, 110°C
5.7 Desiccator with P$_2$O$_5$ drying agent
5.8 Disposable aluminum-weighing dishes

6. REAGENTS
6.1 Deionized distilled (DDI) water
6.2 Hydrofluoric acid (HF), 48%, low trace metal content
6.3 Concentrated hydrochloric acid (HCl), 12 *N*. Use instrumental grade reagents which contain low
   levels of impurities.
6.4 Concentrated nitric acid (HNO$_3$), 16 *N*. Use instrumental grade reagents which contain low levels of
   impurities.
6.5 Boric acid solution, 2.5 percent. Dissolve 25.0 g low trace metal, granular boric acid (H$_3$BO$_3$) in 1000
   mL DDI water.

7. PROCEDURE
HF plus Aqua Regia Dissolution
7.1 Prepare Na-saturated clay as in procedure 7A2i, Preparation of Clay Suspension, Steps 7.8 to 7.19. Clay dispersion by this method eliminates quantitative analysis of Na and P in the clay due to dispersion by sodium hexametaphosphate. Digestion of the entire fine earth (<2-mm) fraction or any fraction not derived by dispersion with sodium hexametaphosphate (or other Na and P-containing dispersing agents) can be quantitatively analyzed for Na and P. Dispersion of clays and cleaning of test tubes and dishware should be with DDI water.

7.2 Pipet a known aliquot of clay suspension containing approximately 100 mg clay into a 25-mL Teflon container. The milliliters of suspension required depends on the clay concentration of the suspension but is generally from 2 to 6 mL. More dilute suspensions should be partially evaporated under a fume hood to concentrate the clay prior to transfer to the Teflon container. Fine-earth (<2-mm) or a specific particle size separate ground to <80-mesh may be used instead of clay. Samples with greater than 3 percent organic C should be ashed in a muffle furnace at 400°C for 2 h prior to analysis to destroy the organic matter. Oven dry the sample (110°C), cool over P$_2$O$_5$, and weigh to 100 ±0.1 mg. If a clay suspension is used, Steps 7.3 to 7.4 are performed. Proceed to Step 7.5 if using fine-earth or other oven-dried material.

7.3 Pipet a duplicate aliquot of suspension (as used in Step 7.2) into a tared Al weighing dish, dry at 110°C, cool in a desiccator with P$_2$O$_5$, and weigh to the nearest 0.1 mg. Use this value as the sample weight in the calculations.

7.4 Dry the Teflon container and clay suspension in an oven for 4 h or until the aqueous portion of the suspension is completely evaporated. Remove from oven and cool on the bench top or in a fume hood. Cooling in a desiccator is not required.

7.5 Pipet 0.75 mL HNO$_3$ and 0.25 mL HCl into the sample and allow to completely wet and then pipet 5 mL HF into sample.

7.6 Place covered Teflon container in stainless steel retainer vessel. Place sample in oven at 110°C for a minimum of 6 h. Samples can be left in the oven overnight at 110°C.

7.7 Remove samples from oven and cool for at least 4 h.

7.8 Under a hood, remove Teflon container from steel retainer vessel, open the Teflon container, and add 15 mL 2.5 percent boric acid solution.

7.9 Quantitatively transfer contents of Teflon container to a 100 mL nalgene volumetric flask and adjust to volume with 2.5 percent H$_3$BO$_3$.

7.10 Cap flask and mix well by inverting at least three times. Allow to stand overnight to dissolve any metal fluorides.

7.11 Invert the volumetric flask to mix and decant approximately 60 mL into a labeled polypropylene container.

7.12 Prepare working standards of a blank, a clay suspension from a SSL reference soil sample, and a National Institute of Standards and Technology (NIST) standard reference material by the same digestion method. Run one of these standards with each set of 20 samples.

7.13 Solutions and standards are analyzed by ICP spectrometry. Refer to procedures 6C7b, 6D6a, 6G11b, 6N5b, 6O5b, 6P3b, 6Q3b, 6S6a, 6V1b, 8K1a, 8L1a, 8M1a, 8N1a, 8O1a, 8P1a, 8Q1a, and 8R1a for analysis of Fe, Mn, Al, Ca, Mg, Na, K, P, Si, Zr, Cu, Zn, As, Ti, Se, Cd, and Pb, respectively.

8. CALCULATIONS

8.1 Data are transferred as an ASCII file from the ICP computer onto a 3.5-in floppy disk via "Report Writer" in the TJA software ThermoSpec, Version 5.06.

8.2 On a MS-DOS based PC computer, import the ASCII file of ICP data into the DOS editor and strip off unnecessary headers and data from standards. Save the file after editing, renaming using a format that can be imported into LOTUS, e.g., rename to .wk3 file for LOTUS 123, Version 3.1.

8.3 Import the file into an established total analysis spreadsheet in LOTUS 123. The spreadsheet has columns for sample number, soil fraction digested, soil weight, concentration of each element in ppm, and the calculated elemental percent. Each line of elemental data for a sample is imported as a single data string.

8.4 Parse the components of each data string into separate columns. Rearrange the data set in order to have all elemental values on a single line for a particular sample. Move the data into the correct columns of the spreadsheet.

8.5 Insert values for elements requiring dilution into the original line of sample data and replace all negative values with zero.

8.6 Input sample weights, or if possible, import sample weights (dried soil weights) from the ASCII file generated by computer attached to balance via RS-232.

8.7 Calculate the percent of an element in the soil from ppm in solution as shown in the Si example as follows:

Si (ppm) in solution	= 75.2 ppm (75.2 µg/mL)
Volume extract	= 100 mL
Sample weight (110°C)	= 100.0 mg

Calculate as follows:

% Si = 75.2µg mL^{-1} x 100 mL x (1 g/ 10^6 µg) x (1/0.1 g soil) x 100 = 7.52 %

8.8 The fraction digested needs to be identified with each sample. Use proper SSL database abbreviations.

8.9 Delete the Na and P data for clay samples dispersed in sodium hexametaphosphate.

8.10 Prepare the file to send to CMS. Save the file as an unformatted ASCII file using LOTUS.

8.11 Enter data for Si, Al, Fe, Mg, Mn, K, Ti, Ca, Zr, P, and Na into the SSL CMS database on a 110°C weight basis as percent of the element in the fraction digested. Data are converted to the oxide form on the data sheet.

8.12 The factor for converting from an elemental form to an oxide form is based on the atomic weights of the element and oxygen. An example is as follows:

Atomic weight Si	= 28.09
Atomic Weight O	= 16.0
Molecular weight SiO$_2$	= 60.09

Calculate percent Si in SiO$_2$ as follows:

Si (%) = (28.09/60.09) x 100 = 46.7 %

There is 46.7 percent Si in SiO$_2$. To convert from percent Si to percent Si oxide (SiO$_2$) in the soil, divide the percent Si by 0.467 or multiply by the inverse of this value. The following table lists the element, the oxide form, and the elemental percent in the oxide form.

Element	Oxide Form	Elemental %
Si	SiO$_2$	46.7
Al	Al$_2$O$_3$	52.9
Fe	Fe$_2$O$_3$	69.9
Mg	MgO	60.3
Mn	MnO	77.4
K	K$_2$O	83.0
Ti	TiO$_2$	59.9
Ca	CaO	71.5
Zr	ZrO$_2$	74.0
P	P$_2$O$_5$	43.6
Na	Na$_2$O	74.2

9. REPORT

Data are reported as percent to the nearest tenth for Fe, Al, Mg, Na, K, and Si; to the nearest hundredth for Mn, Ca, P, and Ti; and to the nearest thousandth for Zr. The remaining trace elements (Cu, Zn, As, Se, Cd, and Pb) are reported in mg kg^{-1} (ppm).

10. PRECISION

The mean, standard deviation, and C.V. are calculated for each element for both the NIST standard and the SSL reference standard.

11. REFERENCES

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MINERALOGY
SURFACE AREA (7D)
ETHYLENE GLYCOL MONOETHYL ETHER (EGME) RETENTION (7D2)

1. APPLICATION

Surface area determines many physical and chemical properties of materials. Water retention and movement, cation exchange capacity, pesticide adsorption, and many biological processes are closely related to specific surface (Carter et al., 1986). Soils vary widely in their reactive surface area because of differences in mineralogical and organic composition and in their particle-size distribution (Carter et al., 1965). Specific surface, defined as surface area per unit mass of soil, is usually expressed in units of m^2 g^{-1} or cm^2 g^{-1} soil. Specific surface has been measured for several clays, e.g., 810 m^2 g^{-1} for smectite and 20 to 40 m^2 g^{-1} for kaolinite and mica.

2. SUMMARY OF METHOD

Ethylene glycol monoethyl ether (EGME) retention is a surface-area determination. A soil sample is dried over phosphorus pentoxide (P_2O_5). The sample is saturated with EGME. A monomolecular layer of EGME is established by desorbing the EGME by vacuum over EGME-saturated $CaCl_2$. The solvate of $CaCl_2$ and EGME helps to maintain an EGME vapor pressure in the desiccator which results in the formation of a monomolecular layer of EGME on sample surfaces.

The weight of a monomolecular layer of EGME on the sample is determined by weighing the dried sample. EGME is determined by weighing the sample and sample plus EGME (Carter et al., 1965). The SSL determines EGME retention by procedure 7D2. The SSL reports EGME retention as mg EGME per g of soil to the nearest mg on a <2-mm base.

3. INTERFERENCES

The loss or contamination of sample and the variation in sample weight may cause erroneous results. Handle the weighing vessels with finger cots or tongs to prevent vessel contamination and the resulting weighing errors. High relative humidity in the laboratory may result in high moisture absorption by sample.

4. SAFETY

Wear protective clothing (e.g., coats, aprons, and gloves) and eye protection (e.g., face shields, goggles, or safety glasses) when handling reagents and working with vacuum desiccators. Follow standard laboratory safety procedures in handling reagents and vacuum devices. The P_2O_5 is corrosive and reacts violently with water. Use caution in cleaning P_2O_5 spills. The EGME is combustible and harmful is swallowed, inhaled, or absorbed through the skin. Keep samples and desiccators with EGME under fume hood at all times.

5. EQUIPMENT

5.1 Electronic balance, ±0.1-mg sensitivity, Mettler AE 160
5.2 Vacuum desiccator, 250 mm, Nalgene No. 5310, with desiccator plate, 230 mm
5.3 Laboratory vacuum or vacuum pump, 0.65 to 0.75 bars
5.4 EGME trap, anhydrous $CaCl_2$ in a large tube between desiccator and vacuum source
5.5 Syringe, polypropylene, 3 mL
5.6 Weighing bottle, cylindrical, low form, 50 x 30 mm

6. REAGENTS

6.1 Ethylene glycol monoethyl ether (EGME), reagent
6.2 Phosphorus pentoxide (P_2O_5), anhydrous
6.3 Calcium chloride ($CaCl_2$), pellets, 40 mesh, reagent grade

7. PROCEDURE

7.1 Dry 3 to 5 g of <2-mm, air-dry soil in a weighing bottle in a vacuum desiccator over P_2O_5 for 2 days.

MINERALOGY
SURFACE AREA (7D)
ETHYLENE GLYCOL MONOETHYL ETHER (EGME) RETENTION (7D2)

7.2 Prepare solvated $CaCl_2$ by weighing 100 g oven-dried $CaCl_2$, without cooling, into a large beaker. Add 20 g EGME and mix by stirring. Transfer to a desiccator in which EGME-saturated samples equilibrate.

7.3 Weigh the P_2O_5-dried soil sample to the nearest 0.1 mg. When working outside the desiccator, cover the sample to avoid moisture adsorption from the atmosphere.

7.4 Use a 3-mL syringe to saturate the soil with EGME. Add 5 drops in excess of saturation.

7.5 Place the uncovered, EGME-soil mixture in a vacuum desiccator over solvated $CaCl_2$. Use a laboratory vacuum of 0.65 to 0.75 bar pressure.

7.6 Loosely cover the tops of weighing bottles with a piece of aluminum foil that is smaller than the inside diameter of desiccator.

7.7 Apply suction for 16 to 24 h.

7.8 Carefully release the suction. Remove weighing bottles and weigh the EGME-soil mixture.

7.9 If a 3-g sample is used, the difference between the EGME-soil mixture and P_2O_5-dry soil is $\approx$ 10 mg EGME/g P_2O_5-dry soil. When this difference is <10 mg, reduce the vacuum time to 1 h day^{-1} and weigh twice daily.

7.10 Repeat the vacuum and weighing procedure until a constant weight is attained. Constant weight is defined as three successive daily weighings within 1 mg of EGME per gram P_2O_5-dry soil. When a constant weight is attained, make calculations.

8. CALCULATIONS

8.1 The EGME retention is calculated as follows:

Retention of EGME (mg g^{-1}) = (Wt$_1$ - Wt$_2$) x (1000/Wt$_3$)

where:
Wt$_1$ = Soil weight with monomolecular layer of EGME + Tare weight of bottle
Wt$_2$ = Soil weight after drying with P_2O_5 + Tare weight of bottle
Wt$_3$ = Soil weight after drying with P_2O_5 - Tare weight of bottle
1000 = Conversion factor (mg g^{-1})

The surface area in units of mg EGME per g of soil is converted to m^2 g^{-1}, the convention commonly used in clay mineralogy. The conversion is as follows:

Surface area (m^2 g^{-1}) = (EGME retention (mg g^{-1}))/0.286

where:
0.286 = Conversion factor (mg EGME m^{-2})

The constant, 0.286, is the amount of EGME (mg) that is required to cover a m^2 of clay surface with a monomolecular layer (Carter et al., 1986). This value is calculated from the measured value of 231.7 mg EGME per g of pure montmorillonite assumed to have 810 m^2 g^{-1} on the basis of other measurements.

9. REPORT
Report EGME as mg EGME per g of soil to the nearest mg.

10. PRECISION
Precision data are not available for this procedure. Two quality control checks, a high and a low standard, are routinely analyzed in EGME. The mean (mg EGME per g soil), standard deviation, and C.V. for the quality control check sample are as follows:

	Mean	n	Std. Dev.	C.V.
High Std	109.0	10	7.4	7.3
Low Std	37.5	10	0.64	4.8

11. REFERENCES
Carter. D.L., M.D. Heilman, and C.L. Gonzalez. 1965. Ethylene glycol monoethyl ether for determining surface area of silicate minerals. Soil Sci. 100:356-360.

Carter, D.L., M. M. Mortland, and W.D. Kemper. 1986. Sampling. In A. Klute (ed.) Methods of soil analysis. Part 1. Physical and mineralogical methods. 2nd ed. Agronomy 9:413-423.

MISCELLANEOUS
SATURATED PASTE, SATURATED EXTRACT, CONDUCTIVITY, RESISTIVITY, SATURATED PH, TOTAL SALT, and PREDICT
(8A, 8A3, 8A3a, 8C1b, 8D5, 8E1, and 8I)

INTRODUCTION

Salt-affected soils, i.e., excessive amounts of soluble salts and/or exchangeable sodium (ES), are common in, though not restricted to, arid and semi-arid regions. These soils are usually described and characterized in terms of the soluble salt concentrations, i.e., major dissolved inorganic solutes (Rhoades, 1982). Salt composition and distribution in the soil profile affect the plant response, i.e., osmotic stress, specific ion effects, and nutritional imbalances. Soil texture and plant species also are factors in this plant response to saline soils.

Traditionally, the classification of salt-affected soils has been based on the soluble salt concentrations in extracted soil solutions and on the exchangeable sodium percentage (ESP) in the associated soil (Bohn et al., 1979). In general, saline soils have been defined as having a salt content >0.1% or an EC $\geq$4 mmhos cm^{-1}; alkali soils have an ESP of $\geq$15%; and saline-alkali soils have properties of both saline and alkali soils (U.S. Salinity Laboratory Staff, 1954). In *Soil Taxonomy*, the ESP and the Na-adsorption ratio (SAR) have been used as criteria for natric horizons. The ESP and SAR are calculated in procedures 5D2 and 5E, respectively.

The measurable absolute and relative amounts of various solutes are influenced by the soil:water ratio at which the soil solution extract is made. Therefore, this ratio is standardized to obtain results that can be applied and interpreted universally. Soil salinity is conventionally defined and measured on aqueous extracts of saturated soil pastes (U.S. Salinity Laboratory Staff, 1954). This soil:water ratio is used because it is the lowest reproducible ratio at which the extract for analysis can be readily removed from the soil with common laboratory equipment, i.e., pressure or vacuum, and because this soil:water ratio is often related in a predictable manner to field soil water contents (Rhoades, 1982). Soil solutions obtained at lower soil moisture conditions are more labor intensive and require special equipment.

The SSL measures salinity on aqueous extracts of saturated soil pastes. The saturated paste is prepared, and the saturation percentage (SP) is determined in procedure 8A. The saturated paste extract is obtained with an automatic extractor in procedure 8A3. Electrical conductivity and soil resistivity are measured in procedures 8A3a and 8E1, respectively. The saturated paste pH is measured in procedure 8C1b. The water-soluble cations of Ca^{2+}, Mg^{2+}, Na^+, and K^+ are measured by atomic absorption in procedures (6N1, 6O1, 6P1, and 6Q1, respectively). The water-soluble anions of Cl^-, SO_4^{2-}, NO_3^-, Fl^-, and NO^{2-}) are measured by ion chromatography in procedures 6K1d, 6L1d, 6M1d, 6U1b, and 6W1b, respectively. The carbonate and bicarbonate concentrations are determined by acid titration procedures 6I1b and 6J1b, respectively. Estimated total salt is calculated in procedure 8D5. The SSL also performs a salt prediction test (procedure 8I) which is used not only to predict those soils that have measurable amounts of soluble salts but also to predict the quantity and the appropriate dilutions for salt analyses of those soils. If salt predictions or conductances are <0.25 mmhos cm^{-1}, soils are considered nonsalty, and generally, no other salt analyses are performed on these soils by the SSL.

The SP, i.e., the amount of moisture in the saturated paste, is an important measurement (procedure 8A). An experienced analyst should be able to repeat the saturated paste preparation to an SP within 5%. The SP can be related directly to the field moisture range. Measurements on soils, over a considerable textural range, (U.S. Salinity Laboratory Staff, 1954) indicate the following general rules of thumb.

SP $\approx$ 4 x 15-bar water

SP $\approx$ 2 x upper end field soil moisture content

AWC $\approx$ SP/4

where:
Sp = Saturation percentage
AWC = Available water capacity

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Therefore, at the upper (saturated) and lower (dry) ends of the field moisture range, the salt concentration of the soil solution is $\approx$ 4x and 2x the concentration in the saturation extract, respectively.

If the soil texture is known, and the 15-bar water content has been measured, the preceding SP relationships may be redefined (U.S. Salinity Laboratory Staff, 1954) as follows:

```
15-Bar          Texture        Relationship
Water
_____

(%)


2.0 - 6.5       Coarse         SP ≈ 6 1/3 x 15 bar
6.6 - 15        Medium         SP ≈ 4 x 15 bar
>15             Fine           SP ≈ 3 1/4 x 15 bar
>15             Organic        SP ≈ 3 2/3 x 15 bar
```

The electrical conductivity of the saturated paste (EC_s) is measured and is commonly reported as resistivity (R_s). The EC_s measurement requires more time, i.e., preparation of saturated soil paste, than the R_s measurement. However, the EC_s is the easier measurement from which to make interpretations, i.e., EC_s is more closely related to plant response (U.S. Salinity Laboratory Staff, 1954). Furthermore, there is a limited correlation between EC_s and R_s, as the relationship is markedly influenced by variations in SP, salinity, and soil mineral conductivity. The EC_s has been related to R_s (U.S. Laboratory Staff, 1954) by the equation as follows:

$$EC_s \approx 0.25/R_s$$

where:
0.25 = Constant for Bureau of Soils electrode cup

Historically, the EC_s is adjusted to 60°F (15.5°C) basis before interpretative use. The EC_s and R_s increase $\approx$ 2% per °C. The SSL determines the EC_s and R_s in procedures 8A3a and 8E1, respectively. The unit EC x 10^3 is called the millimho per centimeter (mmhos cm^{-1}).

The EC_s (mmhos cm^{-1}) may be used to estimate the salt percentage (P_{sw}) in solution (U.S. Salinity Laboratory Staff, 1954) as follows:

$$P_{sw} \approx 0.064 \text{ x } EC_s \text{ (mmhos cm}^{-1}\text{)}$$

The preceding equation may be used to estimate the salt percentage in the soil (P_{ss}) (U.S. Salinity Laboratory Staff, 1954) as follows:

$$P_{ss} \approx (P_{sw} \text{ x } SP)/100$$

The EC_s (mmhos cm^{-1}) may be used to estimate the osmotic potential (OP) in atmospheres of a solution (U.S. Salinity Laboratory Staff, 1954) as follows:

$$OP \approx 0.36 \text{ x } EC_s \text{ (mmhos cm}^{-1}\text{)}$$

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The EC_s (mmhos cm^{-1}) may be used to estimate the total cation or anion concentration (meq L^{-1}) of the solution (U.S. Salinity Laboratory Staff, 1954) as follows:

$$Total\ cations \approx 10 \times EC_s\ (mmhos\ cm^{-1})$$

$$Total\ anions \approx 10 \times EC_s\ (mmhos\ cm^{-1})$$

where:
EC_s at 25°C

A means of cross-checking chemical analyses for consistency and reliability is provided by the interrelations that exist among the various soil chemical determinations (U.S. Salinity Laboratory Staff, 1954). The saturated paste pH (procedure 8C1b) is the apparent pH of the soil:water mixture and is a key indicator in many of these interrelations. The saturated paste pH (procedure 8C1b) is dependent upon the dissolved CO_2 concentration; moisture content of the mixture; exchangeable cation composition; soluble salt composition and concentration; and the presence and amount of gypsum and alkaline-earth carbonates. Some rules of thumb that apply to the saturated paste (U.S. Salinity Laboratory Staff, 1954) are as follows:

Total Cation and Anion Concentrations

1. Total cations ≈ Total anions, expressed on equivalent basis

pH and Ca and Mg Concentrations

2. Concentrations of Ca^{2+} and Mg^{2+} are seldom >2 meq L^{-1} at pH >9.

pH and Carbonate and Bicarbonate Concentrations

1. Carbonate concentration (meq L^{-1}) is measurable only if pH >9.

2. Bicarbonate concentration is rarely >10 meq L^{-1} in absence of carbonates.

3. Bicarbonate concentration is seldom >3 or 4 meq L^{-1} if pH <7.

Gypsum

1. Gypsum is rarely present if pH >8.2.

2. Gypsum has variable solubility in saline solutions (20 to 50 meq L^{-1}).

3. Check for the presence of gypsum if Ca concentration >20 meq L^{-1} and pH ≤8.2.

pH, ESP, and Alkaline-Earth Carbonates

1. Alkaline-earth CO_3^{-} and ESP ≥15 are indicated if pH ≥8.5.

2. ESP $\leq$15 may or may not be indicated if pH <8.5.

3. No alkaline-earth CO_3^- are indicated if pH <7.5.

pH and Exchangeable Acidity

1. Significant amounts of exchangeable acidity are indicated if pH <7.0.

The commonly determined soluble cations and anions in the saturation extract include calcium, magnesium, sodium, potassium, chloride, sulfate, nitrate, fluoride, carbonate, bicarbonate, and nitrite. The less commonly analyzed cations and anions include iron, aluminum, manganese, lithium, strontium, rubidium, cesium, hydronium, phosphate, borate, silicate, bromide, selenate, selenite, arsenate, and arsenite.

The effect of soluble cations upon the exchangeable cation determination is to increase the cation concentration in the extracting solution, i.e., NH_4OAc, buffered at pH 7.0 (procedure 5A8c). The dissolution of salts by the extractant necessitates an independent determination of soluble cations and a correction to the exchangeable cations. Therefore, in soils with soluble salts or carbonates, the soluble cations (meq L^{-1} solution) must be measured separately and the results subtracted from the extractable bases for determination of exchangeable bases as follows:

Exchangeable = Extractable - Soluble

The presence of alkaline-earth carbonates prevent accurate determination of exchangeable Ca and Mg. Refer to procedures 6N, 6O, 6P, and 6Q.

REFERENCES
Bohn, H.L., McNeal, B.L., and O'Connor, G.A. 1979. Soil Chemistry. John Wiley & Sons, NY.
Rhoades, J.D. 1982. Soluble Salts. *In* A.L Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:167-179.
U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

MISCELLANEOUS
SATURATED PASTE, MIXED (8A)

1. APPLICATION

The saturated soil paste is a particular mixture of soil and water, i.e. the soil paste glistens as it reflects light; flows slightly when the container is tipped; and slides freely and cleanly from a spatula except for those soils with high clay content. This soil:water ratio is used because it is the lowest reproducible ratio for which enough extract for analysis can be readily removed from the soil with pressure or vacuum, and because this ratio is often related in a predictable manner to the field soil water content (U.S. Salinity Laboratory Staff, 1954). Upon preparation of a saturated paste, an aqueous extract is obtained, which is used in a series of chemical analyses, e.g., electrical conductivity and concentrations of the major solutes.

2. SUMMARY OF METHOD

A saturated paste is prepared by adding water to a soil sample while stirring the mixture until the soil paste meets the saturation criteria, i.e. the soil paste glistens as it reflects light; flows slightly when the container is tipped; and slides freely and cleanly from a spatula except for those soils with high clay content. The mixture is covered and allowed to stand overnight. The saturation criteria are then rechecked. If the mixture fails to meet these criteria, more water or soil is added until criteria are met. A saturated paste subsample is used to determine the moisture content, i.e., saturation percentage (SP).

3. INTERFERENCES

Special precautions must be taken for peat and muck soils and very fine or very coarse-textured soils (Rhoades, 1982). Dry peat and muck soils, especially if coarse textured or woody, require an overnight wetting to obtain a a definite end point for the saturated paste. After the first wetting, pastes of these soils usually stiffen and lose their glisten. However, upon adding water and remixing, the paste usually retains the saturated paste characteristics. With fine-textured soils, enough water should be added immediately, with a minimum of mixing, to bring the sample nearly to saturation. Care also should be taken not to overwet coarse-textured soils. The presence of free water on the surface of the paste after standing is an indication of oversaturation in the coarse-textured soils (Rhoades, 1982).

4. SAFETY

Use heat-resistant gloves to remove hot moisture cans from the oven. No other significant hazards are associated with this procedure. Follow standard laboratory safety practices.

5. EQUIPMENT
5.1 Aluminum cans, drying
5.2 Spatulas, stainless steel, hardwood handles
5.3 Electronic balance, ±0.01-g sensitivity
5.4 Oven, thermostatically controlled, 105 ± 5°C
5.5 Thermometer, 0° to 200°C
5.6 Plastic food containers, 1920 mL (16 fl. oz.) capacities with recessed lids, Sweetheart Products Group, Owings Mills, MD

6. REAGENTS
6.1 Distilled deionized (DDI) water

7. PROCEDURE

Saturated Soil Paste Preparation
7.1 Place a <2-mm, air-dry, 250-g soil sample in the food container. This sample size is convenient to handle with the 1920-mL (16-oz) food containers and provides enough extract for most purposes. The sample size varies with the number of determinations to be made upon the paste or saturation extract.

7.2 Add enough DDI water to bring the sample nearly to saturation. To reduce soil puddling and to obtain a more definite end point of the saturation criteria, mix with a minimum of stirring. Soils puddle easily when worked at a moisture content near field capacity. If the paste becomes too wet, add more dry soil.

7.3 Occasionally tap the container on the workbench to consolidate the soil:water mixture. At saturation, the soil paste glistens as it reflects light; flows slightly when the container is tipped; and slides freely and cleanly off the spatula except for those soils with high clay content.

7.4 Cover the container and allow the sample to stand overnight.

7.5 Recheck saturation criteria, i.e., ordinarily, free water should not collect on the soil surface; paste should not stiffen markedly; and paste should not lose its glisten upon standing.

7.6 If the paste does not meet the saturation criteria, remix the paste with more DDI water or dry soil. Allow to stand for at least 4 h and recheck the saturation criteria.

<div align="center">

Saturation Percentage Determination
</div>

7.7 Tare a moisture can and cover. Label each moisture can with the appropriate sample number.

7.8 Add ~ 20 to 40 g of the saturated soil paste to the moisture can.

7.9 Cover the can, weigh the can plus sample, and record the weight to the nearest 0.01 g.

7.10 Remove the can cover, place the can in a vented drying oven at 105°C, and leave in the oven overnight (12 to 16 h). A drying period of 24 h or longer is recommended. Do not place moist samples in the oven with other samples that are drying, unless these samples have been in the oven at least 12 to 16 h. Do not overcrowd the drying oven with samples.

7.11 Remove the cans from the oven and cover immediately. Allow the cans to cool for 1 h.

7.12 Weigh the oven-dry paste sample and record the weight. Before calculating the SP, subtract the tare weights from the saturated paste and oven-dry weights. Do not use the SP subsample for other analyses.

8. CALCULATIONS

$$SP = \frac{(Wt_{SP} - Wt_{OD})}{(Wt_{OD})} \times 100$$

where:
SP   = Saturation percentage
Wt_{SP} = Weight of saturated paste
Wt_{OD} = Weight of ovendry soil

9. REPORT
Report the saturation percentage to the nearest 0.1%.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES

Rhoades, J.D. 1982. Soluble Salts. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:167-179.

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MISCELLANEOUS
SATURATED PASTE, MIXED (8A)
SATURATION EXTRACT, AUTOMATIC EXTRACTOR (8A3)

1. APPLICATION

The saturated paste is operationally defined so that it may be reproduced by a trained analyst using limited equipment. The saturated paste extract derived from the saturated paste (procedure 8A) is an important aqueous solution because many soil properties have been related to the composition of the saturation extract, e.g., soluble salt composition and electrical conductivity. These soil properties or characteristics are related in turn to the plant response to salinity (U.S. Salinity Laboratory Staff, 1954).

2. SUMMARY OF METHOD

The saturated paste is transferred to a plastic filter funnel fitted with filter paper. The funnel is placed on a mechanical vacuum extractor (Holmgren et al., 1977), and the saturated paste is extracted). The extract is used in subsequent chemical analyses, e.g., water-soluble cations (procedures 6N1, 6O1, 6P1, and 6Q1) and water-soluble anions (procedures 6I1b, 6J1b, 6K1d, 6L1d, 6M1d, 6U1b, 6W1b).

3. INTERFERENCES

Some saturated pastes are difficult to extract, i.e., soil dispersion and puddling. Repeated extractions may be necessary to obtain sufficient extract. High speed centrifuging or filtration of the extract also may be necessary. Refer to Appendix XIV, Saturation Extract, Centrifuge Procedure. If the extract is to be stored for an extended period, sodium hexametaphosphate may be added to prevent calcium carbonate precipitation in the extract.

4. SAFETY

No significant hazards are associated with this procedure. Follow standard laboratory procedures.

5. EQUIPMENT
5.1 Mechanical vacuum extractor, 24 place, Centurion International Inc., Lincoln, NE
5.2 Mechanical vacuum extractor, MAVCO SAMPLETEX, Lincoln, NE
5.3 Paste extraction cups, 9-cm diameter, for mechanical vacuum extractors
5.4 Syringes, disposable, 60 mL, polypropylene, for extraction
5.5 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (1/8 ID x 1/4 OD x 1 in)
5.6 Polycons, Richards Mfg. Co.
5.7 Milipore filters, 0.2-or 0.45-μm diameter syringe filter
5.8 Filter paper, 3 and 9-cm diameter, Whatman No. 40 or equivalent

6. REAGENTS
6.1 Distilled deionized (DDI) water
6.2 Sodium hexametaphosphate, 1000 ppm PO_3. Dissolve 1.29 g of $(NaPO_3)_6$ in DDI water and bring to 1-L volume.

7. PROCEDURE

7.1 Prepare the saturated paste extract cup to receive the saturated paste (procedure 8A) by placing a 3-cm diameter filter paper circle over the center of the cup followed by a 9-cm diameter filter paper circle. Slightly moisten the filter paper to ensure that it remains in place.

7.2 Place the extraction syringe on the lower disk of the mechanical vacuum extractor.

7.3 Use a clamp to close rubber tubing on the bottom of the paste extraction cup. Carefully transfer the saturated paste into the extraction cup. Gently tap the cup to remove entrapped air in the paste. Place cups on the extractor, connect the syringe and remove the clamp.

7.4 When all cups are ready to extract, place a plastic cover over the extraction cup to retard evaporation.

7.5 Turn on the extractor. Set the extraction time to ≈ 1 h. Refer to Appendix II and III for operation and calibration of mechanical vacuum extractors.

7.6 When the extractor stops, turn off the power.

7.7 If sufficient extract has been obtained, pull the plunger of the syringe down. Do not pull plunger from the barrel of the syringe. Carefully remove the syringe containing the extract. Leave the rubber tubing on the sample tube.

7.8 If insufficient extract has been obtained, re-extract by repositioning the extractor to its starting configuration. Remove excess air in the syringe and restart the extractor. Slowing the extraction time to an overnight extraction may be necessary to obtain sufficient extract. Alternate methods are to extract any "unused" saturated paste in a new extraction cup or to re-extract by removing the top "moist" paste from the extraction cup, mixing with any "unused" paste, and re-extracting with a clean extraction cup.

7.9 If the solution is to be stored for a long period, add 0.1 mL of the 1000-ppm PO_3 per 25 mL of the extract as a preservative. Record the volume of sodium hexametaphosphate that is added to the extract.

7.10 Filtering the saturation extract is recommended to prevent the development of microorganisms. Connect the syringe to a 0.2- or 0.45 μm diameter Milipore filter and express the extract into a polycon.

8. CALCULATIONS
No calculations are required for this procedure.

9. REPORT
The volume of added sodium hexametaphosphate solution is recorded, and the data are used in subsequent analyses to adjust for the additional Na.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Holmgren, George G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.
U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

MISCELLANEOUS
SATURATION PASTE, MIXED (8A)
CONDUCTIVITY, DIGITAL BRIDGE (8A3a)

1. APPLICATION

The electrical conductivity of the saturation extract (EC_s) is used as a criterion for classifying a soil as saline. Other uses of this measurement include the estimation of the total cation concentration in the extract, salt percentage in solution (P_{sw}), salt percentage in soil (P_{ss}), and osmotic pressure (OP). The unit EC x 10^3 is called the millimho per centimeter (mmhos cm^{-1}). For solutions with a low EC_s, i.e., dilute solutions, the EC_s (mmhos cm^{-1}) x 10 ≈ cation concentration (meq L^{-1}) (U.S. Salinity Laboratory Staff, 1954). The EC_s (mmhos cm^{-1}) x 0.064 ≈ (P_{sw}); the (P_{sw} x SP)/100 ≈ P_{ss}; and the EC_s (mmhos cm^{-1}) x 0.36 ≈ OP in atmospheres (U.S. Salinity Laboratory Staff, 1954).

2. SUMMARY OF METHOD

The EC_s of the saturation extract that is prepared in procedure 8A is measured using a conductivity cell and a direct reading digital bridge. The cell constant is set using a standard solution.

3. INTERFERENCES

There are no significant interferences in this procedure. Distilled deionized water is used to zero and flush the conductivity cell. The extract temperature is assumed to be 25°C. If the temperature deviates significantly, a correction may be required.

4. SAFETY

No significant hazards are associated with this procedure. Follow standard laboratory safety procedures.

5. EQUIPMENT
5.1 Conductivity bridge and conductivity cell, Markson Model 1096, Amber Science, Eugene, OR

6. REAGENTS
6.1 Distilled deionized (DDI) water
6.2 Potassium Chloride, (KCl), 0.010 *N*. Dissolve 0.7456 g of KCl in DDI water and bring to 1-L volume. Conductivity at 25°C is 1.412 mmhos cm^{-1}.

7. PROCEDURE

7.1 Calibrate the conductivity meter and cell by drawing the 0.010 *N* KCl solution into the cell.

7.2 Set the meter to "D" Scale and adjust the digital reading to "1.41".

7.3 Flush the cell and fill with DDI water. Verify that digital reading is "0.00".

7.4 Read the electrical conductivity of saturation extract (EC_s) by drawing up the extract into the cell and flush at least once if the cell has not been dried. Draw up extract a second time. Reading is started on the "C" Scale. Higher readings may require the use of the "D" or "E" Scales.

7.5 When the reading has stabilized, record the EC_s. Rinse the cell with DDI water and ensure that the conductivity reading falls to zero.

8. CALCULATIONS

No calculations are required for this procedure.

9. REPORT

Report EC_s to the nearest 0.01 mmhos cm^{-1}.

10. PRECISION
   Precision data are not available for this procedure.

11. REFERENCES
   U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

MISCELLANEOUS
REACTION (pH) (8C)

INTRODUCTION

Soil pH is one of the most frequently performed determinations, and one of the most indicative measurements of soil chemical properties (McLean, 1982). The soil pH is affected by many factors, e.g., nature and type of inorganic and organic matter; amount and type of exchangeable cations and anions; soil:solution ratio; salt or electrolyte content; and CO_2 content (McLean, 1982). The acidity, neutrality, or basicity of a soil influences the solubility of various compounds; the relative ion bonding to exchange sites; and microbial activities. Depending on the predominant clay type, the soil pH may be used as a relative indicator of base saturation (Mehlich, 1934). Soil pH is also a critical factor in the availability of most essential elements for plants.

The SSL performs several pH determinations. These methods are Saturated paste pH, procedure 8C1b; NaF (1 *N* pH 7.2 to 8.1), procedure 8C1d; 1:1 water and 1:2 $CaCl_2$ (final solution: 0.01 *M* $CaCl_2$), procedure 8C1f; 1 *N* KCl, procedure 8C1g; Oxidized pH, procedure 8C1h; and Organic materials, $CaCl_2$ (final solution ~ 0.01 *M* $CaCl_2$), procedure 8C2a.

An increase in the soil:water ratio or the presence of salts generally results in a decrease in the soil pH. The soluble salt content of the soil can be overcome by using dilute salt solutions, e.g., $CaCl_2$ or KCl, instead of distilled water. The use of dilute salt solutions is a popular method for masking seasonal variation in soil pH. The pH readings are usually less with dilute salt solutions than with distilled water but may be equal to or greater in highly weathered tropical soils, i.e., soils with a high anion exchange capacity. When the pH values of various soils are compared, determination by the same method is important (Foth and Ellis, 1984).

The 1 *N* KCl (procedure 8C1g) is an index of soil acidity and is more popular in those regions with extremely acid soils and in which KCl is used as an extractant of exchangeable Al. The KCl pH indicates the pH at which Al is extracted. Similar to the 1:2 $CaCl_2$ pH, the 1 *N* KCl pH readings also tend to be uniform regardless of time of year.

The saturated paste pH (procedure 8C1b) is popular in regions with soils with soluble salts. The water content varies with soil water storage characteristics. The saturated paste pH may be more indicative of the saturated, irrigated soil pH than is the soil pH measurement at a constant soil:water ratio. The saturated paste pH is also that pH at which the saturation extract is removed for salt analysis, and hence, is the pH and the dilution at which the sodium adsorption ratio (SAR) is computed (procedure 5E).

The 1 *N* NaF pH (procedure 8C1d) may be used as an indicator that amorphous material dominates the soil exchange complex. The oxidized pH (procedure 8C1h) may be used to assess the activities of soil microorganisms. In *Soil Taxonomy* (Soil Survey Staff, 1975), the $CaCl_2$ pH (procedure 8C2a) is used to distinguish two family reaction classes in Histosols.

REFERENCES

Foth, H.D., and B.G. Ellis. 1984. Soil fertility. Soil pH and its management. p. 36-61. John Wiley and Sons. NY, NY.

McLean, E.O. 1982. Soil pH and lime requirement. *In* A.L Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:199-224.

Mehlich, A. 1943. The significance of percentage of base saturation and pH in relation to soil differences. Soil Sci. Soc. Am. Proc. 7:167-174.

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys, USDA-SCS Agric. Handb. 436. Appendix III: Tests of organic materials. p. 483. U.S. Govt. Print. Office, Washington, DC.

MISCELLANEOUS
REACTION (pH) (8C)
SOIL SUSPENSIONS (8C1)
SATURATED PASTE (8C1b)

1. APPLICATION

When making interpretations about the soil, the saturated paste pH is usually compared to the 1:1 water pH and the 1:2 $CaCl_2$ pH (procedure 8C1f). The usual pH sequence is as follows: 1:1 water pH > 1:2 $CaCl_2$ pH > saturated paste pH. If saturated paste pH is > 1:2 $CaCl_2$ pH, the soil is not saline. If the saturated paste pH $\geq$ 1:1 water pH, the soil may be Na saturated and does not have free carbonates.

Because of the interrelations that exist among the various soil chemical determinations, the saturated paste pH value may be used as a means of cross-checking salinity data for internal consistency and reliability (U.S. Salinity Laboratory Staff, 1954). Some rules of thumb that apply to the saturated paste pH are as follows:

a. Soluble carbonates are present only if the pH is >9.

b. Soluble bicarbonate seldom >3 or 4 meq L^{-1}, if the pH is $\leq$7.

c. Soluble Ca^{2+} and Mg^{2+} seldom >2 meq L^{-1}, if the pH is >9.

d. Gypsiferous soils seldom have a pH >8.2.

2. SUMMARY OF METHOD

The saturated paste is prepared (procedure 8A3a), and the pH of paste is measured with a calibrated combination electrode/digital pH meter.

3. INTERFERENCES

The difference in the sediment and supernatant pH is called the suspension effect (McLean, 1982). To maintain uniformity in pH determination, measure the pH just beneath the surface of saturated paste. Clays may clog the KCl junction and slow the electrode response. Clean the electrode by rinsing with distilled water and patting it dry with tissue. Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization.

4. SAFETY

No significant hazards are associated with this procedure. Follow standard laboratory safety practices.

5. EQUIPMENT
5.1 Digital pH/ion meter, Accumet Model 950, Fisher Scientific
5.2 Electrode, standard glass body combination, Accu-pHast, Fisher Scientific

6. REAGENTS
6.1 Distilled water
6.2 pH Buffers, pH 4.00, pH 7.00 and pH 9.18, for electrode calibration.

7. PROCEDURE

7.1 Prepare a saturated paste (procedure 8A3a).

7.2 Calibrate the pH meter with pH 7.00 and pH 9.18 buffer solutions. Use the pH 4.00 buffer solution as a linearity check.

7.3 After equipment calibration, gently wash the electrode with distilled water. Dry the electrode. Do not wipe the electrode with a tissue as this may cause a static charge on the electrode.

7.4 Gently lower the electrode in the saturated paste until the KCl junction of the electrode is beneath the surface of saturated paste.

7.5 Allow the pH meter to stabilize before recording the pH. Record pH to the nearest 0.10 unit.

7.6 Gently raise the pH electrode from the paste and wash all particles adhering to the electrode with a stream of distilled water.

8. CALCULATIONS
No calculations are required for this procedure.

9. REPORT
Report saturated paste pH to the nearest 0.1 pH unit.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
McLean, E.O. 1982. Soil pH and lime requirement. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:199-224.

U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

MISCELLANEOUS
REACTION (pH) (8C)
SOIL SUSPENSIONS (8C1)
NaF (1 *N* pH 7.2 - 8.1) (8C1d)

1. APPLICATION
The action of NaF upon noncrystalline (amorphous) soil material releases hydroxide ions (OH^-) to the soil solution and increases the pH of the solution. The amount of amorphous material in the soil controls the release of OH^- and the subsequent increase in pH (Fields and Perrott, 1966). The following reactions illustrate this action and form the basis of procedure 8C1d.

$$Al(OH)_3 + 3 \ F^- >> AlF_3 + 3 \ OH^-$$

$$Si(OH)_4 + 4 \ F^- >> SiF_4 + 4 \ OH^-$$
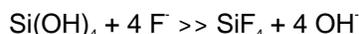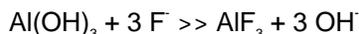
Most soils contain components that react with NaF and release OH^-. However, a NaF pH ≥ 9.4 is a strong indicator that amorphous material dominates the soil exchange complex. Amorphous material is usually an early product of weathering of pyroclastic materials in a humid climate. Amorphous material appears to form in spodic horizons in the absence of pyroclastics.

2. SUMMARY OF METHOD
A 1.000-g sample is mixed with 50 mL of 1 *N* NaF and stirred for 2 min. While the sample is being stirred, the pH is read at exactly 2 min in the upper 1/3 of the suspension.

3. INTERFERENCES
The difference in the sediment and supernatant pH is called the suspension effect (McLean, 1982). To maintain uniformity in pH determination, measure the pH just above the soil sediment. Clays may clog the KCl junction and slow the electrode response. Clean the electrode by rinsing with distilled water and patting it dry with tissue. Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization.
Soils with a 1:1 water pH >8.2 do not give a reliable NaF pH. Free carbonates in a soil result in a high NaF pH. In general, soils with a 1:1 water pH <7.0 are not affected.

4. SAFETY
The NaF is poisonous. Avoid eye contact and ingestion. Skin penetration and irritation are moderately hazardous. Do not eat or drink while using NaF. Thoroughly wash hands after use. Wear protective clothing, e.g., coats, aprons, and gloves, and eye protection, e.g., safety glasses or goggles, when using NaF. Use the fume hood when using NaF. Follow standard laboratory safety practices.

5. EQUIPMENT
5.1 Electronic balance, ±1-mg sensitivity
5.2 Paper cup, 120 mL (4 fl. oz.), disposable, Solo Cup Co., No. 404
5.3 Beaker, plastic, 50 mL
5.4 Beverage stirring sticks, wood, FSN 7340-00-753-5565
5.5 Digital pH/ion meter, Accumet Model 950, Fisher Scientific
5.6 Accu-pHast standard glass body combination electrode, Fisher Scientific
5.7 Stopwatch or timing device with min and s display.

6. REAGENTS
6.1 Distilled water

6.2 pH buffers, pH 4.00, pH 7.00, and pH 9.18, for electrode calibration.

6.3 Phenolphthalein

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6.4 Sodium fluoride (NaF), 1.0 *N*. In a plastic bottle, add 400 g NaF in 8 L of distilled water. Let stand for 2 days with occasional shaking. On the third day, after excess NaF has settled, measure 50 mL of the solution and read pH. The pH should be between 7.2 and 8.1. Add 3 to 5 drops 0.25% phenolphthalein and titrate to pink end point (pH 8.2 to 8.3). If pH is outside the 7.2 to 8.1 range, then adjust pH with either HF or NaOH. If solution has a pH >8.2 or if the titratable acidity is >0.25 meq L^{-1}, use another source of NaF.

7. PROCEDURE

7.1 Weigh 1.000 g of air-dry soil and place in a 120-mL (4-oz) paper cup.

7.2 Calibrate the pH meter with pH 7.00 and pH 9.18 buffer solutions. Use the pH 4.00 buffer solution as a linearity check.

7.3 After equipment calibration, gently wash the electrode with distilled water. Dry the electrode. Do not wipe the electrode with a tissue as this may cause a static charge on the electrode.

7.4 Dispense 50 mL of 1 *N* NaF into a plastic beaker.

7.5 Start stopwatch immediately upon addition of NaF solution to the soil.

7.6 Continuously stir the soil suspension with stirring stick for 1 min.

7.7 Place the pH electrode in the upper 1/3 of supernatant and continue to stir.

7.8 While stirring the soil suspension, read the pH at exactly 2 min.

7.9 Record the pH to ±0.01 pH units.
7.10 Rinse the electrode with distilled water.

7.11 Discard the solution, stirring stick, and cup in safe containers. The paper cup with the NaF solution leaks in about 15 min.

8. CALCULATIONS

No calculations are required for this procedure.

9. REPORT

Report NaF pH to the nearest 0.1 pH unit.

10. PRECISION

Precision data are not available for this procedure. A quality control check sample is included in every 24 analyses. With 22 observations of a quality control check sample, the mean, standard deviation, and C.V. are 11.0, 0.09, 0.8 %, respectively.

11. REFERENCES

Fields, M., and K.W. Perrott. 1966. The nature of allophane in soils. Part 3. Rapid field and laboratory test for allophane. N.Z. J. Sci. 9:623-629.
McLean, E.O. 1982. Soil pH and lime requirement. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:199-224.

MISCELLANEOUS
REACTION (pH) (8C)
SOIL SUSPENSIONS (8C1)
1:1 WATER DILUTION AND 1:2 CaCl₂ (8C1f)
(final solution: 0.01 M CaCl₂)

1. APPLICATION

The 1:1 water and 1:2 $CaCl_2$ pH determinations are two commonly performed soil pH measurements. The $CaCl_2$ soil pH is generally less than the 1:1 water pH. The combination of exchange and hydrolysis in salt solutions (0.1 to 1 M) can lower the measured pH from 0.5 to 1.5 units, compared to the pH measured in distilled water (Foth and Ellis, 1984).

In *Soil Taxonomy*, these pH values are used as a criterion for reaction classes (acid and nonacid) in families of Entisols and Aquepts (Soil Survey Staff, 1975). The acid class is <5.0 pH in 0.01 M $CaCl_2$ (2:1) or ≈ 5.5 in 1:1 water. The nonacid class is ≥5.0 pH in 0.01 M $CaCl_2$ (2:1).

2. SUMMARY OF METHOD

The pH is measured in soil-water (1:1) and soil-salt (1:2 $CaCl_2$) solutions. For convenience, the pH is initially measured in water and then measured in $CaCl_2$. With the addition of an equal volume of 0.02 M $CaCl_2$ to the soil suspension that was prepared for the water pH, the final soil-solution ratio is 1:2 0.01 M $CaCl_2$.

A 20-g soil sample is mixed with 20 mL of distilled water (1:1 w:v) with occasional stirring. The sample is allowed to stand 1 h with occasional stirring. The sample is stirred for 30 s, and the 1:1 water pH is measured. The 0.02 M $CaCl_2$ (20mL) is added to soil suspension, the sample is stirred, and the 1:2 0.01 M $CaCl_2$ pH is measured.

3. INTERFERENCES

The pH will vary between the supernatant and soil sediment (McLean, 1982). Measure the pH just above the soil sediment to maintain uniformity. Clays may clog the KCl junction and slow the electrode response. Clean the electrode. Wiping the electrode dry with cloth, laboratory tissue or similar material may cause electrode polarization. Rinse the electrode with distilled water and pat dry.

Atmospheric CO_2 affects the pH of the soil:water mixture. Closed containers and nonporous materials will not allow equilibration with CO_2. At the time of pH determination, the partial pressure of CO_2 and the equilibrium point must be considered, if doing critical work.

4. SAFETY

No significant hazards are associated with the procedure. Follow standard laboratory safety practices.

5. EQUIPMENT

5.1 Measuring scoop, handmade, ≈ 20-g capability
5.2 Paper cup, 120 mL (4 fl. oz.), disposable, Solo Cup Co., No. 404
5.3 Manual multiple dispenser, Repipet or equivalent, 0 to 30 ml, Custom Laboratory Equipment Inc.
5.4 Beverage stirring sticks, wood, FSN 7340-00-753-5565
5.5 Titration beakers, polyethylene, 250 mL
5.6 Automatic titrator, Metrohm 670 Titroprocessor Series 04, 664 Control Unit, 674 Sample Changer Series 5, and 665 Dosimat Series 14, Metrohm Ltd., Brinkmann Instruments, Inc.
5.7 Digital pH meter, Metrohm model E500, Brinkmann Instruments, Inc.
5.8 Combination pH-reference electrode, Metrohm part no. 6.0210.100, Brinkmann Instruments, Inc.

6. REAGENTS

6.1 Distilled water
6.2 pH buffers, pH 4.00, pH 7.00, and pH 9.18, for electrode calibration.
6.3 Calcium chloride ($CaCl_2$), 0.02 M. Dissolve 23.52 g of $CaCl_2 \cdot 2H_2O$ in distilled water and dilute to 8 L.

7. PROCEDURE

7.1 Use a calibrated scoop to measure $\approx$ 20 g of mineral soil.

7.2 Place the sample in a 120-mL (4-oz) paper cup.

7.3 Dispense 20 mL of distilled water into sample and stir.

7.4 Place paper cup with sample in 250-mL titration beaker, allow to stand for 1 h, stirring occasionally.

7.5 Load beakers into sample magazines and arrange on sample changer table.

7.6 Calibrate the pH meter using the pH 7.00 and pH 4.00 buffer solutions. Use pH 9.18 buffer solution as a linearity check.

7.7 Sample stirring, waiting interval for readings, addition of CaCl$_2$ solution, pH readings, and rinsing of electrode are controlled by computer. Refer to Appendix XV for operation of the automatic titrator.

7.8 The general sequence used by the automated system is as follows:

a. The sample is lifted so that the pH electrode is positioned above the soil sediment.

b. The sample is stirred for 30 s.

c. After 1 min, 1:1 water pH is read and recorded by unit.

d. The 20 mL of 0.02 *M* CaCl$_2$ are added to sample. The sample is stirred for 30 s.

e. After 1 min, the 1:2 CaCl$_2$ pH is read and recorded by unit.

f. The sample is lowered, and the electrode and stirrer are rinsed with distilled water.

g. The next sample is positioned for analysis.

h. The cycle is repeated until all samples have been analyzed.

8. CALCULATIONS
No calculations are required for this procedure.

9. REPORT
Report the 1:1 water pH and the 1:2 0.01 *M* CaCl$_2$ pH to the nearest 0.1 pH unit.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is included in every 24 analyses. For 32 observations of the quality control check sample (1:1 water pH), the mean, standard deviation, and C.V. are 5.7, 0.06, and 1.1%, respectively. For 32 observations of the quality control check sample (1:2 CaCl$_2$ pH), the mean, standard deviation, and C.V. are 5.0, 0.03, and 0.6%, respectively.

11. REFERENCES

Foth, H.D., and B.G. Ellis. 1984. Soil fertility. Soil pH and its management. p. 36-61. John Wiley and Sons. NY, NY.

McLean, E.O. 1982. Soil pH and lime requirement. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:199-224.

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys, USDA-SCS Agric. Handb. 436.

MISCELLANEOUS
REACTION (pH) (8C)
SOIL SUSPENSIONS (8C1)
1 *N* KCl (8C1g)
AUTOMATED SYSTEM
METROHM TITROPROCESSOR 670

1. APPLICATION

The 1 *N* KCl pH is an index of soil acidity. If KCl pH is <5, significant amounts of Al are expected in the solution, and if the pH is very much below 5, almost all the acidity is in the form of Al.

2. SUMMARY OF METHOD

A 20-g soil sample is mixed with 20 mL of 1 *N* KCl. The sample is allowed to stand for 1 h with occasional stirring. The sample is stirred for 30 s, and after 1 min, the KCl pH is read.

3. INTERFERENCES

The difference in the sediment and supernatant pH is called the suspension effect (McLean, 1982). To maintain uniformity in determination, measure the pH just above the soil sediment. Clays may clog the KCl junction and slow the electrode response. Clean the electrode by rinsing with distilled water and patting it dry with tissue. Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization.

4. SAFETY

No significant hazards are associated with the procedure. Follow standard laboratory safety practices.

5. EQUIPMENT
5.1 Measuring scoop, handmade, $\approx$ 20 g
5.2 Paper cup, 120 mL (4 fl. oz.), disposable, Solo Cup Co., No. 404
5.3 Dispenser, 0 to 10 mL, Repipet or equivalent
5.4 Beverage stirring sticks, wood, FSN 7340-00-753-5565
5.5 Titration beakers, polyethylene, 250 mL
5.6 Automatic titrator, Metrohm 670 Titroprocessor Series 04, 664 Control Unit, 674 Sample Changer Series 5, and 665 Dosimat Series 14, Metrohm Ltd., Brinkmann Instruments, Inc.
5.7 Digital pH meter, Metrohm model E500, Brinkmann Instruments, Inc.
5.8 Combination pH-reference electrode, Metrohm part no. 6.0210.100, Brinkmann Instruments, Inc.

6. REAGENTS
6.1 Distilled water
6.2 pH buffers, pH 4.00 and pH 7.00, for electrode calibration.
6.3 Potassium chloride (KCl), 1.0 *N*. Dissolve 74.56 g of KCl in distilled water. Dilute to 1 L.

7. Procedure

7.1 Use a calibrated scoop to measure $\approx$ 20 g of mineral soil.

7.2 Place the sample in a 120-mL (4-oz) paper cup.

7.3 Dispense 20 mL of 1 *N* KCl into sample and stir with wooden beverage stirrer.

7.4 Place paper cup with sample in 250-mL titration beaker, allow to stand 1 h, stirring occasionally.

7.5 Load beakers into sample magazines and arrange on sample changer table.

7.6 Calibrate the pH meter using the pH 7.00 and pH 4.00 buffer solutions.

MISCELLANEOUS
REACTION (pH) (8C)
SOIL SUSPENSIONS (8C1)
1 *N* KCl (8C1g)
AUTOMATED SYSTEM
METROHM TITROPROCESSOR 670

7.7 Sample stirring, waiting interval for reading, pH reading, and rinsing of electrode are controlled by computer. Refer to Appendix XV for operation of the automatic titrator.

7.8 The general sequence used by the automated system is as follows:

a. The sample is lifted so that pH electrode is positioned above the soil sediment.

b. The sample is stirred for 30 s.

c. After 1 min, the KCl pH is read and recorded by unit.

d. The sample is lowered, and the electrode and stirrer are rinsed with distilled water.

e. The next sample is positioned for analysis.

f. The cycle is repeated until all samples have been analyzed.

8. CALCULATIONS
        No calculations are required for this procedure.

9. REPORT
        Report KCl pH to the nearest 0.1 pH unit.

10. PRECISION
        Precision data are not available for this procedure. A quality control check sample is included in every 24 analyses. For 35 observations of the quality control check sample, the mean, standard deviation, and C.V. are 4.1, 0.03, and 0.8 %, respectively.

11. REFERENCES
  McLean, E.O. 1982. Soil pH and lime requirement. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:199-224.

MISCELLANEOUS
REACTION (PH) (8C)
SOIL SUSPENSIONS (8C1)
OXIDIZED pH (8C1h)

1. APPLICATION

The pH of a soil that has been incubated at room temperature and at a moisture content above field capacity is used to assess the potential formation of reducing conditions through the activities of soil microorganisms. If the soil has a ready source of energy for the microorganisms, e.g., fresh organic matter or reduced inorganic compounds such as sulfides, the soil potential is higher. If the soil has no free carbonates and has a significant available source of decomposable organic matter for the microorganisms, the oxidized pH is < 1:1 water pH.

Ochre is the name commonly assigned to oxidized Fe deposits and associated bacterial slimes that can clog drains. Ochre can be so voluminous and gelatinous from water hydration that drains become clogged from masses of these deposits. Drain design, installation, and maintenance can be changed when the ochre forming potentials of drainage sites are known (Ford, 1982). Although not routinely adopted as a standard procedure in determining ochre forming potentials, oxidized pH may be used as an indicator of these potentials.

2. SUMMARY OF METHOD

A soil sample is wetted with distilled water until it is saturated. The soil is mixed periodically and stored at room temperature in a closed container. The pH of the soil:water mixture is read daily. When water unt86 ue ohs

7.5 Read the pH of the saturated soil in 1 h after mixing. Carefully place the electrode into the soil mixture. Ensure that the KCl junction and sensor membrane are in contact with the mixture.

7.6 Allow the pH meter to stabilize before recording the pH. Record the pH to the nearest 0.01 pH unit.

7.7 Close the polycon and store at room temperature (20 to 25°C).

7.8 Mix the sample daily and record pH. Note any bubbling. After pH determination, immediately close the polycon.

7.9 Record the pH daily until the change is <0.03 pH units.

8. CALCULATIONS
No calculations are required for this procedure.

9. REPORT
Report the initial pH and the oxidized pH (end pH) to the nearest 0.1 pH unit.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Ford, H.W. 1982. Some fundamentals of iron and slime deposition in drains. Proc. 2nd. International Drainage Workshop. Washington, DC. Dec. 5-12. 1982.

MISCELLANEOUS
REACTION pH (8C)
ORGANIC MATERIALS (8C2)
CaCl$_2$ (8C2a)
(final solution: ~ 0.01 M CaCl$_2$)

1. APPLICATION
Two family reaction classes in Histosols are distinguished in *Soil Taxonomy* (Soil Survey Staff, 1975). Dysic families have a pH <4.5 in 0.01 *M* CaCl$_2$ in all parts of the organic materials in the control section. Euic families have a pH >4.5 in 0.01 *M* CaCl$_2$ in some part of the control section.

2. SUMMARY OF METHOD
Place 2.5 mL (2.5 cm^3) of the prepared sample in a 30-mL plastic container and add 4 of 0.015 *M* CaCl$_2$, i.e., yields final concentration of $\approx$ 0.01 *M* CaCl$_2$ with most packed, moist organic materials. Mix, cover, and allow to equilibrate at least 1 h. Uncover and measure pH with pH paper or pH meter (Soil Survey Staff, 1975).

3. INTERFERENCES
This test of organic soil material can be used in field offices. Since it is not practical in the field to base a determination on a dry sample weight, moist soil is used. The specific volume of moist material depends on how it is packed. Therefore, packing of material must be standardized in order to obtain comparable results by different soil scientists (Soil Survey Staff, 1975).

Clean the pH electrode by rinsing with distilled water and patting it dry with tissue. Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization.

4. SAFETY
No signifcant hazard has been identifed with this procedure. Follow standard laboratory safety precautions.

5. EQUIPMENT
5.1 Polycons, 30 mL
5.2 Digital pH/ion meter, Accumet Model 950, Fisher Scientific
5.3 Electrode, standard glass body combination, Accu-pHast, Fisher Scientific
5.4 Half-syringe, 6 mL. Cut plastic syringe longitudinally to form a half-cylinder measuring device.
5.5 Metal spatula

6. REAGENTS
6.1 Distilled water
6.2 CaCl$_2$, 0.015 *M*
6.3 pH buffers, pH 4.00 and 7.00, for pH meter calibration.

7. PROCEDURE

Sample Preparation
7.1 Prepare soil material. If the soil is dry, add water and let stand to saturate. Place 50 to 60 mL of a representative sample on a paper towel in a linear mound. Roll the towel around the sample and express water if necessary. Use additional paper towels as external blotters. Remove the sample and place on a fresh paper towel. The sample should be firm but saturated with water.

7.2 Use scissors to cut sample into 0.5- to 1.0-cm long segments.

7.3 Randomly select sample segments for determination of fiber (8G1), solubility in pyrophosphate (8H), and pH (8C2a).

pH Determination

7.4 Use a metal spatula to pack a half-syringe that is adjusted to the 5-mL mark or 2.5-mL (2.5-cm^3) volume with the moist sample.

7.5 Place 2.5 mL (2.5 cm^3) of the prepared sample in a 30-mL polycon and add 4 mL of 0.015 M CaCl$_2$, i.e. yields a final concentration of approximately 0.01 M CaCl$_2$ with most packed moist organic materials.

7.6 Mix, cover, and allow to equilibrate at least 1 h.

7.7 Uncover, mix again, immerse electrode, and measure pH. Rinse electrode with distilled water.

7.8 Alternatively, place pH strip on top of sample so that it wets from the bottom. Close cover and allow to equilibrate approximately 5 min. Remove pH strip with tweezers. Use a wash bottle to gently wash soil from bottom of strip. Compare color of active segment (center) with reference segments and with pH scale on box to determine pH.

8. CALCULATIONS

No calculations are required for this procedure.

9. REPORT

Report the 0.01 M CaCl$_2$ pH to the nearest 0.1 pH unit.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys, USDA-SCS Agric. Handb. 436. Appendix III: Tests of organic materials. p. 483. U.S. Govt. Print. Office, Washington, DC.

MISCELLANEOUS
RATIOS AND ESTIMATES (8D)
TO TOTAL CLAY (8D1)

Divide the cation exchange capacity (CEC-7) (procedure 5A8c), extractable Fe (procedure 6C2), 15-bar water retention (procedure 4B2a or 4B2b), or other measurements by the total clay percentage (procedure 3A1 or 3A2) In the past, the ratios of CEC:clay, Fe:clay, and 15-bar water:clay have been reported as meq g^{-1}, g g^{-1}, and g g^{-1}, respectively.

MISCELLANEOUS
RATIOS AND ESTIMATES (8D)
TO NONCARBONATE CLAY (8D2)

Divide the CEC-7 (procedure 5A8c), extractable Fe (procedure 6C2), or 15-bar water retention (procedure 4B2a or 4B2b) by the noncarbonate clay percentage. Noncarbonate clay is determined by subtracting the carbonate clay (procedure 3A1d or 3A2d) from total clay (procedure 3A1 or 3A2).

MISCELLANEOUS
RATIOS AND ESTIMATS (8D)
Ca to Mg (extractable) (8D3)

Divide extractable Ca^{2+} (procedure 6N2) by extractable Mg^{2+} (procedure 6O2).

MISCELLANEOUS
RATIOS AND ESTIMATES (8D)
ESTIMATED CLAY PERCENTAGE (8D4)

For most soils, clay percentage can be approximated as 2.5 x 15-bar water percentage (procedure 4B2a or 4B2b). Use caution in applying this factor to any particular situation, especially if organic matter or other amorphous material is present in significant quantities.

MISCELLANEOUS
RATIOS AND ESTIMATES (8D)
ESTIMATED TOTAL SALT (8D5)

Use the charts and graphs available in U.S. Salinity Laboratory Staff (1954) to estimate total salt content from the electrical conductivity (EC$_s$) of the saturation extract (procedure 8A3a). The essential relations are summarized in the equations as follows:

Log total salt in soil (ppm) = 0.81 + 1.08 x Log EC$_s$ (mmhos cm^{-1}) + Log SP

where:
EC$_s$ = Electrical conductivity of saturation extract
SP = Saturation percentage of saturation extract

Total salt in soil (%) = Total salt (ppm) x 10^{-4}

These equations are applicable to saturation extracts with an EC$_s$ <20 mmhos cm^{-1}. Deviations occur at higher salt concentrations.

MISCELLANEOUS
RATIOS AND ESTIMATES (8D)
IRON PLUS ALUMINUM, PYROPHOSPHATE EXTRACTABLE TO DITHIONITE-CITRATE EXTRACTABLE (8D6)

Divide the sum of the pyrophosphate-extractable Fe plus Al (procedures 6C8a and 6G10a, respectively) by the sum of dithionite-citrate-extractable Fe plus Al (procedures 6C2 and 6G7, respectively). Pyrophosphate and dithionite-citrate extractable Fe and Al are former criteria for spodic placement (Soil Survey Staff, 1975).

MISCELLANEOUS
RATIOS AND ESTIMATES (8D)
INDEX OF ACCUMULATION (8D7)

Subtract 1/2 the clay percentage (procedure 3A1 or 3A2) of a subhorizon from the CEC at pH 8.2 (procedure 5A3a) and multiply the remainder by the thickness of subhorizon (cm). The combined index of accumulation of amorphous material is a former criterion for spodic placement (Soil Survey Staff, 1975).

REFERENCES
Soil Survey Staff. 1975. Soil Taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA-SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.
U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

CORRIGENDA

MISCELLANEOUS
RATIOS AND ESTIMATES (8D)
ESTIMATED TOTAL SALT (8D5)

Use the charts and graphs available in U.S. Salinity Laboratory Staff (1954) to estimate total salt content from the electrical conductivity (EC_s) of the saturation extract (procedure 8A3a). The essential relations are summarized in the equations as follows:

Total Salt in soil (ppm) = (-4.2333 + (12.2347 X Ec_s) + (0.058 x Ec_s^2) - (0.0003 x Ecs^3)) x 0.000064 x SP

where:
EC_s = Electrical conductivity of saturation extract
SP   = Saturation percentage of saturation extract

MISCELLANEOUS
SOIL RESISTIVITY (8E)
SATURATED PASTE (8E1)

1. APPLICATION

The resistivity of the soil paste is mainly used to estimate the salt content in the soil. The apparatus is simple and rugged, the measurements can be made quickly, and the results are reproducible. Many agencies use the Bureau of Soils electrode cup to estimate the soluble salt content in soils (Davis and Bryan, 1910; Soil Survey Staff, 1951).

There is no simple method to convert saturation extract electrical conductivity to soil paste resistivity or vice versa. There is a limited correlation between EC_s and R_s, as the relationship is markedly influenced by variations in SP, salinity, and soil mineral conductivity.

2. SUMMARY OF METHOD

A saturated paste is placed in an electrode cup. The resistance is measured. The temperature of the paste is measured. The resistance (ohms) is converted to a 60°F (15.5°C) basis.

3. INTERFERENCES

No significant interferences are known to affect the saturated paste resistivity measurement.

4. SAFETY

No significant hazards are associated with this procedure. Follow standard laboratory safety practices.

5. EQUIPMENT
5.1 Conductivity bridge, Model RC 16B2, Beckmann Instruments, Inc.
5.2 Soil cup cell holder, soil cup Cel-M, Industrial Instruments, Inc.
5.3 Bureau of Soils electrode cup, cell constant is defined as 0.25.
5.4 Thermometer, 0 to 100°C

6. REAGENTS

No reagents or consumables are used in this procedure.

7. PROCEDURE

7.1 Fill the electrode cup with the saturated paste (procedure 8A). Gently tap the cup to remove air bubbles. Level the soil paste by striking off the excess with a spatula.

7.2 Place the cup in the cell holder. Make sure that the surfaces of the cup and holder are clean and bright. Use steel wool or fine sandpaper to carefully clean the surfaces.

7.3 Set the conductivity meter to 1000 cycles s^{-1} and adjust the multiplier range and the dial control to obtain the most distinct butterfly pattern on the fluorescent tube.

7.4 Measure resistivity. Adjustment of the sensitivity control also may be necessary.

7.5 Record the resistivity.

7.6 Place a thermometer in the saturated paste. When the temperature is stabilized, record the temperature.

8. CALCULATIONS

Use Table 1 to convert measured resistance to specific resistance at 60°F (15.5°C).

Resistivity (ohms cm^{-1}) = ohms @ 60°C x electrode cup cell factor

9. REPORT

Report saturated paste resistivity in units of ohms at 60°F (15.5°C) to the nearest whole number.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Davis, R.O., and H. Bryan. 1910. The electrical bridge for the determination of soluble salts in soils. USDA, Bur. Soils Bull. 61, 36 pp.

Soil Survey Staff. 1951. Soil Survey Manual. USDA-ARS. Govt. Print. Office, Washington, DC.

Whitney, M., and T.H. Means. 1897. An electrical method of determining the soluble salt content of soils. USDA, Div. Soils Bul. 8, 30 pp., illus.

Table 1. Bureau of soils data for reducing soil paste resistance readings to values at 60°F (Whitney and Means, 1897).

Temp	Ohms								
°F	1 000	2 000	3 000	4 000	5 000	6 000	7 000	8 000	9 000
40	736	1 472	2 208	2 944	3 680	4 416	5 152	5 888	6 634
42	763	1 526	2 289	3 052	3 815	4 578	5 341	6 104	6 867
44	788	1 576	2 364	3 152	3 940	4 728	5 516	6 304	7 092
46	814	1 628	2 442	3 256	4 070	4 884	5 698	6 512	7 326
48	842	1 684	2 529	3 372	4 215	5 058	5 901	6 744	7 587
50	868	1 734	2 601	3 468	4 335	5 202	6 069	6 936	7 803
52	893	1 786	2 679	3 572	4 465	5 358	6 251	7 114	8 037
54	919	1 838	2 751	3 668	4 585	5 502	6 419	7 336	8 253
56	947	1 894	2 841	3 780	4 735	5 682	6 629	7 576	8 523
58	974	1 948	2 922	3 896	4 870	5 844	6 818	7 792	8 766
60	1 000	2 000	3 000	4 000	5 000	6 000	7 000	8 000	9 000
62	1 027	2 054	3 081	4 108	5 135	6 162	7 189	8 216	9 243
64	1 054	2 108	3 162	4 216	5 270	6 324	7 378	8 432	9 486
66	1 082	2 164	3 243	4 324	5 405	6 486	7 567	8 648	9 729
68	1 110	2 220	3 330	4 440	5 550	6 660	7 770	8 880	9 990
70	1 140	2 280	3 420	4 560	5 700	6 840	7 980	9 120	10 260
72	1 170	2 340	3 510	4 680	5 850	7 020	8 190	9 360	10 530
74	1 201	2 402	3 603	4 804	6 005	7 206	8 407	9 608	10 809
76	1 230	2 460	3 690	4 920	6 150	7 380	8 610	9 840	11 070
78	1 262	2 524	3 783	5 044	6 305	7 566	8 827	10 088	11 349
80	1 294	2 588	3 882	5 176	6 470	7 764	9 058	10 352	11 646
82	1 327	2 654	3 981	5 308	6 635	7 962	9 289	10 616	11 943
84	1 359	2 718	4 077	5 436	6 795	8 154	9 513	10 872	12 231
86	1 393	2 786	4 179	5 572	6 965	8 358	9 751	11 144	12 537
88	1 427	2 854	4 281	5 708	7 135	8 562	9 989	11 416	12 843
90	1 460	2 920	4 380	5 840	7 300	8 760	10 220	11 680	13 140
92	1 495	2 990	4 485	5 980	7 475	8 970	10 465	11 960	13 455
94	1 531	3 062	4 596	6 128	7 660	9 192	10 724	12 256	13 788
96	1 569	3 138	4 710	6 280	7 850	9 420	10 990	12 560	14 130
98	1 609	3 218	4 833	6 444	8 055	9 666	11 277	12 888	14 499

MISCELLANEOUS
MINERAL CONTENT (8F)
LOSS ON IGNITION (400°C) (8F1)

1. APPLICATION

The mineral content is the plant ash and soil particles that remain after organic matter removal. The percentage of organic matter lost on ignition can be used to define organic soils in place of organic matter estimates by the Walkley-Black organic C method (6A1c). The determination of organic matter by loss on ignition is a taxonomic criterion for organic soil materials (Soil Survey Staff, 1994). Organic C data by Walkley-Black are generally considered invalid if organic C is >8 percent.

2. SUMMARY OF METHOD

Dry sample overnight at 110°C in moisture can. Cool and weigh. Place sample in a cold muffle furnace and raise the temperature to 400°C. Heat sample overnight (16 hr), cool, and weigh. The ratio of the weights (400°C/105°C) is the mineral content percentage.

3. INTERFERENCES

The sample must be placed in a cold muffle furnace to prevent rapid combustion and sample splattering.

4. SAFETY

Use caution when the muffle furnace is hot. Wear protective clothing and goggles. Handle the heated material with tongs.

5. EQUIPMENT

5.1 Metal weighing tins
5.2 Oven, 105 to 110°C
5.3 Muffle furnace, 400°C
5.4 Electronic Balance, ±0.01-g sensitivity

6. REAGENTS

None.

7. PROCEDURE

7.1 Place a 10- to 15-g sample in a tared weighing tin.

7.2 Dry sample at 105°C overnight.

7.3 Remove sample from oven, cap, and cool in a desiccator.

7.4 When cool, record weight to nearest 0.01 g.

7.5 Place sample and weighing tin in a cold muffle furnace. Raise temperature to 400°C. Heat overnight (16 h).

7.6 Remove sample from oven, cap, and cool in a desiccator.

7.7 When cool, record sample weight to nearest 0.01 g.

8. CALCULATIONS

Mineral Content (%) = (R_w/OD_w) x 100

where:
R_w = Residue weight after ignition
OD_w = Oven-dry soil weight

Organic matter percent can then be calculated as follows:

Organic Content (%) = 100 - Mineral Content (%)

9. REPORT
Report percentage mineral content.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Soil Survey Staff. 1994. Keys to soil taxonomy. 6th ed. USDA-SCS. Govt. Print. Office, Washington, DC.

MISCELLANEOUS
FIBER VOLUME (8G)
WATER DISPERSED (8G1)

1. APPLICATION

The water-dispersed fiber volume is a method to characterize the physical decomposition state of organic materials. The decomposition state of organic matter is used in *Soil Taxonomy* (Soil Survey Staff, 1975) to define sapric, hemic, and fibric organic materials. Sapric material passes through a 100-mesh sieve (0.15-mm openings). Fibers are retained on the sieve. As defined in *Soil Taxonomy*, organic materials that are >2 mm in cross section and that are too firm to be readily crushed between thumb and fingers are excluded from fiber.

2. SUMMARY OF METHOD

The sample is prepared to a standard water content. The unrubbed fiber content is determined in a series of three steps designed to remove the sapric material by increasingly vigorous treatments. The rubbed fiber content is determined by rubbing the sample between the thumb and fingers (Soil Survey Staff, 1975).

3. INTERFERENCES

This test of organic soil material can be used in field offices. Since it is not practical in the field to base a determination on a dry sample weight, moist soil is used. The specific volume of moist material depends on how it is packed. Therefore, packing of material must be standardized in order to obtain comparable results by different soil scientists (Soil Survey Staff, 1975).

4. SAFETY

Use caution when using electrical equipment.

5. EQUIPMENT

5.1 Half-syringe, 6 mL. Cut plastic syringe longitudinally to form a half-cylinder measuring device.
5.2 Sieve, 100 mesh, 7.6-cm diameter
5.3 Eggbeater
5.4 Microscope or hand lens
5.5 Electric mixer, Hamilton Beach no. 35
5.6 Scissors
5.7 Paper towel
5.8 Metal spatula

6. REAGENTS

None.

7. PROCEDURE

Sample Preparation

7.1 Prepare soil material. If the soil is dry, add water and allow to stand until saturated. Place 50 to 60 mL of a representative sample on a paper towel in a linear mound. Roll the towel around the sample and gently squeeze to express water if necessary. Use additional paper towels as external blotters. Remove the sample and place on a fresh paper towel. The sample should be firm but saturated with water.

7.2 Use scissors to cut sample into 0.5- to 1.0-cm length segments.

7.3 Randomly select sample segments for determination of fiber (procedure 8G1), solubility in pyrophosphate (procedure 8H), and pH (procedure 8C2a).

Unrubbed Fiber: Overview

7.4 The unrubbed fiber procedure involves a series of three steps designed to disperse sapric material by increasingly vigorous treatments. All three steps may not be necessary. Following each step that is performed, the percentage estimate of sapric material remaining is visually determined under a microscope or hand lens. The following categories are used to estimate the remaining sapric component.

a. Clean (<1% sapric)
b. Nearly clean (1 to 10% sapric)
c. Some sapric (10 to 30% sapric)
d. Sapric (>30% sapric)

Unrubbed Fiber: Step 1

7.5 Use a metal spatula to pack a half-syringe that is adjusted to the 5-mL mark or 2.5-mL (2.5 cm^3) volume with the moist sample.

7.6 Transfer all the soil material to a 100-mesh sieve and wash under a stream of tap water, adjusted to deliver 200 to 300 mL in 5 s. Wash sample until the water passing through the sieve appears clean. To more clearly determine the end point, catch the effluent in a white plastic container. Periodically empty the container until the effluent runs nearly clean.

7.7 Examine the sample under a microscope or hand lens to determine if sample is free of sapric material.

7.8 If sapric material is >10%, proceed to Unrubbed Fiber: Step 2. If sapric material is <10%, wash the residue to one side of the screen and blot from underneath with absorbent tissue to withdraw water and proceed as follows with Unrubbed Fiber: Step 1.

7.9 Repack the residue into a half-syringe and blot again with absorbent tissue. The moisture content should be ≈ that of the original sample.

7.10 Measure the volume by withdrawing the plunger and reading the value on the syringe scale. Record as a percentage of the initial 2.5-mL (2.5 cm^3) volume.

7.11 Proceed with the Rubbed Fiber determination.

Unrubbed Fiber: Step 2

7.12 Transfer the residue obtained in Unrubbed Fiber: Step 1 to a 500-mL plastic container and fill about half full with water.

7.13 Stir vigorously with an eggbeater for 1 min.

7.14 Transfer to the 100-mesh sieve and repeat procedures in Unrubbed Fiber: Step 1 beginning with 7.9. If sapric material is >10%, proceed to Unrubbed Fiber: Step 3.

Unrubbed Fiber: Step 3

7.15 Transfer residue left from Unrubbed Fiber: Step 2 to an electric mixer container (malt mixer or blender) and fill to about two-thirds with water.

7.16 Mix for 1 min.

7.17 Transfer to a 100-mesh sieve and repeat Unrubbed Fiber: Step 1 beginning with 7.6, the washing procedure.

7.18 Examine the residue under a microscope or hand lens and estimate the percentage of sapric material, if any.

7.19 Record the kind of fiber observed. Typical fibers are herbaceous, woody, and diatomaceous.

7.20 Blot the sample and measure the residue volume.

7.21 Proceed with the Rubbed Fiber determination.

Rubbed Fiber

7.22 Transfer the residue from the unrubbed fiber treatment to the 100-mesh sieve.

7.23 Rub sample between thumb and fingers under a stream of tap water, adjusted to deliver 150 to 200 mL in 5 s, until water passing through the sieve is clean. Clean rubbed fibers roll between the thumb and fingers rather than slide or smear.

7.24 Blot sample and measure volume in half-syringe.

8. CALCULATIONS

Fiber volume (%) = Reading on half-syringe (mL) x 20

where:
Fiber volume = Rubbed + unrubbed fiber

9. REPORT

Record the percentage of unrubbed fiber after each completed step. Report the final unrubbed and the rubbed fiber percentages. Also report fiber type.

10. PRECISION

Precision data are not available for this procedure. Experienced analysts can usually reproduce unrubbed fiber within ± 3 % (absolute) and rubbed fiber within ± 1 to 2% (absolute).

11. REFERENCES

Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys, USDA-SCS Agric. Handb. 436. Appendix III: Tests of organic materials. p. 483. U.S. Govt. Print. Office, Washington, DC.

MISCELLANEOUS
PYROPHOSPHATE COLOR (8H)

1. APPLICATION
Decomposed organic materials are soluble in sodium pyrophosphate. The combination of organic matter and sodium pyrophosphate form a solution color which correlates with the decomposition state of the organic materials. Dark colors are associated with sapric materials and light colors with fibric materials (Soil Survey Staff, 1975).

2. SUMMARY OF METHOD
Organic material is combined with sodium pyrophosphate. After standing, the color is evaluated by moistening a chromatographic strip in the solution and comparing the color with standard Munsell color charts (Soil Survey Staff, 1975).

3. INTERFERENCES
This test of organic soil material can be used in field offices. Since it is not practical in the field to base a determination on a dry sample weight, moist soil is used. The specific volume of moist material depends on how it is packed. Therefore, packing of material must be standardized in order to obtain comparable results by different soil scientists (Soil Survey Staff, 1975).

4. SAFETY
Use caution when handling sodium pyrophosphate.

5. EQUIPMENT
5.1 Polycons, 30 mL, Richards Mfg. Co.
5.2 Chromatographic paper, Schleicher and Schuell no. 470 A-3.
5.3 Munsell Color Book, 10YR and 7.5YR pages.
5.4 Half-syringe, 6 mL. Cut plastic syringe longitudinally to form a half-cylinder measuring device.
5.5 Scissors
5.6 Paper towel
5.7 Tweezers
5.8 Metal spatula

6. REAGENTS
6.1 Sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)

7. PROCEDURE

Sample Preparation
7.1 Prepare soil material. If the soil is dry, add water and let stand to saturate. Place 50 to 60 mL of a representative sample on a paper towel in a linear mound. Roll the towel around the sample and express water if necessary. Use additional paper towels as external blotters. Remove the sample and place on a fresh paper towel. The sample should be firm but saturated with water.

7.2 Use scissors to cut sample into 5- to 10-mm long segments.

7.3 Randomly select sample segments for determination of fiber (8G1), solubility in pyrophosphate (8H), and pH (8C2a).

Pyrophosphate
7.4 Dissolve 1 g (heaping 1/8 tsp) of sodium pyrophosphate in 4 mL of water in a 30-mL polycon container. Allow to equilibrate for 5 min.

7.5 Use a metal spatula to pack a half-syringe that is adjusted to the 5-mL mark or 2.5-mL (2.5-cm^3) volume with the moist sample.

7.6 Transfer soil material cleanly into the container that holds the pyrophosphate solution.

7.7 Mix thoroughly using a wooden stirrer or metal spatula. Cover and let stand overnight.

7.8 Mix sample again next morning.

7.9 Use tweezers to insert a strip of chromatographic paper vertically into the sample to a 1-cm depth. Let stand until the paper strip has wetted to a 2-cm height above slurry surface. Generally, sample needs to stand ≈ 5 min but may stand longer if cover is closed. Remove the paper strip with tweezers. Cut strip and leave in the slurry that portion to which the soil adheres.

7.10 Place the strip on a piece of blotting paper and press gently with tweezers to make even contact.

7.11 Remove paper strip with tweezers and compare color of the strip to Munsell color charts.

8. CALCULATIONS
No calculations.

9. REPORT
Report color using Munsell color notation.

10. PRECISION
Precision data are not available for this procedure. Experienced analysts can usually reproduce results within ± 1 color chip.

11. REFERENCES
Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA-SCS Agric. Handb. 436. Appendix III: Tests of organic materials. p. 483. U.S. Govt. Print. Office. Washington, DC.

MISCELLANEOUS
SALT PREDICTION (8I)

1. APPLICATION

Salt prediction is used not only to predict which soils have measurable amounts of soluble salts but also to predict the quantity and the appropriate dilutions for salt analyses of those soils. If salt predictions or conductances are <0.25 mmhos cm^{-1}, soils are considered nonsalty, and generally, no other salt analyses are performed on these soils by the SSL.

2. SUMMARY OF METHOD

A soil sample is mixed with water and allowed to stand overnight. The electrical conductivity (EC) of the mixture is measured using an electronic bridge. The EC is used to indicate the presence of soluble salts (U.S. Salinity Laboratory Staff, 1954).

3. INTERFERENCES

No significant interferences are known to affect the prediction EC.

4. SAFETY

No significant hazards are associated with this procedure. Follow standard laboratory safety practices.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity
5.2 Conductivity bridge and conductivity cell, Markson Model 1096, Amber Science, Eugene, OR
5.3 Condiment cups, 60 mL (2 fl. oz.), clear, with polylids, Anchor Hocking Plastics, Inc., St. Paul, MN
5.4 Dispenser, Repipet or equivalent, 0 to 10 mL

6. REAGENTS

6.1 Distilled deionized (DDI) water
6.2 Potassium chloride (KCL), 0.010 *N*. Dry KCl overnight or at least 4 h in oven (105°C). Dissolve 0.7456 g of KCl in DDI water and bring to 1-L volume. Conductivity at 25°C is 1.41 mmhos cm^{-1}.

7. PROCEDURE

7.1 Weigh 5.0 g of <2-mm, air-dry soil in a 60-mL (2-oz) condiment cup.

7.2 Add 10 mL of DDI water to sample using a Repipet dispenser.

7.3 Swirl to mix, cap, and allow to stand overnight.

7.4 Standardize the conductivity bridge using DDI water (blank) and 0.010 *N* KCl (1.41 mmhos cm^{-1}).

7.5 Read conductance of supernatant solution directly from the bridge.

7.6 Record conductance to 0.01 mmhos cm^{-1}.

8. CALCULATIONS

8.1 No calculations are required for this procedure.

8.2 Use the following relationship to estimate the total soluble cation or anion concentration (meq L^{-1}) in the soil.

EC (mmhos cm^{-1}) x 10 = Cation or Anion (meq L^{-1})

8.3 Use the following relationship to estimate the total soluble cation or anion concentration (meq g^{-1} oven-dry soil) in the soil.

EC (mmhos cm^{-1}) x 20 = Cation (meq g^{-1} soil)

EC (mmhos cm^{-1}) x 20 = Anion (meq g^{-1} soil)

9. REPORT
    Report prediction conductance in mmhos cm^{-1} to the nearest 0.01 mmhos cm^{-1}

10. PRECISION
    Precision data are not available for this procedure.

11. REFERENCES
    U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

APPENDIX

APPENDIX I

LABORATORY PREPARATION CODES

Use Table 1 with the SSL preparation procedures 1B1, 1B2, 1B5, 1B6, and 1B7. Gravel codes are also defined in Table 1. In the "Code" column, "Char" refers to characterization sample. Laboratory preparation and >2-mm porosity are defined in footnotes on laboratory data sheet.

Table 1. Laboratory preparation codes and procedural summaries.

Code		Laboratory Preparation
Char	**>2mm**	
S	**Blank**	Weigh sample at field moisture content and record weight. Air-dry, weigh, and record weight. Sieve >2-mm fractions, weigh, record weights, and discard. Report all analytical results on <2-mm basis. Refer to procedure 1B1, Standard Air-dry.
S	**P**	Lab preparation is same as S-blank. However, report clod parameters and Cm (correction factor for >2-mm content moist soil) on an whole soil basis. Refer to procedure 1B1, Standard Air-dry.
N	**Blank**	Lab preparation is same as S-blank except do not record the weight of the >2-mm fraction. All analytical results are reported on a <2-mm basis. Refer to procedure 1B1, Standard Air-dry.
M	**Blank**	Lab preparation is same as S-blank except sieve <2-mm moist subsample for 15-bar moist analysis. Use <2-mm air-dry soil for all other analyses. Report all analytical results on <2-mm basis. Refer to procedure 1B2, Field Moist.
S	**K**	Lab preparation is same as S-blank except grind the 2- to 20-mm fraction to <2 mm and keep for CO_3 analyses, etc. Report the analytical results for the ground 2- to 20-mm fraction on a 2- to 20-mm basis and all other analytical results on a <2-mm basis. Refer to procedure 1B5, Coarse Fragments.

APPENDIX I

LABORATORY PREPARATION CODES

Code		Laboratory Preparation
Char	**>2mm**	

S   **R**   Lab preparation is same as S-blank except recombine the 2- to 20-mm fraction with the <2-mm fraction and grind the entire sample to <2 mm. Report all analytical results for ground sample on a <2-mm basis. Refer to procedure 1B5, Coarse Fragments

G   **P**   Weigh sample at field moisture content and record weight. Air-dry, weigh, and record weight. Grind entire sample to <2 mm. Report all analytical results for ground sample on a whole soil basis. Refer to procedure 1B6, Whole Soil.

W   **P**   Weigh sample at field moisture content and record weight. Air-dry, weigh, and record weight. Sieve >2-mm fractions, weigh, and record weights. Recombine the >2-mm fractions with the <2-mm fraction and grind entire sample to <2 mm. Report all analytical results on a whole soil basis. This procedure is no longer performed at the SSL.

H   **Blank**   Obtain a moist whole soil subsample for Histosol analysis. Obtain a <2-mm moist subsample for 15-bar moist analysis. Weigh remaining sample at field moisture content and record weight. Air-dry, weigh, and record weight. Sieve >2-mm fractions, weigh, record weights, and discard. Pulverize subsample of <2-mm air-dry soil to a <80-mesh size and use for lab analyses. Use <80-mesh air-dry for all analyses except AD/OD, 15-, 1/10- and 2-bar analyses. For the AD/OD, 15-, 1/10- and 2-bar analyses, use <2-mm air-dry soil. Use <2-mm moist subsample for 15-bar moist. Report all analytical results except fabric on a <2-mm basis. Refer to procedure 1B7, Organic Material.

APPENDIX I

LABORATORY PREPARATION CODES

Code		Laboratory Preparation
Char	**>2mm**	
A (L)	**Blank**	Lab preparation is same as N-blank except pulverize subsample of <2-mm air-dry soil to a <80-mesh size and use for lab analyses. Use <80-mesh air-dry for all analyses except AD/OD and 15-bar analyses. For the AD/OD and 15-bar analyses, use <2-mm air-dry soil. All analytical results are reported on a <2-mm basis. Refer to procedure 1B1, Standard Air-dry.

Gravel codes

P =   porous >2-mm material that is considered soil is used for clod or core measurements.
V =   volume estimate is used to calculate the weight percentage of a >2-mm fraction. If that fraction is porous (P), code the samples with "P" rather than with "V".

Socket Set Screws

Top View

(15)

(4)

(14)

Fil. Hd. Mach. Scr.
No. 6-32   N.P. 3/8 Long
(4 required)

Precision Knurled Head
Thumb Screw
No. 10-32 1/2 Long

(6)

(16)

(3)

(4)

(2)

(1)

(11) diameter -
1.27 cm

(6) Precision Knurled
Head Thumb Screw
No. 10-32 1/2 Long

(12) Parallel Rails
diameter - 63 mm

(13) diameter - 63 mm
(scale optional)

(6) Precision Knurled
Head Thumb Screw
No. 10-32 1/2 Long
(place on opposite
side)

(19)

Thumb Screw
No. 1/4-20
1/2 Long

Nos. 1, 2, 14, 15, and 16 are
12.5 mm thick.

No. 19 is 3 cm square.

1	3	5 cm

Scale

Shaw Pipet Rack

APPENDIX III

<div style="text-align:center">

MECHANICAL VACUUM EXTRACTOR
OPERATION
INTERNATIONAL CENTURION, 24-PLACE

</div>

1. Locate control wheel on mechanical vacuum extractor. Use wheel to adjust the rate of extraction. In order to determine the rate of extraction, count the number of links on the chain that pass the upper toothed wheel. Use the following chart to determine the rate of extraction for a full plunger stroke.

Time: 1/2 h
Rate: 53 links min^{-1}
Rate: 8 links 9 s^{-1}

Time: 3/4 h
Rate:35 1/2 links min^{-1}
Rate: 6 links s^{-1}

Time: 1 h
Rate: 26 links min^{-1}
Rate: 10 links 23 s^{-1}

Time: 2 h
Rate: 13 links min^{-1}

Time: 4 h
Rate: 4 1/2 links min^{-1}

Time: 8 h
Rate: 1/3 links min^{-1}

Time: 12 h
Rate: 2 links min^{-1}

Time: 16 h
Rate: 1 2/3 links min^{-1}

2. Individual machines vary slightly in extraction rate. Mark the graduated speed scale with the wheel position to turn to the required speed.

REFERENCES
Centurion International Inc. 1977. Instruction Manual. Mechanical Vacuum Extractor, 24-place. Lincoln, NE.

MECHANICAL VACUUM EXTRACTOR
OPERATION
MAVCO SAMPLETEK

Overview

The soil extraction controller is a microprocessor-based device that allows accurate timing functions to be performed on extraction machines.

Indicators

There is an eighty character display which is used for communication to the operator and a LED indicator that illuminates when an operation is in progress.

Input

1. All operator input is accomplished through the use of a sixteen key pad located on the front panel. The key definitions are as follows:

a. Keys 0 to 9 are used for numeric input.

b. Key "A" adjusts the starting point of an extraction process by moving the table up rapidly. This key may be used at anytime.

c. Key "B" is not used.

d. Key "C" cancels any operation that is in progress and clears the display. This key also clears any errors.

e. Key "D" is not used.
f. Key "*" pauses an operation that is in progress.

g. Key "#" returns to operation from adjust or pause.

h. To use Keys "A", "C", and "*", press and hold for one second, then release. The associated function will then begin.

Options

1. Three options are available as follows:

a. Option 1 = Repeat previous extraction process.

b. Option 2 = Extraction option.

c. Option 3 = Retract option.

Operation

1. Power is applied to the controller through the AC connector located on the side. The power switch is also located there. When power is applied, one of two things will happen as follows:

a. If an operation is in progress when power is removed, then the operation will resume.

MECHANICAL VACUUM EXTRACTOR
OPERATION
MAVCO SAMPLETEK

b. The operator will be prompted to enter an option. Refer to the discussion on Options.

2. If Option 1 is entered, this is the only input required.

3. If Option 2 is entered, the sequence is as follows:

a. Prompt mL = Volume of sample to be taken in mL. Enter a two-digit number here. 10 to 60 mL is valid.

b. Prompt Hours = Number of hours in the extraction period. Enter a two-digit number here. 00 to 59 is valid. A minimum time of 1 min per 2 mL is required.

4. The extraction process will begin and the busy LED will light. The plate rises, causing a sample to be extracted for the amount of time entered above. The volume of the sample will be equal to the mL entry. The operation will continue until the sample time is complete or the operator presses the "C" Key or the Stroke Limit is reached.

5. If Option 3 is entered, the table will extract to the home position. The retract operation may be cancelled by pressing the "C" Key.

6. When any of the above operations have completed, the busy LED will extinguish and/or the following prompt will appear as follows: "Operation Complete, Press Any Key". When any key is pressed, the prompt "Option = " will appear.

REFERENCES
Mavco Industries, Inc. 1995. Operation Guide. Sampletek Programmable Sample Extractor Model 524.
        5300 N. 57th St., Lincoln, NE.

APPENDIX V

SULFUR AND CARBON ANALYZER
OPERATION
LECO MODEL SC-444

Set-up

1. Set the system and furnace power "On-Off" switch to the "On" position with sharp, positive motion.

2. If system is already on, touch screen to elevate furnace temperature to operating temperature.

3. Turn on the oxygen supply and set delivery pressure to 30 PSI.

4. Touch the Maintenance icon then Ambient Monitor icon. Check that the temperature, voltages, and pressure used in the system fall within the set range limits.

5. Touch the Front Panel icon and check status of instrument.

Calibration

6. The system electronics must be allowed to warm up for a minimum of 2 h after electrical power is applied, and the furnace must be at operating temperature before attempting analysis.

7. When true analytical performance is expected, the calibrations are as follows:

a. When the instrument has been idle for a length of time, or when fresh anydrone has been installed, 3 to 5 "conditioning" analyses should be run at the start of the day.

b. A system blank may be necessary if low C analyses are performed.

c. The system should be calibrated.

d. The balance should be calibrated.

e. The standards are defined.

8. Calibration procedure is as follows:

a. Touch the Calibration icon then the Define Standard icon. Enter the standard and its value.

b. Run 3 to 5 "conditioning" analyses.

c Run 3 to 5 blanks.

d. Analyze 3 to 5 samples of a known standard at various weight levels (e.g. 0.2, 0.5, 0.75 g).

e. Return to main menu, touch the Calibration icon.

f. Select the results to used to for calibration. Select process. The plot that appears on the calibration screen indicates the measured mg of sulfur or carbon in relation to the theoretical mg of S or C for each sample weight.

g. Choose the linear fixed calibration curve.

SULFUR AND CARBON ANALYZER
OPERATION
LECO MODEL SC-444

h. Verify that the calibration results are within 2 percent of the actual value.

i. Exit to main menu.

Shut-down

9. Touch Logoff icon to place instrument in standby mode.

10. Close the valve on the O_2 supply cylinder.

REFERENCES

Leco Corp. 1994. Instruction Manual. SC-444 Sulfur and Carbon Analyzers. Leco Corp., 3000 Lakeview Ave., St. Joseph, MI.
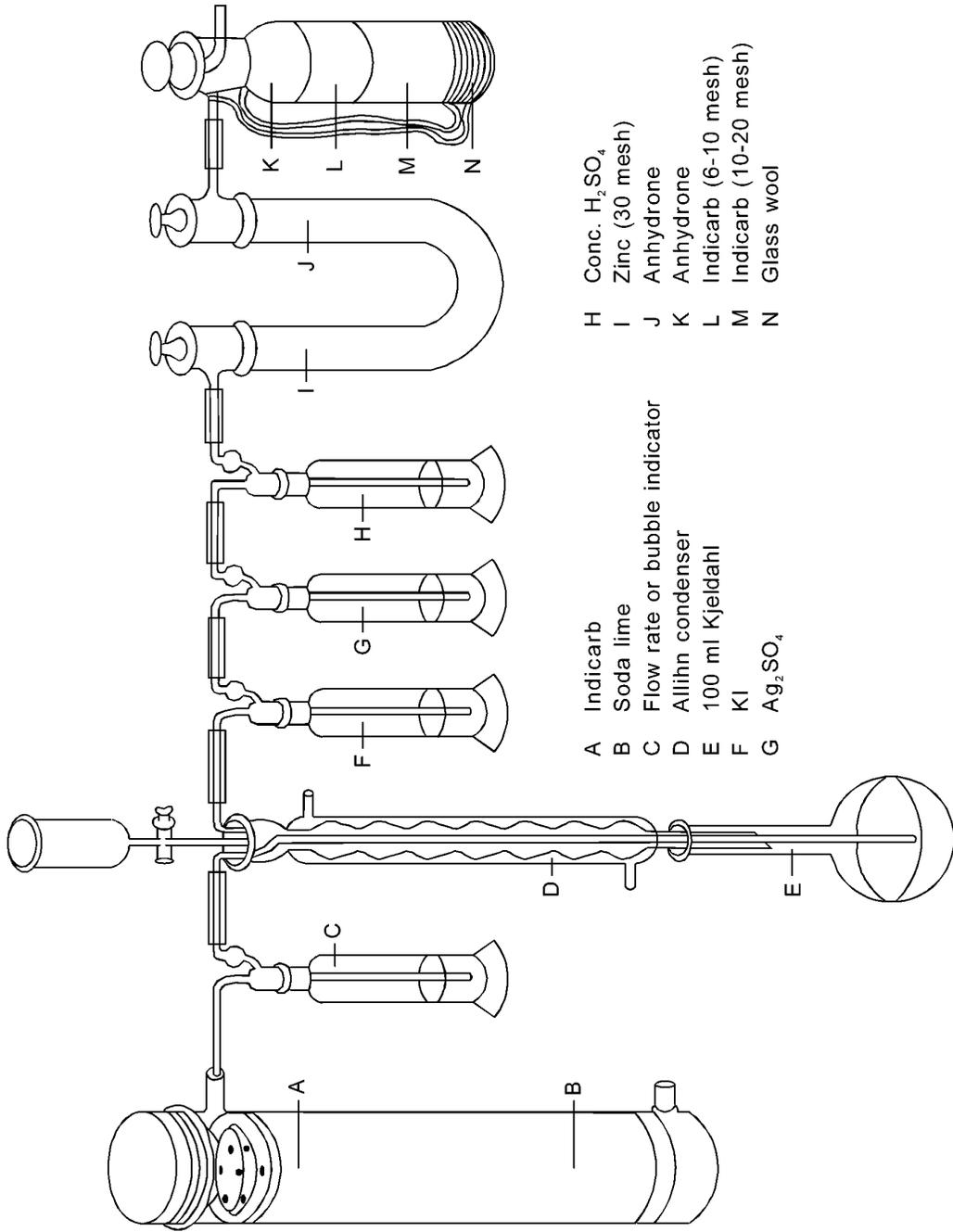
A   Indicarb
B   Soda lime
C   Flow rate or bubble indicator
D   Allihn condenser
E   100 ml Kjeldahl
F   KI
G   Ag$_2$SO$_4$

H   Conc. H$_2$SO$_4$
I   Zinc (30 mesh)
J   Anhydrone
K   Anhydrone
L   Indicarb (6-10 mesh)
M   Indicarb (10-20 mesh)
N   Glass wool

Apparatus for gravimetric organic carbon determinations of 0.1 M sodium pyrophosphate extracts.

APPENDIX VII

NITROGEN ANALYZER
LECO FP-428
MODEL 601-700-400

GENERAL INFORMATION

The FP-428 is a microprocessor-based software-controlled instrument that determines nitrogen in a variety of materials including grain, stock, feed, oil, rubber, and soil. There are three phases during the "Analyze" cycle which are the "Purge", "Burn", and "Analyze" phases. The "Burn" and "Analyze" modes are the same for both sample delivery methods.

In the "Sample Drop Purge" phase, the encapsulated sample is placed in the loading head, sealed, and purged of any atmospheric gases that have entered during sample loading. The Ballast Volume (zero volume at this point) and gas line are also purged. The liquid injector method offers a sealed delivery.

In the "Liquid Injector Purge" phase, the liquid sample is dumped into a system that is not open to the atmosphere. Therefore, the purging takes place only within the lines of the injector and not within the determinator. First, the liquid is removed from the furnace line and released into the purge cup. The injector and syringe are then purged. Finally, the furnace line is purged. Purging liquid released into the furnace is allowed to escape into the system without being analyzed.

During the "Burn" phase, the sample is dropped into a hot furnace (950°C) and then flushed with pure oxygen for a very rapid combustion. The products of combustion, mainly CO_2, H_2O, NO_x, and N_2, are passed through the thermoelectric cooler to remove most of the water then collected in the Ballast Volume. The Ballast Volume has a free floating piston which moves up during the collection of the gas products and is forced back down during gas removal. All the gas products in the Ballast Volume are allowed to become a homogeneous mixture at a pressure approximately 975 mm and a constant temperature.

In the "Analyze" phase, the piston is forced down and a 10 mL aliquot of the sample mixture is collected through the loop of the doser valve. The sample aliquot is swept through hot copper to remove oxygen and change NO_x to N_2, then through Lecosorb and Anhydrone to remove carbon dioxide and water, respectively. The remaining combustion product, nitrogen, is measured by the thermal conductivity cell.

The final result is displayed as percent nitrogen (or protein if selected). Results can also be calculated on a dry basis by entering a known moisture content.

Start-up

1. Turn instrument to "Analyze" mode. Allow system to warm up approximately 20 minutes. Both the furnace and the oven lights will flash on and off when the system is warmed up.

2. Touch Globe to "Log On".

3. Touch "User".

4. Enter operator's name. This data input brings up the main menu. Press "Enter".

5. Touch "View". Touch "System Folders".

6. Open "System Diagnostics" Open "Ambient Monitor".

7. Check to determine if the furnace temperature is near 950°C for soils. Check to determine if the t-cell output is near 1.0 and not > 2.5.

8. When system is warmed up, press "Escape" which puts the operator back into "System Diagnostics".

NITROGEN ANALYZER
LECO FP-428
MODEL 601-700-400

9. Open "Leak Check". The first check is oxygen followed by a helium check. Do a ballast check if the oxygen leak test fails. If the ballast leak check fails, the leak is in the combustion system.

10. See bar graph on monitor. If arrow moves to "Good", press "Escape" and do a helium check.

11. If arrow moves to the Warn Zone, the carrier or analyze gas may be leaking. Check to determine if the furnace is 950°C.

12. If the arrow moves to the Leak Zone, pressure is escaping from the system. Check combustion area including the furnace tube, "O" rings, and sliding block.

13. Press "Escape" to exit.
14. Go into "System Update" and open "Set Counters". Check to determine if the crucible reduction tube and aliquot tubes are not near their limit. If so, repack columns or change crucible as instructed in the manual.

15. Reset counters to zero. Limits are shown on the monitor, a warning is printed on the hard copy of the data reminding the operator to change the crucible or tubes.

16. Press "Escape". Press "Exit" to main menu.

Calibration

1. Touch "Log In". Touch "Id's".

2. Toggle down to "Blank". Press "Escape". Touch "Balance". Touch "Manual". Enter 0.500 g.

3. Enter about 4 to 5 blanks at 0.500 g each.

4. Using surgical or latex gloves, remove a tin foil cup with tweezers and place into a ball.

5. Blanks and samples can be placed in 10-hole sample holder in manual mode.

6. Touch "Id's again and toggle up to "Calibration Standard". Calibration standard (EDTA) = 9.59 percent N. Press "Exit".

7. Go to "Balance". Touch "External". Remote appears on monitor. Using gloves and tweezers, remove one tin foil cup from container, place on balance in sample holding cup, and tare balance. With small spatula, weigh approximately 200 mg of EDTA into foil cup.

8. Press "Print" on balance. Weight appears on monitor.
9. Fold into a "Hershey Kiss" with a flat bottom. Place in a sample holder. Repeat 3 to 4 times.

10. If any sample is lost from the foil cup, press "Remove" and previous weight is discarded. Discard sample foil cup.

11. To review weights or answers, press "Escape", then "View".

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12. Touch "Answer" or "Weight Stack" to see that the appropriate weight has been entered. Make sure instrument is in "Manual" not "Auto" mode.

13. Using tweezers, place a blank into sliding block hole and press "Analyze" (on monitor). Monitor will then que operator to press "Analyze" again which is the loader control button under the sliding block.

14. Analyze all blanks and EDTA calibration standards.

15. When completed, touch "View", "System Folders" and then "System Update".

16. Press "Standard Blank". Press "Enter".

17. Toggle arrow to the blanks that have been analyzed. Press "Include Sample" to highlight these 4 to 5 blanks. NOTE: When using 200-mg sample-size, the crucible will only hold 30 samples. Blanks are excluded.

18. Press "Process Results" and the note the new blank calibration.

19. Press "Standard Calibration".

20. See calculator on monitor, press "Enter". Highlight EDTA standards that have just been determined. Press "Process Results".

21. Press "Print". Press "Escape".

22. Go to the top of screen. Press "Exit" to main screen.

23. Press "Log In". Press "ID's". Toggle to Organic C/N Standard No. 12 (0.14 percent N). Other standards include Saturation Extract Standard No. 37 (0.07 percent N) or other known soil standards.

24. Go to balance "Remote".

25. Weigh 1 to 2 soil standards.

26. Go back into "ID's". Toggle to "Unknown Samples". Touch "Balance" remote (external). Press "Exit". Use Tab to sample ID code, enter sample #.

27. Weigh 200 mg soils as before with EDTA. Press "Print" on the balance.

28. Continue weighing samples and entering sample numbers.

29. To begin operation, place a sample into sliding block as before, press analyze and loader control button.

30. Continue to weigh sample while samples are being analyzed.

31. For use of carousel, see instruction manual.

APPENDIX VII

NITROGEN ANALYZER
LECO FP-428
MODEL 601-700-400

Standards used with LECO FP-428

1. Blanks are tin foil cups only. Enter 0.500 g sample weight.

2. Calibration standards are as follows:

a. EDTA, ethylenedinitrilo tetraaceticacid, disodium salt, dihydrate ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$). EDTA = 9.59 percent N with 100.2 percent purity.

b. Organic C/N Standard No. 12 = 0.14 percent N. Property of USDA-NRCS, Soil Survey Laboratory.

c. Saturation Extract Standard No. 37 = 0.07 percent N. Property of USDA-NRCS, Soil Survey Laboratory.

d. LECO Orchard Leaves Standard = 2.94 percent N (±0.03 percent).

3. All standards (excluding the calibration standard) have been oven-dried over night and placed in small vials in a desiccator. Be sure to cap standards after each use. Absorption of H_2O can provide erratic calibration. At the end of the day, place standards back in the desiccator. If humidity within the laboratory is high, it be necessary to maintain some oven-dried standards for immediate use.

REFERENCES
LECO Corp. 1992. Instruction Manual for LECO FP-428 Model 601-700-400. Version 2.1. LECO Corp., 3000 Lakeview Avenue, St. Joseph, MI.

APPENDIX VIII

STANDARDIZATION OF ACIDS

1. APPLICATION
   The standardization of weak mineral acids routinely is used to establish or check the normality of the acid. Many methods have been used to standardize an acid. In most cases, a primary standard is titrated or back titrated to a set end point. The titer is then used to calculate the normality of the acid.
   A primary standard is a substance that is used to accurately determine the concentrations of active reagents. A primary standard must have high purity (>99.98%). A secondary standard is a substance of accurately determined concentration by standardization with a primary standard, e.g., the concentration of the secondary standard, NaOH solution, is determined by standardization with the primary standard, high purity benzoic acid. Refer to Table 1 for a list of some common acids and bases. A list of some primary standards are as follows:

Benzoic acid - ($C_6H_5CO_2H$). Molecular weight = 122.123 Dissolve about 0.5 g in 50% ethanol and titrate to phenolphthalein end point.

Borax - ($Na_2B_4O_7 \cdot H_2O$). Molecular weight = 381.360. Methyl red indicator. Dissolve in water. Weak acid.

Mercuric oxide - (HgO) Molecular weight = 216.599. Bromthymol blue indicator. Dissolve 0.5 g with 15 g of KBr in 25 mL of DDI water, excluding CO_2.

Potassium bicarbonate - ($KHCO_3$). Molecular weight = 100.116. Bromcresol green indicator, first tint of green end point.

Potassium biodate - ($KH(IO_3)_2$). Molecular weight = 389.912. Bromthymol blue end biodate point. Strong acid. Low solubility.

Potassium biphthalate - ($KHC_8H_4O_4$). Molecular weight = 204.224. Phenolphthalein indicator. Weak acid.

Potassium bitatrate - ($KHC_4H_4O_6$). Molecular weight = 188.178. Phenolphthalein bitatrate indicator. Molding problem.

Sodium carbonate - (Na_2CO_3). Molecular weight = 105.988 Bromocresol green indicator, first green end point.

2. SUMMARY OF METHOD
   Dissolve approximately 0.1 g of sodium carbonate in distilled deionized (DDI) water. Titrate the solution and blanks with the acid to be standardized. Calculate the normality of the acid from the mean blank and titers. Report the mean normality and standard deviation for the acid standardization.

3. INTERFERENCES
   Clean the electrode by rinsing with distilled water. Wiping the electrode dry with a cloth, laboratory tissue, or similar material may cause electrode polarization.
   Slow electrode response time may cause over shooting the end point. A combination of slowing the buret speed and increasing the time delay may help. Cleaning the electrode with detergent may decrease the response time. If all else fails, changing the electrode generally solves the problem.
   Many reagents need to be dried in an oven and stored in a desiccator. Contamination of the primary standard is a possibility, especially when drying, storing, or weighing the reagent. When weighing the primary standard, do not touch the weighing vessel. Keep the standard in a desiccator with fresh desiccant to prevent hydration of standard.

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4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents. Dispense concentrated acids in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Follow the manufacturer's safety precautions when using the automatic titrator.

Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary.

5. EQUIPMENT
5.1 Oven, thermostatically controlled, 250°C
5.2 Thermometer, 0 to 250°C
5.3 Weighing bottles, 40 x 50 mm
5.4 Desiccator
5.5 Electronic balance, ±0.1-mg sensitivity, Mettler model AE 160 or equivalent
5.6 Automatic titrator, Metrohm 686 Titroprocessor Series 04 or 670 Titroprocessor Series 11, 665 Dosimat Series 14, 674 Sample Changer, 664 Control Unit, Series 05, Metrohm Ltd., Brinkmann Instruments, Inc.
5.7 Combination pH-reference electrode, Metrohm part No. 6.0210.100, Metrohm Ltd., Brinkmann Instruments, Inc.
5.8 Titration beakers, borosilicate, 250 mL, Metrohm Ltd., Brinkmann Instruments, Inc.

6. REAGENTS
6.1 Distilled deionized (DDI) water
6.2 pH buffers, pH 4.00, pH 7.00 and pH 9.18 for electrode calibration
6.3 Sodium carbonate, anhydrous, >99.5% pure, dried at 100°C for 1 h, stored in a desiccator
6.4 Anhydrone (magnesium perchorate), 5 to 20 mesh, desiccant **6.5** Bromcresol green indicator. Dissolve 0.10 g of bromcresol green (tetrabromo-m- cresolsulfonphthalein) in 7.15 mL of 0.02 *N* NaOH. Dilute to 250 mL with DDI water. Use bromcresol green indicator if endpoint is determined manually.

7. PROCEDURE

Acid Standardization

7.1 Remove primary standard (dry Na_2CO_3) from desiccator and place on analytical balance.

7.2 Weigh the Na_2CO_3 standard plus its weighing vessel. When weighing the standard, do not touch the weighing vessel.

7.3 On the Standards Acid form, record the Na_2CO_3 weight to the nearest 0.1 mg. Record this weight as "Beginning Bottle Weight". Refer to the example of the Standard Acids form.

7.4 Remove the Na_2CO_3 standard from the balance and place ~ 0.1 g of Na_2CO_3 into a clean, dry 250-mL titration beaker.

7.5 Replace the Na_2CO_3 standard and weighing vessel on analytical balance and record weight on Standard Acids form as "Ending Bottle Weight". Refer to the example of the Standard Acids form.

APPENDIX VIII

STANDARDIZATION OF ACIDS

7.6 Subtract the "Ending Bottle Weight" from the "Original bottle weight" and record as "Sample weight 1", i.e., Na_2CO_3 weight determined by difference.

7.7 Record the "Ending Bottle Weight" in "Sample weight 1" as the "Original bottle weight" for "Sample weight 2". Refer to the example of the Standard Acids form. Continue this weighing procedure until all samples of the primary standard have been weighed, i.e., at least 14 samples of the primary standard. Refer to the example of the Standard Acids form.

7.8 To each 250-mL titration beaker, add 100 mL of DDI of water.

7.9 Add 100 mL of DDI water. To at least four empty beakers (generally 8), add 100 mL of DDI water (blanks).

7.10 Fill and rinse the buret with the acid being standardized. Flush the acid through the tubing by operating the buret through at least two fill and rinse cycles.

7.11 Calibrate the pH electrode with the 7.00, 4.00 and 9.18 pH buffers. Refer to Appendix XV and the 686 Titroprocessor manual for a discussion of electrode calibration.

7.12 Set up the automatic titrator to titrate in the set end point mode ("Set"). Refer to Appendix XV for the operation of the 686 Titroprocessor. The "Set" pH parameters are listed as follows:

```
Parameter        Value

Ep2 pH           4.6
Dyn change pH    1.5 pH units
Drift            0.4 mV s⁻¹
Time Delay       10 s
Temp             25°C
Stop             Vol 35 mL
Buret speed      2.5
 setting
```

7.13 The end point is the 4.60 pH end point.

7.14 The titers and other titration parameters are recorded on the printer of the Titroprocessor.

7.15 An acceptable standard deviation is ± 0.0005 for the *N* of the acid.

8. CALCULATIONS

8.1 $Titer_{blank} = A/B$

where:
A = Blank titers
B = Number of blanks

8.2 $N_{1...} = (A \times 18.867)/(C - D)$

APPENDIX VIII

STANDARDIZATION OF ACIDS

where:

$N_{1...}$ = Normality of primary standard samples (1,2,3, etc.)
A = $Na_2CO_{31...}$ = Weight (g) of Na_2CO_3 added to primary standard samples (1,2,3, etc.)
C = $Titer_{1...}$
D = $Titer_{blank}$

8.3 $N_{acid} = (N_{1...})/A$

where:

$N_{1...}$ = Normality of primary standard samples (1, 2, 3, etc.)
A = Number of primary standards titrated

8.4 Std. Dev. = $(N_{1...} - N_{acid})/(A - 1)$

where:

$N_{1...}$ = Normality of primary standard samples (1, 2, 3, etc.)
A = Number of primary standards titrated

9. REPORT

Report the normality (N) of standardized acid to four significant figures, e.g., $N = 0.1234$. Also report the standard deviation for standardized acid. Record the date of standardization in the Standards Acids binder.

10. REFERENCES

Metrohom Ltd. Instruction Manual. 686 Titroprocessor Series 04. Metrohm Ltd., CH-9100 Herisau, Switzerland.

APPENDIX VIII

STANDARDIZATION OF ACIDS

Table 1. Common commercial strengths of acids and bases.

Name	Molecular Weight	Moles per Liter	Grams per Liter	Percent by Weight	Specific Gravity
Acetic acid,	60.05	17.4	1045	99.5	1.05
Glacial acetic acid	60.05	6.27	376	36	1.045
Butyric acid	88.1	10.3	912	95	0.96
Formic acid	46.02	23.4	1080	90	1.20
		5.75	264	25	1.06
Hydriodic acid	127.9	7.57	969	57	1.70
		5.51	705	47	1.50
		0.86	110	10	1.1
Hydrobromic acid	80.92	8.89	720	48	1.50
		6.82	552	40	1.38
Hydrochloric acid	36.5	11.6	424	36	1.18
		2.9	105	10	1.05
Hydrocyanic acid	27.03	25	676	97	0.697
		0.74	19.9	2	0.996
Hydrofluoric acid	20.01	32.1	642	55	1.167
		28.8	578	50	1.155
Hydrofluosilicic acid	144.1	2.65	382	30	1.27
Hypophosphorus acid	66.0	9.47	625	50	1.25
		5.14	339	30	1.13
		1.57	104	10	1.04
Lactic acid	90.1	11.3	1020	85	1.2
Nitric acid	63.02	15.99	1008	71	1.42
		14.9	938	67	1.40
		13.3	837	61	1.37
Perchloric acid	100.5	11.65	1172	70	1.67
		9.2	923	60	1.54

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STANDARDIZATION OF ACIDS

Name	Molecular Weight	Moles per Liter	Grams per Liter	Percent by Weight	Specific Gravity
Phosphoric acid	98	14.7	1445	85	1.70
Sulfuric acid	98.1	18.0	1766	96	1.84
Sulfurous acid	82.1	0.74	61.2	6	1.02
Ammonia water	17.0	14.8	252	28	0.898
Potassium hydroxide	56.1	13.5	757	50	1.52
		1.94	109	10	1.09
Sodium carbonate	106.0	1.04	110	10	1.10
Sodium hydroxide	40	19.1	763	50	1.53
		2.75	111	10	1.11

ACID: _____ DATE: _____

$N = (g\ Na_2CO_3 \times 18.867)/(Titer - Blank)$

Titer	Titer-Blank	Normality			
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 1					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 2					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 3					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 4					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 5 ------					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 6					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 7					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 8					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 9					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 10					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 11					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 12					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 13					
Beginning Bottle Weight ------ Ending Bottle Weight ------ Sample Weight 14					

Standard Deviation   Mean

APPENDIX IX

KJELTEC AUTO SAMPLER SYSTEM
TECATOR KJELTEC 1035 ANALYZER AND 1038 SAMPLER

      The Kjeltec Auto Sampler is composed of two basic modules: Kjeltec 1035 Analyzer and 1038 Sampler. The principle of operation is that a digestion tube with cooled digested sample is loaded onto the splash head by the Sampler. The analytical cycle is started by the program "Analyse". When using the 1035 Analyzer as a stand alone unit, the "Analyses" program will not start unless the first tube is in place and the Analyzer safety door is closed. Receiver solution is dispensed into the titration vessel from the tank by the pump. Dilution water is dispensed into the tube from the tank by the pump. The steam valve opens and delivers steam to the tube, and at the same time the cooling water valve opens and delivers water into the condenser. Alkali is dispensed into the tube from the tank by means of the pump. The liberated gas is condensed in the condenser and delivered to the titration vessel containing receiver solution. Depending on the color of the indicator, titrant is dispensed by the burette from the tank into the titration vessel. When the distillate level in the titration vessel, reaches the level pin, the microprocessor decides if the endpoint has been reached by means of the photocells. If so, it compensates for the volume of titrant added to achieve a constant distillation volume. When distilling for a fixed time, the cycle will stop at the time regardless of endpoint or titrant added.

      Thereafter the drain valve opens and the titration vessel drains while the steam continues to flush the system. When the titration vessel is drained, the steam valve closes and the pinch valve actuates allowing the contents of the tube to be removed to the expansion vessel. The tube emptying valve opens allowing the waste to flow out to the collection tank. The result is presented on the display, printed out on the printer and stored in memory. The Sampler will remove the empty tube and the next analytical cycle will begin. When all tubes programmed into the memory have been analyzed, a cleaning process takes place.

Warm-up Process

1. Check solutions:

a. ~ 0.05 *N* HCl

b. Distilled water

c. Boric acid, 4 percent solution with mixed indicators.

d. 1 *N* NaOH

2. Press green buttons on top and bottom of machine

3. Replace sample drip-tray and tube guide. Turn water on half-way.

4. Press "Sampler" for priming pumps and placing tubes rack with tubes on machine. "A to Load Position" appears in window.

5. Press "Enter" for "A", "B", or "C" or scroll down for menu.

6. Press "Sampler". "Tube to Position" appears in window.

7. Press "Enter". "Tube=O Wing=A" appears in window.

8. Press "Enter". Press "1". "Tube=1 Wing=A" appears in window. Press "Enter". Tube moves into position. "Tube Up" appears in window.

KJELTEC AUTO SAMPLER SYSTEM
TECATOR KJELTEC 1035 ANALYZER AND 1038 SAMPLER

9. Press "Manual".

10. Press "Alkali". Press two times (2x).

11. Press "Rec. Sol." Press eight times (8-10x). Solution should be deep rose color.

12. Press "Burette". Press "Enter". Press five times (4-5x) (enter). "Up-Titr" appears in window.

13. Scroll down. Press "Enter". Press five times (4-5x) (enter). "Down-Cont" appears in window.

14. Press "Manual".

15. Press "Steam". Press one time, wait five minutes. Rinse titrant vessel with water (where rose solution flows in).

16. Turn printer on.

17. Scroll. Press "Sampler". Press "Enter". "Tube Down" appears in window.

18. Scroll. Press "Enter". "A to Load Position" appears in window.

19. Press "Enter". Tube should remove self.

Run Samples

1. Check batch # and sample # needed.

2. Check blank # needed.

3. Check solutions needed.

4. Press "Sampler". Press "Enter". Load rack of tubes. "A to Load Position" appears in window.

5. Press "Weigh". Need to enter current statistics. Example: Batch=20 Tube=1-4 blank 0.000g F=1.00 #7. Distillation always=#7 (blank=0). "Batch=20 Tube= 1" appears in window for example.

6. Scroll. Press "Enter" "Tube=2". "Batch=20 Tube=2" appears in window.

7. Scroll down to next change. Press "Enter".

8. Tubes 1-4=blanks. Example: Tubes 5-16=soil samples. Batch=20 Tube=5. 2.5 g F=1.00 #7. "Batch=20 Tube=5" appears in window.

9. Scroll down thru #16. Example: Samples 17&18=CC,DC. Weight=0.000 0.000g F=1.00 #7 #17-20=blanks. "Batch=20 Tube=16" "Batch=20 Tube=17 appear in window.

10. Scroll to 20. "Batch=20 Tube=20".

11. Scroll. Press "Analyze". Press "Enter". Change Blank.

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12. Press "Enter" Example:Blank=.35

13. Press "Enter". "Batch=20 Wing=A" appears in window.

14. Press "Enter" four times. "Start Batch 20" appears in window. Press "Enter". Start sample analysis. Start "Tube 1" appears in window. Machine starts and runs automatically for Batch=20 Tubes=1-20.

15. Three doors on Kjeltec should not be opened while instrument is operating. These doors are labelled.

16. For emergency, open one of the doors to stop machine immediately.

17. "Stop" button will stop machine after current sample is finished running.

Shut-Down Process

1. Press "Sampler". Press "Enter". Tray moves back to center. "A to Load Position" appears in window. Remove rack of tubes.

2. Clean sample bay. Close door.

3. Press "Paper Feed" to remove data. Turn printer off.

4. Turn machine off by pressing two green buttons. Fill titrant vessel with water (receives pink solution).

5. Remove tube guide and sampler drip tray.

6. Replace drip tray if present. Drip tray usually not used. Wrong tray if marked with purple tape. Rinse rubber adaptor. Replace tube guide. Clean glassware.

REFERENCES
Tecator. 1995. Manual. Kjeltec Auto 1035/38 Sampler System. Perstorp Analytical Inc., Hoganas, Sweden.

APPENDIX X

ATOMIC ABSORPTION SPECTROSCOPY

The SSL presently uses a Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer with a Model 5000 Automatic Burner Control, Model AS-50 Auto Sampler, and Series 7000 Computer. The SSL also uses a Thermo Jarrell Ash Model Smith-Hieftje 4000 Automated Atomic Absorption (flame) Spectrophotometer (4 lamp configuration) with host computer and printer. The information provided in this section assumes that these equipment are used. However, much of the information in this section is applicable to other atomic absorption (AA) equipment.

The five basic components of the AA are as follows:

a. Light source
b. Burner system
c. Monochromator
d. Detector
e. Display

The operator of the AA may adjust several of these components to optimize the AA for the performed analyses. Each component is presented as a separate topic.

Light Source

The main sources used for the AA are the hollow cathode lamp (HCL) and the electrodeless discharge lamp (EDL). The HCL is an excellent, bright, stable line source for most elements. However, for some volatile elements, where low intensity and short lamp lifetime are a problem, an EDL is available. The EDL is typically more intense than an HCL. Therefore, an EDL may offer better precision and lower detection limits for some elements. An HCL has a finite lifetime. With extended use, the metal atoms from the cathode are removed. Lamps for volatile elements age faster because of more rapid cathode sputtering.

The cathode of an HCL is constructed from a very pure metal which results in a very pure emission spectrum. The construction of a cathode from a mixture or alloy of several metals is possible. The resulting "multi-element" lamp may be used as a source for all the metals contained in the cathode. Not all metals may be used in combination because of the metallurgical properties or spectral interferences. The emission intensity for a particular element in a multi-element lamp is not so great as the same element in a single-element lamp. This may result in a poorer signal/noise ratio which may influence the precision and detection limit of the analyses. When working close to the detection limit or when the best precision is required, select a single-element lamp. A multi-element lamp is adequate for routine analyses that are well above the detection limit. Other considerations are the cost of the lamps for infrequent analyses and the reduction in time in changing and optimizing AA lamps.

Each HCL has a maximum and operating lamp current for continuous operation. The recommended operating currents are those which have been proved empirically to be appropriate for most analytical situations. However, satisfactory results may be possible by using less than the recommended current. Use of a lower current reduces the light output resulting in a higher AA gain setting. This does not harm the lamp. In fact, the life of the lamp is extended. If precision is not affected, a slightly lower lamp current is acceptable. As an HCl ages, increasing the lamp current to the maximum current rating, i.e., equal to a new lamp, in order to achieve additional light emission equal may be necessary. Increasing the lamp current may accelerate the aging of the lamp but may be a necessary compromise to obtain enough emission for good performance. Analytical sensitivity may be poorer at higher current settings. A HCL failure occurs when the fill gas is depleted and the lamp no longer "lights". Higher lamp currents accelerate the gas depletion and cathode sputtering and should be avoided until the age of the lamp requires a current increase.

Warm-up time for an HCL is short, and with the Perkin-Elmer 5000 AA, no warm-up is required. For a single-beam AA, a short warm-up period is recommended.

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Sometimes an EDL provides greater light output and longer life than a corresponding HCL. For certain elements, i.e., As, SE, P, the EDL provides improved sensitivity and lower detection limits. There are EDL's for 18 elements (Al, Sb, As, Bi, CD, Cs, Ge, Pb, Hg, P, K, Rb, Se, Te, Tl, Sn, Ti, and Zn). Since the light source is greater in an EDL, the AA performance benefits are better with an optical system that is designed to take advantage of these benefits. The Perkin-Elmer 5000 EDL may be directly interchanged with an HCL. They require a separate power supply. To use this EDL, connect the proper lamp to the power supply with the supplied cable. Switch on the power and turn the power meter control clockwise approximately 3/4 of maximum power. When the lamp lights, the power meter increases to the right, i.e., off scale. If the lamp doesn't light, turn on the igniter lamp and hold it in front of the lamp for a second or two. After the lamp lights, reduce the power. If a quick warm-up is required, set the power to 2 to 3 W above the recommended setting for 5 min. If the warm-up time is no problem, set the power to 1/2 to 1 W below the recommended setting. Power slightly increases as warm-up occurs in 30 to 40 min.

The EDL power supply may be operated in the continuous mode for routine operations and also may be modulated with external synchronization from the AA or internally modulated from the line frequency. The recommended lamp power setting is selected for optimum performance under most conditions that require maximum intensity with maximum sensitivity. For many applications, such as flame AA, maximum intensity is not required. In those cases, lamp operation at a slightly lower power, i.e., 1/2 to 1 W less, does not degrade the performance and may extend the lamp life. In other cases, particularly when working with the graphite furnace, additional intensity may lead to improved performance. Increasing the power slightly, i.e., 1/2 to 1 W above the suggested value, may increase the intensity but also may result in reduced sensitivity (5 to 10%) and lamp life. When the lamps are operated in the modulated mode, they have a more restricted operation range. The power settings in excess of those frequently recommended may lead to oscillation, whereas at lower power settings, the lamp may drop into its "low mode", i.e., a condition in which spectral lines of the element of interest are not emitted. As a result, the lamp may be damaged. For modulated operation, the stated lamp power setting is recommended.

Burner System

The AA mixing chamber is made of molded Ryton that is polypropylene coated. The system may be operated with either a flow spoiler or an impact bead. The flow spoiler is a molded polypropylene vane with three support arms which press-fit to the mixing chamber walls. One arm should point straight down when installed. The Pyrex impact bead inserts into a positioning hole in the end-cap. When seated, the impact bead is directly aligned approximately 2 to 3 mm behind the nebulizer venturi. No further impact bead adjustment is required. For elements using an air-acetylene flame, the impact head generally improves the sensitivity and detection limits approximately 2x the flow spoiler. For elements that require nitrous oxide-acetylene flame, the impact bead generally contributes to poorer precision and detection limits. Use the flow spoiler as follows:

a. analyses of solutions with high dissolved solids.
b. analyses of solutions that attack glass, e.g., HF, NaOH.
c. analyses that require a nitrous oxide-acetylene flame.

Use the impact bead when 2x sensitivity improvement is required.

There are three available titanium burner heads. Titanium is corrosion resistant and free of most elements that are commonly determined by AA.

The 10-cm burner head is designed for use with the air-acetylene flame. This burner provides the best sensitivity for air-acetylene elements because of its long path length.

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ATOMIC ABSORPTION SPECTROSCOPY

The 5-cm burner head or nitrous oxide burner head is required for nitrous oxide-acetylene operation. This burner also may be used with air-acetylene or air-hydrogen and may be rotated up to 90° to provide reduced sensitivity.

The three-slot burner head also may be used for air-acetylene or argon-hydrogen-entrained air flames and is designed for analyses of samples with high concentrations of dissolved solids.

The two most common oxidant/fuel combinations used in AA are the air-acetylene and nitrous oxide-acetylene. Other flames that may be used are air-hydrogen and argon-hydrogen-entrained air.

Air-acetylene is the preferred flame for the determination of approximately 35 elements by AA. Usually, ordinary welding grade-acetylene is adequate. However, welding-grade acetylene that is dissolved in acetone is supplied. As the tank pressure falls, the acetone concentration that enters the flame increases. This increase may produce erratic results when determining elements that require a fuel-rich flame or elements with analytical wavelengths in the low UV range. Acetone that passes into the gas control box may damage valves and tubing. Acetylene tanks should be replaced when the tank pressure falls below 75 PSI. Acetylene tanks should be stored and operated in a vertical position to prevent liquid acetone from reaching the cylinder valve. If welding-grade acetylene is not adequate, AA-grade acetylene is available.

The nitrous oxide-acetylene flame has a maximum temperature of approximately 2900°C and is used for the determination of elements which form refractory oxides. The nitrous oxide-acetylene flame also is used to overcome chemical interferences that may be present in flames at the lower` temperatures. Light emission from the nitrous oxide-acetylene flame is very strong at certain wavelengths which may cause fluctuations in the determinations performed at these wavelengths, particularly if the lamp emission for the element is weak. Only the nitrous oxide burner head can be used with the nitrous oxide-acetylene flame. Eye protection from the UV light emitted by the flame is also necessary. Do not look at the flame without eye protection. Other flames that may be used for AA are the air-hydrogen and argon-hydrogen-entrained air flame. The air-hydrogen flame burns at approximately 2000°C. The temperature of the argon-hydrogen-entrained air flame is extremely low (300 to 800°C). Both flames are essentially colorless. A Na solution may be aspirated to determine if the flame is ignited. Air-hydrogen may be used for the determination of the alkali metals (Cs, Rb, K, and Na) as its lower flame temperature reduces ionization interferences. The argon-hydrogen-entrained air flame may be used for arsenic and selenium determination. However, because of the low temperature of these flames, numerous chemical and matrix interferences may be encountered. For this reason, these flames are not commonly used for AA.

Initial operation conditions, i.e., pressure and flow settings for fuel and oxidant, are listed in manufacturer's instruction manual. Some of the operating combinations are as follows:

Burner head = 10 cm
Fuel = C_2H_2 Oxidizer = Air
Flow settings (spoiler): Fuel = 25/35 Oxidizer = 40/45
Flow settings (bead): Fuel = 20 or 25 Oxidizer = 30

Burner Head = 5 cm
Fuel = C_2H_2 Oxidizer = Air
Flow Settings (Spoiler): Fuel = 20 Oxidizer = 25
Flow Settings (Bead): Fuel = 15 Oxidizer = 20

Burner Head = 5 cm
Fuel = C_2H_2 Oxidizer = N_2O
Flow Settings (Spoiler): Fuel = 32 Oxidizer = 20
Flow Settings (Bead): Not recommended

ATOMIC ABSORPTION SPECTROSCOPY

       Burner head adjustment relative to the AA light path is necessary to obtain maximum sensitivity. The burner height is adjusted by initially lowering the burner head well below the light beam and then zeroing the readout. Slowly raise the burner until the head just intercepts the beam, i.e., a positive reading is indicated. The burner should be lowered slowly until the readout returns to zero. For elements that require a fuel-rich flame, the burner height may require optimization, i.e., aspirating a standard solution with the flame on and then slowly lowering the burner until a maximum signal is obtained. Readjust zero after lowering the burner. The lateral and rotational burner adjustment must be made with the flame on and while aspirating a standard solution. The burner is adjusted to obtain maximum absorption.

       For many elements, the fuel/oxidant ratio must be adjusted for maximum sensitivity. Aspirate a standard solution and adjust the "Fuel". Check zero after each flow change and readjust if necessary. To adjust the nebulizer, set-up the AA for the determination of Cu, Mg, or other elements which have an absorbing wavelength above 250 nm and whose sensitivity is not dependent on the fuel/oxidant ratio. Do not select an element that requires nitrous oxide-acetylene flame. Aspirate a standard solution of the

APPENDIX X

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Display

The digital display of the AA is controlled by a microprocessor. The 6 digit display with polarity and adjustable decimal can display absorbance, concentration, or emission intensity. Absorbance readings to about 2A, concentration readings to 9999 with two additional decimal location zeros, and continuously variable scale expansion form 0.01 to 100x are available. In addition, the intergration/peak monitoring time is adjustable from 0.2 to 60 s. Time-averaged integration, non-averaged integration (peak area), and peak height measurement modes with a choice of automatic updated readings or individual readings with time-averaged integration are available.

The keyboard entry can control integration time, scale expansion, lamp current, lamp, wavelength, slit width, and slit height. All keyboard entries may be stored on magnetic cards for automated input.

REFERENCES
Perkin-Elmer Corp. 1983. Atomic Absorption Spectrophotometer Manual Rev. Model 5000 Atomic
    Absorption Spectrophotometer. Perkin-elmer Corp., Norwalk, CT.
Perkin-Elmer Corp. 1982. Analytical Methods for Atomic Absorption Spectrophotometer Manual Rev.
    Model 5000 Atomic Absorption Spectrophotometer. Perkin-Elmer Corp., Norwalk, CT.

APPENDIX XI

ATOMIC ABSORPTION (AA)
OPERATION
PERKIN-ELMER AA 5000

AA Start-up

1. For most elements, install and use the short burner head parallel to light beam. For Mg, Na, and HF-K analyses, install and use short burner head at a 30° angle to light beam. Pin must be in place with 2 hooks attached.

2. The elements, Al and Si, require N_2O instead air. To use nitrous oxide gas (N_2O), plug in regulator heater for 5 min prior to opening gas valve. Before turning on N_2O, install spectrometer program that requires N_2O.

3. Open the acetylene gas tank and the N_2O tank, if needed.

4. Turn on air which is behind burner control unit.

5. Turn power on for automatic burner control.

6. Turn power on for spectrometer. If power is "On", then turn "Standby" to "Run".

7. On spectrometer keyboard, turn "Print" off.

8. Turn on automatic sample changer.

9. Use appropriate magnetic strip to input required program. The magnetic strips contain programs that set the machine and the individual element parameters. The parameters are as follows:

a. Program number
b. Peak reading time
c. Lamp number and mA
d. Wavelength
e. Slit
f. Gas settings
g. Print beginning number of sample
h. Absorbance or concentration
i. Hold
j. Standard concentration
k. Print

10. If program is not on a magnetic strip, operational set-up is as follows:

a. Key in number of required lamp and press "Lamp #".
b. Key in lamp milliamps (Ma) and press "Lamp Ma"
c. Key in wavelength and press "Wavelength Peak".
d. Key in slit setting and press "Slit High".
e. Set fuel and oxidant levels on burner control unit.
f. Press "Conc" and "Hold".
g. Enter "8" and press "t".
h. Enter concentration of required standard.
i. Press "1" and "Print" to start the numbering on print out.
j. Select a number for program storage and press "Store".

ATOMIC ABSORPTION (AA)
OPERATION
PERKIN-ELMER AA 5000

k. To store on magnetic strip, insert strip and press "Store".

11. Allow spectrometer to warm up for ~ 30 min.

12. Check drain bottle and tubing. Flame extinguishes when bottle is full. Bottle should not be empty. Fill bottle to the line indicated, i.e., about 1/2 full. Loop should be 3/4 full of water.

13. Turn on printer. Printer must be "On Line" to print data.

Ignition and Adjustments

1. Ignite flame by pressing "Flame On".

2. Aspirate distilled deionized (DDI) water.
Press "Manual" on autosampler. "Manual" raises and lowers aspirator wire.

3. Check flame for any interferences or contaminants at burner head contact. If there are problems, extinguish flame and clean.

4. For optimization, select an element that requires a blue (oxidizing), air-acetylene flame and has a wavelength control setting >250 nm. The recommended optimization elements are as follows: Cu, Mg, Ni or Pb. The elements that are not recommended are as follows: Ca, Sr, Ba, or elements whose absorbance is sensitive to the fuel-air ratio. Do not adjust nebulizer with nitrous oxide-acetylene flame.

5. The SSL uses the following elements for optimization.

a. Mg for analysis of cations, salts, and HF-K.
b. Fe or Cu, if available, for analysis of Fe, Al, and Mn.

6. Set spectrometer to "Cont", "Abs".

7. Aspirate DDI water, and zero the emissions with right knob on front of nebulizer unit. Turn up to point whereby burner causes blockage of light beam. Turn down to "0" plus an additional 1/4 turn.

8. Press "AZ", i.e., auto-zero.

9. Aspirate blank and press "AZ".

10. Aspirate optimization standard, e.g., Mg. Open aspirator (nebulizer) until the emissions read "0", and the air blows into sample. Turn back nebulizer until emissions reach the highest possible value. If burner head is parallel, adjust left knob on nebulizer unit until emissions reach the highest possible value. Readjust right knob until reach highest emissions.

11. Set "Hold" and enter "6" and "t".

12. Aspirate standard and record 3 to 5 readings or until stable.

13. In logbook for specific element, record machine parameters as follows:

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OPERATION
PERKIN-ELMER AA 5000

a. Absorbance

b. Burner height

c. AA-BG reading

d. Gain

e. Energy

14. Switch program to the element of interest. This resets all of the machine parameters.

15. Set "Cont", "Abs", and "Print Off".

16. Key in "0.5" and press "t".

17. Aspirate blank and press "AZ".

18. Set "Hold" and enter "6" and "t".

19. Aspirate standard and take 5 or more readings or until stable.

20. Record machine parameters in logbook for the element of interest.

21. On autosampler, enter the parameters as follows:

a. Program number of element of interest.

b. Position numbers for recalibration, e.g., 7, 13, and 24.

c. Last sample number, if <50.

d. Read delay = 6 s.

22. On autosampler, press "Manual" to lower aspirator and then press "Start".

23. "Manual" raises and lowers aspirator wire.

24. "Manual" also is used to run autosampler manually. Select the sample on the carousel to run. Key in sample position number and press "Manual". Sampler moves to that position. Press "Start" to erase program number that is set for autosampler.

AA Shut-down

1. To clean system, aspirate DDI water for 3 to 5 min.

2. Press "Flame Off".

3. If N_2O has been used, unplug heater on tank and allow to cool several minutes.

4. Turn off gases.

5. Turn off air.

6. Bleed off gases by pressing "Check Flow". If N_2O has been used, release pressure setting valve on tank.

APPENDIX XI

ATOMIC ABSORPTION (AA)
OPERATION
PERKIN-ELMER AA 5000

7. Turn power off for automatic burner control unit.

8. On spectrometer keyboard, key in "0" and press "Ma".

9. Turn spectrometer to "Standby".

10. Turn power off for burner control box.

11. Turn off autosampler.

12. Remove burner head. Soak burner head in water and detergent and rinse well.

13. Turn off printer.

Additional Notes

1. If conductivities of saturated paste extracts are >2400, dilutions may be necessary.

2. For acetate extracts, check the HCl effervescence test in "Coarse Fragments" book. The HCl effervescence test indicates Ca in excess of the CEC. If the HCl effervescence test is positive, dilution is not usually necessary if the Ca reading is over-calibrated.

3. Make solution dilutions, e.g., NaOAc and dithionite-citrate, to simulate the original matrix and then dilute 1:40 with lanthanum ionization suppressant.

REFERENCES

Perkin-Elmer Corp. 1983. Atomic Absorption Spectrophotometer Manual Rev. Model 5000 Atomic Absorption Spectrophotometer. Perkin-Elmer Corp., Norwalk, CT.
Perkin-Elmer Corp. 1982. Analytical Methods for Atomic Absorption Spectrophotometer Manual Rev. Model 5000 Atomic Absorption Spectrophotometer. Perkin-Elmer Corp., Norwalk, CT.

APPENDIX XII

ATOMIC ABSORPTION (AA)
OPERATION
THERMO JARRELL ASH
SMITH-HIEFTJE 4000
AUTOMATED AA SPECTROPHOTOMETER

AA Start-up

1. For most elements, install and use the air/acetylene burner head parallel to light beam. For Mg and Na, install air/acetylene burner head at a 30 angle to light beam.

2. The elements Al and Si require N_2O instead of air. To use N_2O, plug in regulator heater for 5 min prior to opening gas valve. Use the N_2O/acetylene burner head.

3. Open the acetylene gas tank and the N_2O tank, if needed.

4. Turn power on to the machine. The computer will go through a brief self-checking procedure and then automatically boot up the ThermoSpec software.

5. Use arrow keys on the computer to highlight wavelength calibration under the set-up heading. Press enter. The instrument will go through its wavelength calibration procedure.

6. Install burner head by selecting the correct burner head, air/acetylene or N_2O/acetylene.

7. Insert the burner head into the neck of the premix chamber. Make sure that the hole in the burner's collar engages the rotation adjustment pin, then push the burner down firmly in order to engage the interlock switch.

8. Align burner with light beam. Use a small index card to intercept the hallow-cathode light beam above the burner head at the focal point of the beam. Position the card approximately two-thirds along the length of the burner head from the hallow cathode area. Raise the burner head with the burner height control until the red spot appears to rest just on the surface of the burner. Use the burner controls to make the focal point of the beam coincide with the burner slot. Move the card along the full length of the burner slot, while making sure the beam is centered over the slot for the entire length of the burner head.

Ignition and Adjustment
(Air/Acetylene Flame)

1. At the acetylene cylinder, set the external fuel pressure to 15 psi.

2. Turn the gas control selector switch to the air position.

3. Turn the oxidant flow control knob counterclockwise to replace the oxidant flow until the ball in the oxidant flow meter stops dropping.

4. Place the aspirator tube in a graduated cylinder containing distilled water.

5. Set the aspiration rate as follows:

a. Rotate the knurled knob of the nebulizer assembly counterclockwise until bubbles exit the aspiration tubing.

**ATOMIC ABSORPTION (AA)
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THERMO JARRELL ASH
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AUTOMATED AA SPECTROPHOTOMETER**

b. Gradually rotate knurled knob clockwise until the bubbles stop.

c. Rotate the knurled knob between one-quarter to one-half of a turn clockwise. The oxidant flow meter should read 12 to 14 SCFH.

d. Measure the aspiration rate with a graduated cylinder. Optimal aspiration rate is 4 to 6 mL min^{-1}.

e. Ignite the flame by pressing and holding the pilot button until ignition occurs.

f. Optimize the stoichometry of the flame for maximum sensitivity by adjusting the fuel flow rate while aspirating a standard.

**Ignition and Adjustment
Nitrous Oxide/Acetylene Flame**

1. Insert the nitrous oxide burner head.

2. At the acetylene cylinder, set the external fuel pressure to 15 psi.

3. At the nitrous oxide cylinder, set the N_2O pressure to 50 psi.

4. Repeat Steps 1 - 5d for ignition and adjustment of air/acetylene flame.

5. Set the fuel flow meter to a setting of 4 to 7 SCFH with the fuel flow control.

6. Ignite the flame by pressing and holding the pilot bottom until ignition occurs. Do not aspirate water. Allow warm-up period of 3 to 5 min.

7. Turn the selector switch to N_2O/fuel. The long narrow flame will become bluish with a 1-in red feather. Aspirate with distilled water.

**AA Shut-down
(Air/Acetylene)**

1. Increase fuel flow to 4 to 5 SCFH and aspirate with distilled water for 30 s.

2. Turn gas flow selector from fuel/air to air.

3. Wait for the flame to go out, then switch the gas flow selector to off.

4. Turn off the instrument. Use arrow keys on the computer to highlight standby. Push enter to put instrument in standby mode.

5. Turn power off.

6. Turn off gases at cylinder.

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ATOMIC ABSORPTION (AA)
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THERMO JARRELL ASH
SMITH-HIEFTJE 4000
AUTOMATED AA SPECTROPHOTOMETER

7. Remove burner head and soak in water and detergent. Rinse well.

AA Shut-down
(Nitrous Oxide/Acetylene)

1. While aspirating distilled water, turn gas flow selector switch from N$_2$O/fuel to air/fuel. Allow 15 s for the flame to stabilize, then switch to air.

2. Wait for the flame to go out, then remove capillary from the distilled water.

3. Wait 10 s, then turn the gas flow selector to off.

4. Turn off the instrument. Use arrow keys on the computer to highlight standby. Push enter to put instrument in standby mode.

5. Turn power off.

6. Turn off gases at cylinder.

7. Remove burner head and soak in water and detergent. Rinse well.

REFERENCES
Smith-Hieftje 1000/4000/8000 Automated AA/AE Spectrophotometer. 1991. Operator's Manual. Thermo
    Jarrell Ash Corp., 8E Forge Parkway, Franklin, MA.

APPENDIX XIII

INDUCTIVELY COUPLED PLASMA
OPERATION
THERMO JARRELL ASH ICAP 61E

Background of Instrument and Software

The ICAP 61E is a simultaneous plasma emission spectrometer consisting of three components as follows:

a. Computer-controlled polychrometer capable of accepting up to 63 channels or elements.
b. Floor mounted power unit (RF generator).
c. Host computer and printer.

The power to the SSL ICP is generated through a line conditioner, a Unity Model UT5K manufactured by Best Power Technology, Inc. The polychrometer is kept under a constant vacuum, even while not in use. This vacuum is maintained by a pump on the back side of the instrument, which is operated 24 h per day. An Ar purge gas also continually flows through the polychrometer in order to maintain a constant atmosphere in the instrument and to prevent dust invasion. Currently, the SSL has the capability to analyze the following elements with this instrument: Na, Mg, B, Al, Si, P, S, K, Ca, Ti, Mn, Fe, Cu, Zn, As, Se, Cd, Pb, and Zr.

The ICP is operated by "ThermoSPEC" Spectrometer Operation System, software version 5.06. The following choices are submenus on the main menu. A brief synopsis of each submenu follows:

a. Operations - for standardizing the instrument, analysis of samples, and setting up an autosampler table.
b. Development - to establish operational parameters for a particular analytical method, establish sample check limits, and integrate quality control samples.
c. IMS - features the Report Writer which allows data to be reproduced as a report, on paper or a floppy disk, following a run; has the peak search library to allow a user to determine peak positions for an element.
d. Setup - One submenu is the Plasma Control panel which displays instrument parameters, e.g., gas flow, pump speed, during operation and provides selection for startup and shutdown. Another submenu is selected to run a Hg profile for ICP calibration.
e. Exit - To exit the software and return to DOS.

ICP Set-up

1. Attach the torch, spray chamber, and nebulizer to bottom of torch. Place a bonnet on top of the torch. Gas lines and drain tube should be attached as illustrated on the drawing displayed in torch chamber. For samples containing HF, use the polypropolyene spray chamber, HF-resistant tip, and "high flow only" torch.

2. Adjust Ar flow rates as follows: Nebulizer Purge = 2.0; Tube Purge = 1.0.

3. Press the Instrument Reset button on the front panel of the polychrometer.

4. Connect the pump winding (orange double stop tubing) to the peristaltic pump.

5. Turn on the coolant water pump on the backside of the ICP.

6. Turn on the switch of the surge protector. This switch controls the computer and printer. The ThermoSPEC software should boot up automatically. If not, type at the C prompt, "STNRUN" to access the software.

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THERMO JARRELL ASH ICAP 61E**

7. Ensure that a method exists for your particular analysis. Elements to be determined in extracts from each SSL laboratory extraction procedure will have a separate method file created for ICP analysis. This method is stored as a file on the computer. To develop a new method or modify an existing method, select "Development" on the main menu of ThermoSPEC software and choose "Method" on the submenu. Some of the information that is included in the method for an ICP analysis is: elements selected for analysis; names and concentrations of standards; choices in storing and printing analysis data; and plasma parameters such as gas flow rates, RF power level, and peristaltic pump parameters.

8. If the analyses will be determined using the autosampler, create an autosampler table by selecting "Autosampler Setup" from "Operations" on the main menu. In this table, you can specify a name for a sample based on it's position in the tube rack. The table also allows for a dilution factor to be inserted for each sample, as well as the automatic insertion of standards, blanks, or quality control samples between groups of samples.

ICP Ignition and Adjustment

1. From the main menu on the ThermoSPEC software, select "Plasma Control Panel" from the "Setup" submenu. Press F1 (Start Up). The instrument will purge with Ar for 90 s, after which time it will ignite automatically. If the instruments ignites, ensure that filtered, distilled water flows into the nebulizer via the peristaltic pump. Never allow the torch tip to run without liquid flowing through system. Allowing the system to run dry will irreparably damage the tip.

2. If the instrument fails to ignite, check for air leaks around the nebulizer and spray chamber while purging during Startup procedure. Also, with regard to the HF-resistant spray chamber, allow the peristaltic pump to thoroughly wet the spray chamber for 5-10 minutes prior to attempting to relight. Other possible options to assist ignition are to adjust the nebulizer gas flow rate or the RF power.

Mercury Profile

1. Perform a Polychromator Profile to obtain optimal alignment of the polychromator. A mercury lamp (435.835 nm), controlled by a lever located on the polychromator front control panel that is used for this purpose. Push the lever on the control panel to the left. Select "Profile" from the submenu "Setup" on the main menu of the ThermoSPEC software. Press F3 (Automatic), then F1 (Run) to run the profile.

2. When the profile is complete, press F1 (Calculate Spectrum Shift) to determine the appropriate vernier position. The vernier, located on the front of the polychromator, is adjusted to this reported setting.

3. After readjusting the vernier, press the Escape key on the computer to repeat the Hg profile. Rerun the profile repeatedly until the result of the calculated spectrum shift is equal to the vernier setting. This Hg profile can be performed prior or after the torch is ignited, and should be repeated at least twice daily to readjust the instrument to changes in room temperature, pressure, and humidity.

Observational Height Adjustment

1. The purpose of this adjustment is to optimize the vertical position of the spectrometer optics (purged optical path tube) in relation to the torch. This adjustment needs to be made whenever the torch or center tube is replaced. A 1 ppm Zn solution in the same chemical matrix to be used for the particular analysis must be prepared.

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2. A method must be created via "Method" from the "Development" submenu as described in Step (7). Create a method for only Zn with the same instrument operational parameters selected in the method that will be used for sample analysis.

3. While the torch is lit, press ESC on the computer keyboard to return to the software main menu. Choose "Analysis" from the "Operations" submenu. Select the Zn method for analysis.

4. Return to "Methods" on the main menu, select the Zn optimization method, and choose F7 (Scans). Press F5 (Wavelength Scan), then F1 (Instr). Aspirate the 1 ppm Zn solution, and press F1 (Run).

5. When the wavelength scan is complete, check the numeric intensities of peak and background. It is desirable to obtain a high peak size in relation to the background. Adjust the vertical torch position and rerun scan until the peak/background ratio is maximized.

6. Once the torch is lit, press the ESC button on the computer keyboard to return to the software main menu. Choose "Analysis" from the "Operations" submenu. Select the appropriate method for analysis. This method was created from the "Development" submenu as described by Step (7).

7. Once this method is selected, the instrument operational parameters will change to those established in the method.

Nebulizer Adjustment

1. Return to the control panel screen (press CTRL-F6) and check the suitability of the nebulizer gas pressure by aspirating a 500 ppm solution of Y (yttrium). Adjust the nebulizer pressure so the top of the Y bullet lines up with the top of the torch bonnet.

Operation

1. Ensure the autosampler pump is operating and the rinse solution has filled the tube of the rinse station.

2. Choose "Analysis" from Operations of the main menu. Select the appropriate method. Initialize the autosampler by typing "ia" on the command line. Then type "ra" to rinse the autosampler tube.

3. Press F9 (Autosampler). Choose the appropriate autosampler table for the run, and press F1 (Run).

Shut-down

1. When analyses are complete, the autosampler will automatically return to the rinse position. Allow it to rinse several minutes.

2. Go the control panel by pressing CTRL F6, and press F5 to extinguish the torch. After the torch is off, press F6 to shutdown the instrument.

3. Disengage the pump tubing from the ICP and autosampler.

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OPERATION
THERMO JARRELL ASH ICAP 61E

4. Turn off the coolant water pump behind the instrument.

5. Turn off the switch on the surge protector.

REFERENCES

Thermo Jarrell Ash Corp. 1991. Operator's Manual. ICAP 61E Spectrometer, 8E Forge Parkway, Franklin, MA.

APPENDIX XIV

SATURATION EXTRACT
CENTRIFUGE METHOD

1. APPLICATION

The saturated paste is operationally defined so that it may be reproduced by a trained analyst using limited equipment. The saturated paste extract derived from the saturated paste (procedure 8A) is an important aqueous solution because many soil properties have been related to the composition of the saturation extract, e.g., soluble salt composition and electrical conductivity. These soil properties or characteristics are related in turn to the plant response to salinity (U.S. Salinity Laboratory Staff, 1954).

2. SUMMARY OF METHOD

The saturated paste is transferred to a custom-made, centrifuge extraction cup and fitted with filter paper. The saturated paste is centrifuged to obtain extract. The extract is used in subsequent chemical analyses, e.g., water-soluble cations (procedures 6N1, 6O1, 6P1, and 6Q1) and water-soluble anions (procedures 6I1, 6J1, 6K1c, 6L1, 6M1, 6U1, and 6W1).

3. INTERFERENCES

Some saturated pastes are difficult to extract, i.e., soil dispersion and puddling. Repeated extractions may be necessary to obtain sufficient extract. Filtration also may be necessary with some extracts.

4. SAFETY

No significant hazards are associated with this procedure. Observe standard laboratory procedures.

5. EQUIPMENT

5.1 Centrifuge, International No. 2, Model V, International Equip. Co., Boston, MA.
5.2 Centrifuge buckets, No. 353, International Equip. Co., Boston, MA.
5.3 Swinging bucket rotor, Model 976, International Equip. Co., Boston, MA.
5.4 Centrifuge extraction cup, custom-made to fit No. 353 centrifuge bucket, Glassco Corp, P.O. 3309, Knoxville, TX. Refer to Figures 1 and 2. Centrifuge extraction cup dimensions are as follows:

a. Type 1 PVC
b. O.D. = 95.25 mm (3 3/4 in)
c. I.D. = 80.96 mm (3 3/16 in)
d. Centrifuge tube length = 127 mm (5 in)
e. Centrifuge tube inserted lip = 3.18 mm (1/8 in)
f. Centrifuge tube base thickness = 12.7 mm (1/2 in)
g. Centrifuge tube base perforations = 2.38 mm (3/32 in)
h. Collection cup length = 31.75 mm (1 1/4 in)
i. Collection cup base thickness = 6.35 mm (1/4 in)

5.5 Filter paper, 8-cm diameter
5.6 Polycons, Richards Mfg. Co.
5.7 Milipore filters, 2-μm diameter

6. REAGENTS

No reagents are required for this procedure.

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7. PROCEDURE

7.1 Prepare the saturated paste extract cup to receive the saturated paste (procedure 8A) by placing a 8-cm diameter filter paper in the bottom of the upper part of the extraction cup. Slightly moisten the filter paper to ensure that it remains in place.

7.2 Carefully transfer the saturated paste into the extraction cup. Gently tap the cup to remove entrapped air in the paste.

7.3 Place pairs of extraction cups on a beam balance to equalize the weights.

7.4 Place the pairs of cups in the centrifuge buckets.

7.5 Centrifuge the saturated paste at 1800 RPM for 30 min.

7.6 If insufficient saturation extract has been obtained, recentrifuge saturated paste.

7.7 Filtering the saturation extract is recommended to prevent the development of microorganisms. Connect the syringe to a 0.2-μm diameter Milipore filter and express the extract into a polycon.

8. CALCULATIONS
No calculations are required for this procedure.

9. REPORT
No values are reported.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
U.S. Salinity Laboratory Staff. 1954. L.A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. U.S. Dept. of Agric. Handb. 60. U.S. Govt. Print. Office, Washington, DC.

A Outer dia
B Inner dia
C Wall thic
D Centrifug
E Centrifug
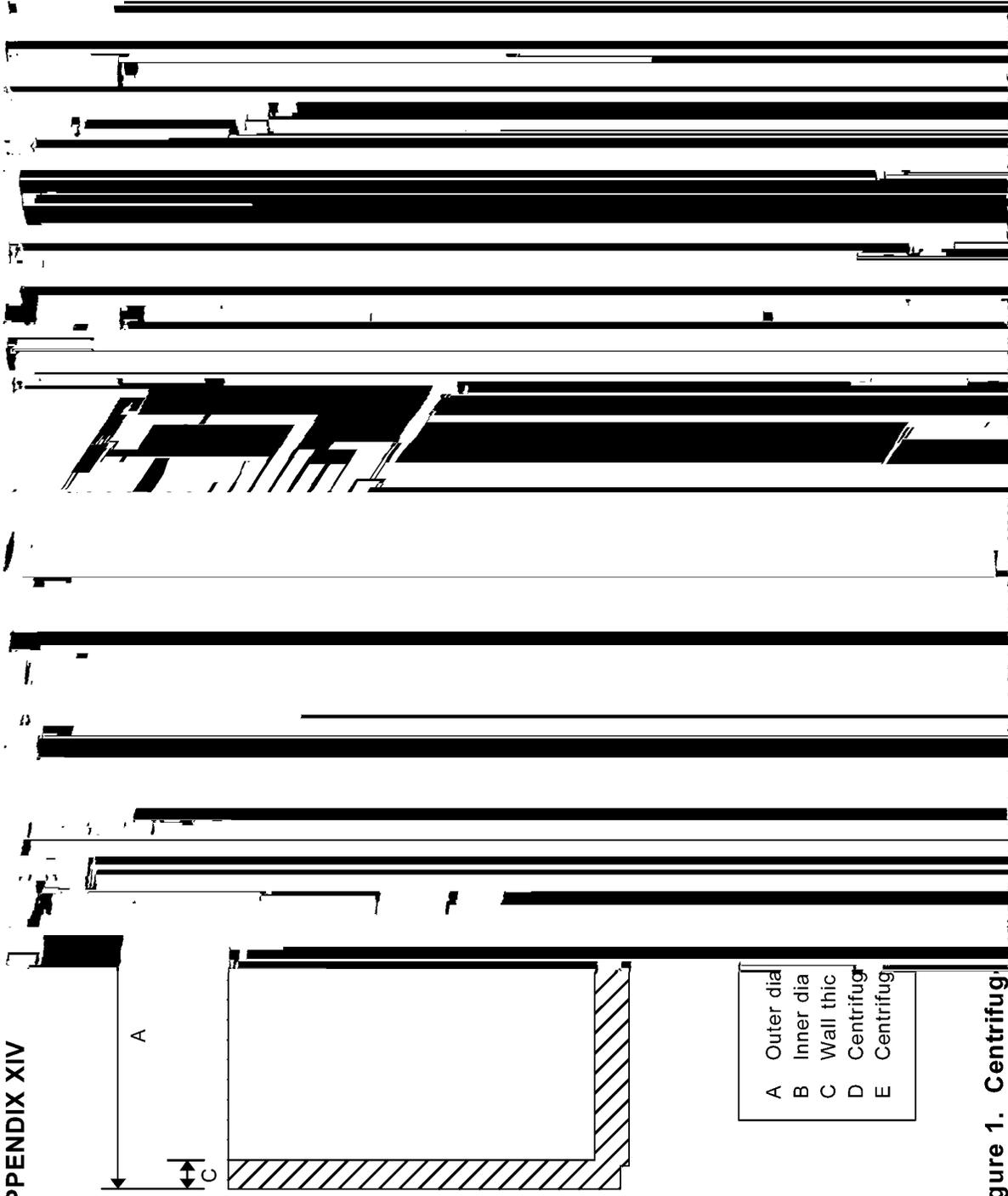
Figure 1. Centrifug

APPENDIX XV

AUTOMATED TITRATOR
OPERATION
METROHM 670 and 686 TITROPROCESSOR, 664 CONTROL UNIT, 674 SAMPLE
CHANGER, and 665 DOSIMAT

The SSL uses automated titrators manufactured by Metrohm. The 670 and 686 Titroprocessors use the same accessory components. The difference between the two units is that the 670 has a more sophisticated control system. Both units have four operation modes as follows:

a. Set equivalence titration
b. General equivalence titration
c. Monotonic equivalence titration
d. Measurement of pH voltage and temperature

The set equivalence titration ("Set") is the mode most generally used by the SSL and is described below. The 686 Titroprocessor is used for extractable acidity (6H5a), carbonate/bicarbonate (6I1b and 6J1b)), standardization of acids, and exclusively for organic C (6A1c). The 670 Titroprocessor is interchangeable with extractable acidity, carbonate/bicarbonate, and standardization of acids. The 670 Titroprocessor has the capacity to perform pH (8C1f and 8C1g) in the measurement mode, a capability that the 686 unit does not have. Refer to the specific SSL method for additional information on operational settings. Refer to the instruction
manual for operation in other modes.

The 686 and 670 Titroprocessor units operate in a similar manner. Operational settings are described below for both units. Reference to any differences are provided separately. Two end points may be specified for each titration and are measured in mV or pH. The time delay to sense the titration end point ranges from 9 to 99s. Pulse range (titration rate) and drift are specified.

Operational Settings for 686 and 670 Titroprocessors

Parameter: Ep_1 pH
Definition: 1st end point
Initial Value: Off
Range: 0 to ±20.00

Parameter Ep_1U
Range: 0 to ±20.00 mV

Parameter: Dyn pH 1
Definition: Pulse Range
Initial Value: Off
Range: 0 to ±20.00

Parameter: Dyn U 1
Range: 0 to ±2000 mV

Parameter: Drift 1
Definition: Next aliquot of titrant added
Initial Value: 10 mV/s
Range: 0.3 to ±99.9 mv s^{-1}

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Parameter: t(delay) 1
Definition: Delay time
Initial Value: 10 s
Range: 0 to ±99 s

Parameter: EP_2pH
Definition: 2nd end point
Initial Value: Off
Range: 0 to ±20.00

Parameter: EP_2U
Range: 0 to ±2000 mV

Parameter: Temperature
Definition: Titration temperature
Initial Value: 25.0°C
Range: 20 to 200°C

Parameter: Stop V
Definition: Stop volume, if no end point
Initial Value: 99.99 mL
Range: 0 to 999.999 mL

Setting Parameters for 686 Titroprocessor

1. Press "Set" key to initiate the mode.

2. Press "Parameters" key to input parameters. Input the appropriate values for each of the parameters and then press "Enter".

3. To store method, press "User Methods" key until "Store" is displayed. Enter the number of the method and press "Enter."

4. To recall method, press the "User Methods" key until "Recall" is displayed. Enter the method number and press "Enter."

Setting Parameters for 670 Titroprocessor

1. Enter methods page by entering "P1" on the keyboard.

2. Enter the method number of the method to modify. This automatically moves the unit to page 8 of the method.

3. Enter "P3" to access the method of operations page.

4. Enter the appropriate value for the various parameters for the titration. Refer to the SSL method for appropriate values to enter.

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AUTOMATED TITRATOR
OPERATION
METROHM 670 and 686 TITROPROCESSOR, 664 CONTROL UNIT, 674 SAMPLE CHANGER, and 665 DOSIMAT

5. Enter "P8" to return to page 8 of the method.

6. The titrations may be started or other operations may be performed at this point.

Optimizing Parameters for 686 and 670 Titroprocessor

1. The dynamic change pH (pulse range), drift (change pH to pulse), and dV/dt (buret speed) are the most important parameters to optimize for fast precise titrations.

2. The dynamic change in pH ranges from 0 to ±20.00. A small change in pH produces a flat titration curve, whereas a large change in pH produces a steep curve. This change is the difference between the shoulder of the titration curve and the end point.

3. The drift may range from 0 to 20.00 pH units. A large drift titrates faster, whereas small drift obtains a more satisfactory equilibrium. A new feeding pulse from the buret is emitted if the drift condition is fulfilled.

4. The dV/dt is the feed speed from the buret and ranges from 0 to 10. A large number feeds the titrant faster than a small number. The dV/dt is not stored and is adjusted on the 665 Dosimat.

5. The time delay, i.e., t(delay), senses the end point and may range from 0 to 99 s. A large number increases the time that the titrator waits to sense whether or not the end point has drifted.

6. A rule of thumb of setting parameters is to optimize the dynamic change in pH and then select the drift.

7. Select high values for dynamic change in pH and slightly higher drift.

8. Set the dV/dt to a middle position.

9. Always optimize parameters for the smallest possible sample concentration in order to prevent an over titration.

10. Set t(delay) when and if the end point remains stable.

REFERENCES
Metrohm Ltd. Instructions for use. 686 Titroprocessor Series 04. Metrohm Ltd., CH-9100 Herisau, Switzerland.
Metrohm Ltd. Instructions for use. 670 Titroprocessor Series 11. Metrohm Ltd., CH-9101 Herisau, Switzerland.
Metrohm Ltd. Instructions for use. 673/674 Sample Changer and 664 Control Unit Series 05. Metrohm Ltd., CH-9100 Herisau, Switzerland.
Metrohm Ltd. Instructions for use. 665 Dosimat Series 14. Metrohm Ltd., CH-9101 Herisau, Switzerland.

APPENDIX XVI

CHROMATOGRAPH
OPERATION
DIONXEX 2110i ION CHROMATOGRAPH
WITH ANION SELF-REGENERATING SUPPRESSOR (ASRS-1)

INTRODUCTION

The term chromatography is derived from the Greek words meaning "color" and "write"; however, the color of compounds is incidental to the separation process by chromatography (Day and Underwood, 1980). A good definition of chromatography is difficult to formulate as it is a collective term applied to methods which are diverse and yet share certain common features (Day and Underwood, 1980). Chromatography is a process whereby components of a sample are distributed between two phases. Keuleman (1959) defined chromatography as follows: "... a physical method of separation, in which the components to be separated are distributed between two phases, one of these phases constituting a stationary bed of large surface area, the other being a fluid that percolates through or along a stationary bed". The stationary phases may be either a solid or a liquid, and the moving phase may be either a liquid or a gas. Four categories of chromatography are as follows: liquid-solid; gas-solid; liquid-liquid; and gas-liquid. In all the chromatographic techniques, the solutes to be separated migrate along a column (or, as in paper or thin-layer chromatography, the physical equivalent of a column), and the basis of the separation lies in different rates of migration for the different solutes (Day and Underwood, 1980). The rate of migration of a solute is the result of two factors, one tending to move the solute and the other to retard it. In Twsett's (1906) original process, the tendency of solutes to adsorb on the solid phase retarded their movement, while their solubility in the moving liquid phase tended to move them along. A slight difference between two solutes in the firmness of their adsorption and in their interaction with the moving solvent becomes the basis of a separation when the solute molecules repeatedly distribute between the two phases over and over again throughout the length of the column.

The SSL uses ion chromatography which is an extension of ion exchange methods combined with liquid chromatography and conductimetric detection techniques. Ion exchange is used to separate complex mixtures of chemical compounds into individual ionic species. Conductimetric detection is the method of choice because of its sensitivity, linearity, and universal detection capabilities. However, conductivity can not be used in conventional ion-exchange chromatography because the ions of interest are eluted and separated by a background eluent which is also of an ionic character. These background ions are also detected by the conductimetric detector which makes it difficult to distinguish between sample and eluent ions. The combination of ion exchange chromatography and conductimetric detection is made possible by an ion suppression column following the ion separation column.

The SSL uses a DIONEX Model 2110i Ion Chromatograph (DIONEX, 1984, 1992). This unit is a fully automatic dual-channel system composed of the following: analytical pump (2); automated sampler; chromatography module; conductivity detectors (2); self-regenerating suppressor (ASRS-1) and controller (SRC-1); computer interface (2); and AI-450 Chromatography Software Program Release 3.32, Microsoft Windows™ Operating Environment (DIONEX, 1993).

Start-Up

1. Determine if eluent box is full.

2. Check generator and air pressure (4.5 to 5.0 psi).
3. Hit "Power" button and listen for air sound.

4. Hit "Eluent" button (blue square). Red light comes on.

5. Hit "B On" button (blue square). Listen for air sound.

6. Check pump. Pump needs oil (1 drop) every 6 months. Note date of service. Listen for noises that may be related to air in system.

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WITH ANION SELF-REGENERATING SUPPRESSOR (ASRS-1)

7. Place syringe in eluent box, fill, and close.

8. Remove air from syringe and place in eluent box. Open eluent box and keep pressure firm on syringe.

9. Open top knob. Change flow rate from 2.0 to 8.8 psi.

10. Keeping firm pressure on syringe with left hand, hit the "Start/Stop" button to start the pump.

11. Tap the tubing near the top knob to remove air bubbles.

12. Inject most of the syringe.

13. Change flow rate to 2.0 mL min^{-1}.

14. Close top knob.

15. Turn off "Eluent" lever.

16. If there is an air knock, repeat process or use isopropanol technique. The previous steps are critical. Using a high flow rate when the top knob is not opened can damage the pump.

17. Allow system to warm-up for 15 to 20 min.

Calibration and Sample Analysis

18. Samples are put in Autosampler after correct dilution. Dilutions are based on Predict reading and HCO_3 reading.

19. Use computer "Windows" Program to set-up schedule as follows:

a. Go to Method. Use "Salt 1" Method for regular samples. Go-to and set-up schedule.
b. Go to Run.
c. Turn chromatograph from "Manual" to "Auto".
d. Hit "Run". Check baseline of blanks and standards at the beginning of each run. Check the acid flow, conductivity, flow rate, and first group of standards.

20. Use the following values as a guide for calibration parameters. Parameters will vary with column length, flow rate, and eluent strength. These guidelines are as follows:

a. Air pressure = 5.0 psi
b. Conductivity = 22.0 to 28.0 mS
c. Flow rate = 2.0 mL min^{-1}
d. Pressure limit low = 0-900 in 10 psi increments
e. Pressure limit high = 0-1900 in 100 psi increments
f. Pump pressure = 560 to 1200 psi
g. Temperature compensation = 1.7
f. The following anions are routinely determined in the Salt 1 Method:

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F^- = Fluoride
Cl^- = Chloride
NO_3^- = Nitrate
NO_2^- = Nitrite
SO_4^{2-} = Sulfate

Shut-Down

21. Shut-down is scheduled into "Windows" Program.

22. Hit "Manual" to escape from "Windows" Program. Turn off computer, pump, and power to chromatograph.

23. Turn off eluent valve to avoid spills.

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Tswett, M. 1906. Ber. Deut. Botan. Ges., 24:235.

APPENDIX XVII

FLOW INJECTION ANALYSIS
LACHAT QUIKCHEM AE, AUTOMATED ION ANALYZER

INTRODUCTION

Flow injection analysis (FIA) is a continuous flow method in which highly precise sample volumes are introduced into an analytical stream. Samples and reagents are transported through flexible plastic tubing by the action of a peristaltic pump. For successful analysis, it is vital that the sample solution be injected rapidly as a pulse or plug of liquid and that these injections not disturb the flow of the carrier stream. Immediately after injection with a sampling valve, the sample zone in a flow injection apparatus has the rectangular concentration profile. As it moves through the tubing, band broadening or dispersion takes place. Flow injection analyses are usually performed under conditions in which dispersion by both convection and radial diffusion occurs. The radial dispersion from the walls toward the center serves the important function of essentially freeing the walls of analyte and thus eliminating cross-contamination between samples.

Dispersion is defined by the equation $D = C_o/C$ where C_o is the analyte concentration of the injected sample and C is the peak concentration at the detector. Dispersion is readily measured by injecting a known concentration Co and then measuring the absorbance in the flow-through cell. After calibration, C is calculated from Beer's Law. Dispersion is influenced by three interrelated and controllable variables, primarily sample volume, tube length, and pumping rate.

The SSL uses the LACHAT QuikChem AE Automated Ion Analyzer with XYZ Sampler; reagent pump; automated dilution station; system unit with up to seven sample processing modules configured for performing flow injection analysis with photometric detection; and QuikChem Data System;

Start-Up

1. Refer to the operating and software reference manuals for LACHAT set-up and operation. The following normal boot-up and start-up diagnostics of system are recommended by LACHAT (1991).

a. Turn main power switch "ON". Some diagnostic messages appear showing the results of the computer hardware test. There should be 640 kB of RAM. If there is a "Disk Boot Failure", push the boot button on the left of the system unit and try again.
b. The injection valves cycle twice. The valve state displays in the lower LH corner show the results, LO for the Load state, and IN for the inject state. All valves that are present should end up in the IN state after the test. In a box in the lower RH corner appears a table of valve test results. All valves present should test "OK". Valve 1 is on sample processing unit 1, closest to the rear of the system unit, valve 2 is on sample processing unit 2, and so. Valves not present will test as "--".
c. The detectors (1. to 7., and "Reference") diagnostic symbols are their output in terms of the 12-bit ADC count measured from each detector. The count is proportional to light power for absorbance detectors and should range between 100 to 4000. The counts for the alpha detector in each channel is in the middle column and for the beta detector, used with the optical dilution option, in the right-most column.

The symbol "--" with 0 counts may indicate that the detector is not connected to the buss board, not installed, no power to the detector, source light bulb burnt out or not pushed into socket, fiber optic not installed or not pushed in all the way when installed underneath the detector head.

A wavy line symbol with <20 counts may indicate that the fiber optic may not be pushed in all the way. Or, a bubble left in the flow cell from shut-down causes this. It will be OK upon starting a method and getting liquid into the flow cell.

The symbol "ok" with <100 counts may be normal for the wavelength. A leftover bubble can cause this as in the wavy line symbol.

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The symbol "OK" with <4000 counts is normal.

The ** symbol with <4096 counts is getting near the 4096 limit of the ADC. This is usable and may occur occasionally at red wavelengths near 660 nm. This symbol may also appear if the interference filter is not pushed in all the way.

The ++ symbol with 4096 counts may indicate that the ADC is at its limit (overrange). This almost always occurs because the interference filter is not mounted in the detector head or is not pushed in all the way. If the filter is mounted, this can indicate a damaged photodiode or detector op amp, usually caused by connecting or disconnecting the detector's cable to the buss board with the power on.

Operation

1. If method requires the heater module, set heater to appropriate temperature and allow 15 to 20 min to warm up.

2. Place correct interference filter into detector head. Refer to specific method.

3. Transfer calibration standards into plastic vials and place in descending order in XYZ sample trays marked "Standards".

4. Set appropriate speed on reagent pump.

5. On computer main menu, select "Methods" and then "Analysis Select and Download". On method list, select appropriate method. System unit receives the downloaded method and initializes it.

6. Pump reagents into manifold. Continue this step and observe baseline. A good baseline needs to be smooth and at zero absorbance. Scatter is indicative of air bubbles and irregular reagent flow. Also observe for any back-pressure in manifold tubing. Refer to method for specific recommendations for pumping reagents into manifold.

7. On computer main menu, select "Samples", "Tray Definition and Submit", and then "Edit" to create new sample tray followed by "Submit" to run new sample tray.

8. Parameters specific to method are defined within the "Method Definition" menu. Some of these parameters may be modified from the QuikChem Methods. Modifications are primarily related to the criteria and strategies for calibration standards and to injection timing. The QuikChem method numbers are printed on the sampling processing modules, e.g., 12-115-01-1-A, orthophosphate in soils.

9. Refer to the method for specific parameters in relation to calibration standards. Some calibration parameters are as follows:

a. Determine the standards, number of standards, and data format, e.g., there are 7 calibration standards (20.0, 12.00, 4.00, 2.00, 0.800, 0.400, and 0.000 mg P L^{-1}) with a data format of ####.###, i.e., data rounded to 3 places.
b. Determine the segments/boundaries for the calibration standards, e.g., the segments are A - C (20.0 to 4.00 mg P L^{-1}); C - E (4.00 to 0.800 mg P L^{-1}); and E - G (0.800 to 0.000 mg P L^{-1}).
c. Determine the protocol (replications) for the calibration standards, e.g., AA BB CCC DDDD EEEE FFFF GG

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FLOW INJECTION ANALYSIS
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d. Determine the check standard, e.g., 20.0 mg P L^{-1}. Maximum number of consecutive trays between check standard is one; maximum number of consecutive samples between check standard is 60; and maximum elapse time between check standards is 2 h.
e. Determine the calibration strategy for segments, e.g., calibration strategy for segments are A - C, C - E, and E - G are normal, normal, and very low, respectively. The normal strategy may require a minimum correlation coefficient of 0.95. The very low strategy may require a minimum correlation coefficient of 0.90. Both may require a maximum standard deviation in slope of 50%. A calibration passes only when both criteria are met. Strategies are user designated. In addition, calibration strategies are based on either a specific chord or the full chord. Chord 0 is full chord, and chord 1 - 5 are sections of peak from start of peak to end of peak.

10. Refer to the method for specific parameters in relation to timing. Some timing parameters are as follows:.

a. Determine cycle period (s)
b. Determine inject to start of peak period (s). To see if peaks are being timed correctly, scan across correlation coefficients for all chords 1 - 5. The most peak area should be between chords 2 - 4 with the most signal-to-noise ratio in chords 1 and 5.
c. Determine inject to end of peak period (s)
d. Use automatic timing, where standard assumptions are in effect. Manual timing may be helpful in some methods.

11. Refer to the method for specific parameters in relation to data presentation. Some data presentation parameters are as follows:

a. Top Scale Response (absorbance)
b. Bottom Scale Response (absorbance)

12. Refer to the "Method Definition" of the method of interest for other parameters not discussed here.

Shut-down

1. Refer to the method for specific recommendations for shut-down procedure. Generally, upon the completion of run, place the transmission lines into distilled deionized water and/or other solutions, e.g., NaOH-EDTA, and pump for the recommended time.

2. Remove transmission lines from the solution and drain all lines completely dry.

3. Turn power switch "OFF". Remove pump tubes from the pump cartridges.

Routine Maintenance

The following recommendations for routine maintenance are provided by LACHAT (1991).

1. One of the most common problems is chemical spills on the sampler, pump, reaction module, and detector head. If a spill occurs, clean the spill immediately.

2. Every 50 h (or 2500 samples), wipe the rollers clean with isopropanol. To ensure a longer life for the pump, spray a lint-free cloth with a silicone spray and, with the pump running, hold against the rollers.

FLOW INJECTION ANALYSIS
LACHAT QUIKCHEM AE, AUTOMATED ION ANALYZER

3. Move the flare/union assemblies from the valve and clean each port with a wet cotton swab weekly.

4. Every 500 h (25000 samples), replace the flares at each port of the valve. Clean the unions at each port of the valve and replace the O-rings if necessary.

5. All manifolds should be flushed for approximately 5 min with distilled deionized water after each use. Air can be pumped through after the water to dry the manifold tubing. Refer to specific methods for special cleaning procedures. Every 500 h of use, clean each fitting and replace O-rings as necessary. A small (#66) drill bit is used to clean any clogged fittings. O-rings should be free of cracks or indentations.

6. Replace pumps approximately every 300 h of use. If the pump tubes become damaged, cracked, brittle, of flat, replace sooner. Silicon pump tubes wear out much faster than the standard PVC tubes and should be replaced accordingly. Never leave the pump tubes cartridges which have pump tubes mounted on them snapped onto the pump unless the rollers are moving. If the rollers are stationary, they will flatten the tubes and render them useless.

REFERENCES
LACHAT Instruments. 1990. QuikChem AE software reference manual, Version 11. LACHAT
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LACHAT Instruments. 1991. Operating manual for the QuikChem AE automated ion analyzer. LACHAT
     Instruments, 6645 West Mill Road, Milwaukee, WI.

APPENDIX XVIII

HIGH SPEED REFRIGERATED CENTRIFUGE
OPERATION
INTERNATIONAL IECB-22M

On the centrifuge, there are three switches as follows: POWER ON/OFF; START; AND STOP/OPEN. All other controls are located on the control panel at the top-rear of the cabinet. The Operating Mode Key is to the right of the cabinet (turn to manual setting). The POWER ON/OFF is usually in the OFF mode. When turned on, the STOP/OPEN indicator switch will glow red. There are three different rotor sizes that are used for different size tubes.

Start-up and Run

1. Set temperature control. Control glows red. Example: 26°C..

2. Set speed setting. Green indicator light. Example: 10000 RPM.

3. Note rotor number. Green indicator light. Example: Rotor No. 874

4. Set time switch. Green indicator light. Time mode period runs from 1 s to 99 hr and 59 min. Example: 10:00 for 10-min run.

5. Some messages may appear as follows:

Latch
Key-Symbol
Imbalance
Brushes
0-Temperature
Off
Manual
Program Set
Program Run

6. Set acceleration. Acceleration speed (green indicator light) ranges from 0=slow to 9=maximum. Example: Acceleration speed = 5

7. Set brake. Brake (green indicator light) ranges from 0=coasting to 9=fast.

8. Set program if used. To activate, turn key to Program Set or Program Run setting.

9. Push STOP/OPEN to open lid of centrifuge. Latch indicator light glows gold.

10. Remove cover letter B. Unscrew bolt and lift cover.

11. Insert even number of samples to balance rotor evenly.

12. Replace cover and bolt.

13. Close lid to centrifuge. Hold both front and back of lid and push down.

14. Press START. It may take a minute for the centrifuge to accelerate to speed setting. If the machine malfunctions, it will shut off at speed 800 RPM.

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HIGH SPEED REFRIGERATED CENTRIFUGE
OPERATION
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15.

APPENDIX XIX

UV-VISIBLE SPECTROPHOTOMETER
OPERATION
DU-7 SPECTROPHOTOMETER

Set-up

1. The DU-7 spectrophotometer operates from A 190- to 800-nm wavelength range. Refer to the manufacturer's manual for additional information on the operation of the unit. To perform routine operation the instructions are as follows:

a. Connect power source (110 V AC).
b. Press "Idle" key.
c. Turn on appropriate light source, "UV" or "VIS". Allow the lamps to warm-up for at least 30 min before any measurements are performed.

Creating a Program

2. The six available operating modes from the keyboard are as follows:

a. Single wavelength
b. Dual wavelength
c. Multi wavelength
d. Scan
e. Rep scan
f. Time drive

3. For most applications, the single wavelength mode is used. If another option is selected, refer to the manufacturer's manual. Create a program in the single wavelength mode as follows:

a. Press the "Single Wavelength" button.

b. Use the arrow keys to position cursor over the parameters. When at the "Function" parameter, use the "Sel" key to select the absorbance ("Abs") function. Press "Enter" to retain the selected function.

c. At the "Wavelength" parameter, key in the number and press "Enter".

d. At the "Concentration" parameter, use the "Sel" key to select "None" and press "Enter".

e. Press the "List" key to display all Programs and Scans in memory.

f. Press "Store" and "Sel" keys until "Program" appears and press "Enter".

g. Key in program number and press "Enter".

Recalling a Stored Program

4. Press "List" to display all programs.

5. Press the required operation mode, i.e., single wavelength, scan, rep scan, etc.

6. Key in program number and press "Enter". The parameters are recalled and displayed on the CRT.

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UV-VISIBLE SPECTROPHOTOMETER
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Operating in the Single Wavelength Mode

7. The operation parameters are as follows:

a. "Start" calibrates the instrument.
b. "Run" records the sample measurement.
c. "Auto Zero" rezeros the instrument.
d. "Copy" prints the CRT screen

8. Install and plug in sample changer before using the DU-7 is powered-up.

9. Install the sipper sampling accessory which contains the peristaltic pump, the flow-through cell, and the assorted attached tubing.

10. Connect cable to sipper top.

11. Connect tubing to arm of sample changer.

12. Connect drain line to waste container.

13. Power-up the DU-7.

14. In the single wavelength mode, three additional parameters, "Fill Time", "# of Samples", and "Auto Zero", are required. Input these parameters by using the arrow key and pressing "Enter". The "Fill Time" determines the time that the pump motor runs in the fill cycle (0.1 to 99.9 s). A 10-s time interval generally is adequate. The "# of Samples" parameter is the total number of sample tubes and does not include blank or reference solutions. The "Auto Zero" parameter automatically rezeros the instrument after every 1, 2, 5, or 11 sample readings. The "None" is an option when rezeroing is not required.

15. Place the sample, blank, and reference tubes in the sample changer. The sequence is blank, reference, samples (Auto Zero Number), blank, reference, samples, etc. until all tubes are in place. The last cartridge in the sample changer is the red "Stop" cartridge.

16. Press the "Start" key to read the blank or reference tube.

17. After the instrument reads the 1st tube, press "Run". The instrument reads samples, blanks, and references until the "# of Samples" parameter has been completed.

REFERENCES
Beckmann Instruments, Inc. Instruction Manual. DU-7 UV-Visible Spectrophotometer, Beckmann
Instruments, Inc.

APPENDIX XX

X-RAY
OPERATION
PHILIPS XRG-3000 X-RAY DIFFRACTOMETER
PHILIPS APD SOFTWARE, VERSION 3.5B

Diffractometer Start-up

1. Ensure the KV and MA controls are fully counter clockwise (at lowest settings).

2. Turn the key-operated LINE switch located on front of generator to "on". This step must be done prior to step (3).

3. Turn on the water in the cooling tank using the "On/Off" switch on the tank. The water flow should be 50-60 gal h^{-1} and the cooling water should maintain the tube temperature to approximately 60°F.

4. Depress the red ON button on the generator to initiate the voltage.

5. Use the following warm-up settings. Turn voltage up first, then current.

Voltage (kv)	Current (ma)	Time (min)
20	5	5
30	10	5
40	20	5

The target (working) settings for the voltage and current for Cu tube x-ray tubes at the SSL are 40 kv and 20 ma. If other tubes are used, manufacturer instructions should be consulted.

Batch Run Set-up

1. The APD software operates via MS-DOS. Enter APD via Microsoft Windows. To do this, open the Program Manager window and select the X-ray diffraction icon. This will open a window with several programs. Two are as follows:

a. *APD-XRAY DIFFRACTION*
Use this exclusively for sample analysis. Enter "APD-XRAY DIFFRACTION" to set up and run the required analysis.

b. *APD-DATA AND GRAPHICS*
Use this exclusively for manipulating and printing data and graphics for XRD analyses for production.

2. The computer must be electronically "connected" to the diffractometer instrument controller. If not, commands sent via the computer will not cause any diffractometer operation. To make a connection, enter "Utilities" from the main menu, then "Diffractometer Commands". To connect, type "//", then press the ENTER key. The goniometer should move to the 0° two-theta position, then return to 5° two-theta. The "C" prompt should be displayed if a connection is made. Return to the main menu of APD by typing exit, then pressing the ESCAPE key twice.

3. Data for specific types of projects (e.g., rCP95, RZ94, etc.) are stored in subdirectories on the "D" partition of the hard drive. Select the correct subdirectory on the computer for analytical data storage or

X-RAY
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PHILIPS XRG-3000 X-RAY DIFFRACTOMETER
PHILIPS APD SOFTWARE, VERSION 3.5B

retrieval. From the main menu, select "System Preparation" and then "System Parameters". Enter the desired subdirectory (e.g., "D:\CP95\"). Press ESCAPE key to return to the main menu.

4. For sample analysis using the sample changer, an appropriate Identify and Batch files must be assigned for the samples. Setup these files in "Edit" from the main menu. Identify Program files specify the analytical parameters used for a specific run, such as run length, continuous or step scan, step size, number of steps. The current identify program for a normal production scan is called by the file name "X".

5. Batch Program files are created for each run and include the sample changer positions, Identify Program name, sample ID, and MS-DOS data file name. Enter the "Edit" submenu and then "Batch file" to create a file. Our typical runs for production consist of 32 samples, a soil standard, and a quartz standard. When creating a batch file, there are established SSL naming conventions as follows:

a. Batch File Name
Abbreviated project name and letter signifying sequential run for project. (e.g., C4VA077A)

b. Sample Identification Project Name and run number (e.g., VA077.569)

c. Data file Name
SSL sample number (e.g., 92P0457)

6. Press the ESCAPE key to return to the main menu.

Sample Analysis

1. Load the samples into the sample holder. Place the sample holder into the sample changer attached to the goniometer. Make sure that sample number 1 is showing through the window of the sample changer.

2. Open the shutter for window 4 by turning knob to "infinity" on shutter control box and pressing red shutter button.

3. On the computer, enter the "Data Collection" submenu, and then "Batch Measurement". Use function key F5 to list all names of batch files created and choose from the list. Select the correct batch file to analyze, then press F1 to start the run. When analysis of a sample is complete, a DOS file is created with the extension ".RD", which refers to "raw data".

Data Calculations and Graphics

1. If the x-ray unit is operating under APD-XRAY DIFFRACTION window, you can shift to another window (e.g., APD-DATA AND GRAPHICS) by hitting "Alt" and "Tab" keys simultaneously. Do this quickly or the XRD run may be disrupted. This will return you to the X-ray diffraction window in Program Manager.

2. Enter APD-DATA and GRAPHICS. You will not immediately enter APD, but will enter a subroutine called X-MENU, which allows selection of specific users or subdirectories.

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3. Select user. By doing so, you will have the correct subdirectory selected for data retrieval and will not have to enter "System Preparation, System Parameters" as was required in step (8).

4. A DI file is created to allow the software to compile peak positions and intensities. From Main Menu, enter "Pattern Treatment", then "Peak Search". Use F5 to select scan file name. From the Peak Search screen, a smooth file can be created as well. This will result in creation of a file with the extension ".SM". Run the peak search, then press F9 to print the diffraction intensities data file. This diffraction intensities file is saved with the extension ".DI".

5. To plot one or more x-ray traces, select "Graphics" from the main menu, then use F5 to select files that should be grouped together. Smoothed, raw data, or DI files can be selected for plotting. Use F9 to print "Hard copy of Graph".

Diffractometer Shut-down

1. Reverse the diffractometer start-up procedure to cool down the tube and prepare the instrument to be shutoff. For weekends or extended periods between sample runs, the SSL policy is to leave the generator on and turn the x-ray tube down to 20 kv and 5 ma. To turn the tube down completely to shut-down the generator procedure below:

```
Voltage      Current      Time
(kv)          (ma)       (min)

30            10           5
20             5           5
 0             0          off
```

2. Depress the red OFF button to turn voltage off.

3. Turn the water on the cooling tank to OFF.

4. Turn the key-operated LINE switch to OFF.

REFERENCES
Philips Electronic Instruments Co. 1975. Instruction Manual. XRG-3000 X-Ray Generator. Philips
        Electronic Instruments Co., 6575 West Loop South, Suite 270, Bellaire, TX.
Philips Electronic Instruments Co. 1992. Software Operation Manual. PC-APD. Version 3.5. Philips
        Electronic Instruments Co., 6575 West Loop South, Suite 270, Bellaire, TX.

APPENDIX XXI

MINERALOGY CODES

Resistant Minerals

AE=Anatase
AG=Antigorite
AN=Andalusite
BY=Beryl
CD=Chalcedony(Chert,
 Flint, Jasper, Agate, Onyx)
CE=Cobaltite
CH=Cliachite (Bauxite)
CN=Corundum
CR=Cristobalite
CT=Cassiterite
DI=Diatoms
FE=Iron Oxides(Goethite,
 Magnetite, Hematite)
GE=Goethite
GI=Gibbsite
GN=Garnet
HE=Hematite
KK=Kaolinite
KY=Kyanite
LE=Lepidocrocite
LM=Limonite
LU=Leucoxene
MD=Resistant Mineraloids

MG=Magnetite
MH=Maghemite
MZ=Monazite
OP=Opaques
OR=Other Resistant Minerals
PN=Pollen
PO=Plant Opal
PY=Pyrophyllite
QC=Clay-Coated Quartz
QI=Iron Oxide-Coated Quartz
QZ=Quartz
RA=Resistant Aggregates
RE=Resistant Minerals
RU=Rutile
SA=Siliceous Aggregates
SL=Sillimanite
SN=Spinel
SO=Staurolite
SP=Sphene
SS=Sponge Spicule
TD=Tridymite
TM=Tourmaline
TP=Topaz
ZR=Zircon

Weatherable Minerals

AC=Actinolite
AH=Anthophyllite
AL=Allophane
AM=Amphibole
AO=Aragonite
AP=Apatite
AR=Weatherable Aggregates
AU=Augite
BC=Biotite-Chlorite
BG=Basic Glass
BR=Brucite
BT=Biotite
CA=Calcite
CB=Carbonate Aggregates
CC=Coal
CL=Chlorite
CM=Chlorite-Mica
CO=Collophane
CY=Chrysotile

GY=Gypsum
HB=Hydrobiotite
HG=Glass-coated Hornblende
HN=Hornblende
HY=Hypersthene
ID=Iddingsite
JO=Jarosite
KH=Halloysite
LA=Lamprobolite
LC=Analcime
MC=Montmorillonite-Chlorite
ME=Magnesite
MI=Mica
ML=Melilite
MM=Montmorillonite-Mica
MS=Muscovite
MT=Montmorillonite
MV=Montmorillonite-Vermiculite
NE=Nepheline

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MINERALOGY CODES

CZ=Clinozoisite
DL=Dolomite
DP=Diopside
EN=Enstatite
EP=Epidote
FA=Andesite
FB=Albite
FC=Microcline
FD=Feldspar
FF=Foraminifera
FG=Glass Coated Feldspar
FK=Potassium Feldspar
FL=Labradorite
FM=Ferromagnesium Mineral
FN=Anorthite
FO=Oligioclase
FP=Plagioclase Feldspar
FR=Orthoclase
FS=Sanidine
FZ=Feldspathoids
GA=Glass Aggregates
GC=Glass Coated Grain
GG=Galena
GL=Glauconite
GM=Glassy Materials
GO=Glaucophane
GS=Glass

NX=Non-Crystalline
OG=Glass Coated Opaques
OT=Other
OV=Olivine
OW=Other Weatherable Minerals
PD=Piemontite
PG=Palygorskite
PI=Pyrite
PL=Phlogopite
PR=Pyroxene
QG=Glass-Coated Quartz
SE=Sepiolite
SG=Sphalerite
SI=Siderite
SM=Smectite
SR=Sericite
ST=Stilbite
TA=Talc
TE=Tremolite
TH=Thenardite
VC=Vermiculite-Chlorite
VH=Vermiculite-Hydrobiotite
VM=Vermiculite-Mica
VR=Vermiculite
WE=Weatherable Minerals
ZE=Zeolite
ZO=Zoisite

Glass Count Minerals and Mineraloids

BG=Basic Glass
DI=Diatoms
FG=Glass-coated Feldspar
GA=Glass Aggregates
GC=Glass-coated Grains
GM=Glassy Materials
GS=Glass

HG=Glass-coated Horneblende
OG=Glass-coated Opaques
OT=Other
PO=Plant Opal
QG=Glass-coated Quartz
SS=Sponge Spicule

APPENDIX XXII

THERMAL ANALYZERS
TA INSTRUMENTS THERMOGRAVIMETRIC ANALYZER (TGA 51)
AND DIFFERENTIAL SCANNING COLORIMETER (DSC 910S)

Start-up

1. Turn on power strip which controls power to all instrument components.

2. Turn on power and heater to instrument controllers for both the TGA and DSC. Use switch on back of MIM's. Allow 60 min warm-up.

3. Turn on N_2 gas at tank and adjust flow on dual flow meter to 110 mm (100 cm^3 min^{-1}) for the TGA and 70 mm (56 cm^3 min^{-1}) for the DSC.

4. Turn on the fan on TGA unit.

5. Turn on the DSC autosampler using the switch on the rear of the instrument and turn on the house air attached to the autosampler at the outlet with the green lever.

6. Turn on the vacuum which has glass filter column attached to use for cleaning TGA pans and other small spills.

7. Turn on computer and press F1 (Start TA System).

8. The System Configuration screen is displayed. Ensure that two TA Module Interfaces (representing the DSC and TGA) are on-line, as well as the DSC autosampler. If any one of the three is not on-line, the computer has been started prior to turning on the instrument controllers or autosampler. If this event occurs, ensure the three components are on and reboot the computer.

Thermogravimetric Analyzer (TGA 51) Operation

1. Press F12 (Instrument Control). Press the right arrow key to highlight the small TGA window at the top of screen.

2. Press F4 (Go to Experimental Parameters).

3. Press F1 (Sample Info) to type in sample name, operator name, miscellaneous comments, and DOS filename. Press F8 (Accept this Form).

4. Ensure the correct method is selected for the analysis. If not, press F2 (Go to Method Editor) to select a different method. Use the ESC key to return to the Experimental Parameters screen.

5. Press ESC key again to return to the Instrument Control screen.

6. Press F6 (Go to Signal Control).

7. Ensure the platinum sample pan is empty on the TGA. If clean, skip to step 19. If not, loosen the silver-colored retaining ring on the quartz furnace tube while the tube is inserted into the furnace. Gently slide the balance housing to the right exposing the balance and sample pan.

8. Using the silver forceps, very carefully remove sample pan from glass rod (WARNING: Glass rods extremely fragile).

THERMAL ANALYZERS
TA INSTRUMENTS THERMOGRAVIMETRIC ANALYZER (TGA 51)
AND DIFFERENTIAL SCANNING COLORIMETER (DSC 910S)

9. Clean sample pan with the plastic nozzle attached to the house vacuum.

10. Replace sample pan to glass rod, and reinsert pan and balance into the furnace tube. Tighten retaining ring.

11. Examine "signal A" on the computer screen and press F1 (Auto Zero A). This will tare the empty sample pan.

12. Repeat steps 15 and 16 to remove the sample pan. Place pan on lab bench top and add approximately 10-12 mg sample into center of pan.

13. Replace the sample pan onto the glass rod and insert into furnace tube.

14. Press the ESC key to return to the Instrument Control screen.

15. Press F1 (Start) to begin analysis.

16. When analysis is complete, allow the furnace temperature to cool to <350°C, then remove quartz furnace tube from furnace. Pull furnace from TGA base and invert on rails on top of fan to cool.

17. When furnace cools to <40°C, a second analysis can be performed or a second furnace can be installed to immediately analyze a second sample.

Analysis and Plotting of TGA Data

1. Press F11 (Data Analysis).

2. Press F1 (Get New Program) and F8 to accept.

3. While viewing the list of data analysis programs, use the up and down arrow keys to select the TGA Standard Data Analysis program. Press F3 to accept.

4. Press F1 to start the program.

5. A window will appear to select a data filename for analysis. The name can be typed into the window. For example, type "C:STDKK.01". Or press the following sequence of keys to select a filename from the list of stored data files: (a) F11 (Data Analysis), (b) F8 (Go to File Utilities), (c) F1 (directory), (d) F8 (Accept the form). A list of filenames will appear and the desired file can be highlighted by using the up and down arrow keys. When the appropriate file is selected, press F3 (Select File). Press ESC key to return to Data Analysis option, and F1 (Resume Program). Press ALT and f keys simultaneously to automatically insert name of selected file into the small window. Press F8 twice to select file.

6. A window of unit and curve options are presented. The standard TGA graph plots temperature (°C) versus signal A (weight percent). The derivative of the weight percent with respect to temperature is also selected as a second curve.

7. Press F8 to accept and F1 to plot all data points (No Limits).

APPENDIX XXII

THERMAL ANALYZERS
TA INSTRUMENTS THERMOGRAVIMETRIC ANALYZER (TGA 51)
AND DIFFERENTIAL SCANNING COLORIMETER (DSC 910S)

8. Press F5 (Analyze curve) for various data analysis options. F1 (Step Transition) or F2 (Weight Change) are typical options. Select one option and enter.

9. Once a data analysis option is selected, press F1 to choose analysis on weight loss curve, and establish temperature limits of the calculation by using the left and right arrow keys (CTRL-arrow key for large steps along the curve). Use the TAB key to change from the low to the high temperature limit. Press F8 twice to accept.

10. Press ESC key to return to main menu options, and select F4 to plot.

11. Press top-left, white-colored key on plotter key pad to turn plotter on. Insert paper and press second white key on plotter to load paper.

12. On computer, press F1 (Plotter) to plot the data graphic.

Differential Scanning Calorimeter (DSC 910S) Operation - Single Sample

This DSC is equipped with an auto sampler (920 AutoDSC), but can be used for single sample analysis without using the autosampler, or used for multiple samples (described beginning at step 52).

1. On the autosampler, press the HALT button to stop the automatic mode, and press the "manual" button to initiate the manual mode.

2. Press F12 on the computer to display the Instrument Control window. Press the left arrow key to highlight the small DSC window at the top of screen.

3. Press F4 (Go to Experimental Parameters).

4. Weigh a sample into a tared Al sample pan on the Mettler AT200 balance. Use the bronze forceps to handle the sample pan. Unlike the TGA, the sample weight must be manually entered into the DSC program.

5. Place the sample in the DSC cell. The front node in the cell is for the sample and the back node is for the reference pan. The reference is generally an empty Al pan. The sample is left uncovered and uncrimped for analysis.

6. Cover the cell using the three lids.

7. Press F1 (Sample Info) to type in sample name, sample weight, operator name, miscellaneous comments, and DOS filename. Press F8 to accept.

8. Ensure the correct method is selected for the analysis. If not, press F2 (Go to Method Editor) to select a different method.

9. Press ESC key to return to the Instrument Control screen.

10. Press F1 (Start) to begin analysis.

THERMAL ANALYZERS
TA INSTRUMENTS THERMOGRAVIMETRIC ANALYZER (TGA 51)
AND DIFFERENTIAL SCANNING COLORIMETER (DSC 910S)

11. When sample analysis is completed, cool the cell with air. Turn on by pressing "Air" on the autosampler keypad, selecting "1", and pressing Enter.

12. When cell cools to < 25°C, turn the air off by pressing "Air" on the keypad, selecting "0", and pressing Enter.

13. Remove the lids from the sample cell, and remove the used sample pan.

14. Another sample can be analyzed at this time.

Differential Scanning Calorimeter (DSC 910S) Operation - Multiple Samples Using Autosampler

1. If the autosampler is in the manual mode (as used for a single run), press the "HALT" key on the autosampler to stop the manual mode. Press the "automatic" key to begin the automatic mode.

2. With the Instrument Control window displayed on the computer monitor, press the left arrow key to highlight the small DSC window at the top of screen.

3. Press F7 (Go to Autosampler).

4. Press F6 (Go to Sequence Utilities), F1 (Edit Run Sequence).

5. The sample information for each sample of a sequential run can be inputted from this screen. The screen format is very similar to the format described for a single analysis above. Use F5 (Insert Run) to create additional runs in the sequence. Use 15 to 35°C with a 3 min delay for load temperature.

6. When all run in a sequence have been inputted, press F8 (Accept Sequence).

7. Press the ESC key to return to the Autosampler Status screen.

8. Press F1 (Start Run Sequence).

Analysis and Plotting of DSC Data

1. Press F11 (Data Analysis).

2. Press F1 (Get New Program) and F8 to accept.

3. While viewing the list of data analysis programs, use the up and down arrow keys to select the DSC Standard Data Analysis program. Press F3 to accept.

4. Press F1 to start the program.

5. A window will appear to select a data filename for analysis. The name can be typed into the window. For example, type "C:STDKK.01". Or press the following sequence of keys to select a filename from the list of stored data files.(a) F11 (Data Analysis), (b) F8 (Go to File Utilities), (c) F1 (directory), (d) F8 (Accept the form). A list of file will appear and the desired file can be highlighted by using the up and down arrow keys. When the appropriate file is selected, press F3 (Select File). Press ESC key to return

THERMAL ANALYZERS
TA INSTRUMENTS THERMOGRAVIMETRIC ANALYZER (TGA 51)
AND DIFFERENTIAL SCANNING COLORIMETER (DSC 910S)

to Data Analysis option, and F1 (Resume Program). Press ALT and f keys simultaneously to automatically insert name of selected file into the small window. Press F8 twice to select file.

6. A window of options will be presented. The standard DSC graph plots temperature ($^{\circ}$C) versus signal A (watts per gram). The derivative of the W g^{-1} with respect to temperature is also selected as a second curve.

7. Press F8 to accept and F1 to plot all data points (no limits). If file size exceed buffer capacity, next select option F2 (Linear Smoothing).

8. Press F5 (Analyze curve) for various data analysis options. F1 (Peak Integration) is a typically chosen option.

9. Once a data analysis option is selected, establish temperature limits of the calculation by using the left and right arrow keys (CTRL-arrow key for large steps along the curve). Use the TAB key to change from the low to the high temperature limit. Press F8 to accept.

10. Press ESC key to return to main menu options, and select F4 to plot.

11. Press top-left key on plotter key pad to turn plotter on. Insert paper and press second white key on plotter to load paper.

12. On computer, press F1 (Plotter) to plot the data graphic.

Shutdown of Thermal Analyzers

1. If both instruments have cooled to room temperature from the final run, remove sample material from TGA pan and remove sample pan from the DSC. Instruments can be shutdown following final run of the day if temperatures are < 300°C.

2. Turn off N$_2$ gas.

3. Turn off DSC autosampler, TGA fan (if furnace cooled below 300°C), house air, house vacuum, and instrument controllers.

4. Turn off computer and power strip.

5. Cover the TGA and the DSC.

SOIL SURVEY LABORATORY METHODS
(methods no longer used and in new method format)

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH4OAc, pH 7.0 (5A8)
AUTOMATIC EXTRACTOR (CEC-7)
STEAM DISTILLATION (5A8b)

1. APPLICATION

The CEC determined with 1 N NH_4OAc buffered at pH 7.0, is a commonly used method and has become a standard reference to which other methods are compared (Peech et al., 1947). The advantages of using this method are that the extractant is highly buffered so that the extraction is performed at a constant, known pH (7.0) and that the $NH4^+$ on the exchange complex is easily determined.

2. SUMMARY OF METHOD

Displacement after washing is the basis for this procedure. The CEC is determined by saturating the exchange sites with an index cation ($NH4^+$); washing the soil free of excess saturated salt; displacing the index cation ($NH4^+$) adsorbed by the soil; and measuring the amount of the index cation ($NH4^+$). A sample is leached using 1 N NH_4OAc and a mechanical vacuum extractor (Holmgren et al., 1977). The extract is weighed and saved for analyses of the cations. The NH_4^+ saturated soil is rinsed with ethanol to remove the NH_4^+ that was not adsorbed. Steam distillation and titration are used to determine the NH_4^+ adsorbed on the soil exchange complex. The CEC by NH_4OAc, pH 7 is reported in meq/100 g oven-dry soil in procedure 5A8b (Soil Conservation Service, 1984).

3. INTERFERENCES

Incomplete saturation of the soil with NH_4^+ and insufficient removal of NH_4^+ are the greatest interferences to this method. Ethanol removes some adsorbed NH_4^+ from the exchange sites of some soils. Isopropanol rinses has been used for some soils in which ethanol removes adsorbed NH_4^+. Soils that contain large amounts of vermiculite can irreversibly "fix" NH_4^+. Soils that contain large amounts of soluble carbonates can change the extractant pH and/or can contribute to erroneously high cation levels in the extract.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the vacuum extractor and the Kjeltec Auto 1030 Analyzer.

5. EQUIPMENT
5.1 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE
5.2 Syringes, polypropylene, disposable, 60 mL, for sample tube, extractant reservoir, and tared extraction syringe.
5.3 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (1/8 ID x 1/4 OD x 1 in) for connecting syringe barrels.
5.4 Polycons, Richards Mfg. Co.
5.5 Kjeltec Auto 1030 Analyzer, Tecator, Fisher Scientific Inc.
5.6 Digestion tubes, straight neck, 250 mL
5.7 Analytical filter pulp, Schleicher and Schuell, no. 289
5.8 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.
5.9 Electronic balance, ±1-mg sensitivity

6. REAGENTS
6.1 Distilled deionized (DDI) water

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH$_4$OAc, pH 7.0 (5A8)
AUTOMATIC EXTRACTOR (CEC-7)
STEAM DISTILLATION (5A8b)

6.2 Ammonium acetate solution (NH$_4$OAc), 1 *N*, pH 7.0. Add 1026 mL of glacial acetic acid (CH$_3$COOH) to 15 L DDI water. Add 1224 mL of conc. ammonium hydroxide (NH$_4$OH). Mix and cool. Dilute with DDI water to 18 L and adjust to pH 7.0 with CH$_3$COOH or NH$_4$OH.

6.3 Ethanol (CH$_3$CH$_2$OH), 95%, U.S.P.

6.4 Nessler's reagent. Add 4.56 g of potassium iodide (KI) to 30 mL DDI water. Add 5.68 g of mercuric iodide (HgI$_2$). Stir until dissolved. Dissolve 10 g of sodium hydroxide (NaOH) in 200 mL of DDI water. Transfer NaOH solution to a 250-mL volumetric flask and slowly add K-Hg-I solution. Dilute to volume with DDI water and thoroughly mix. Solution should not contain a precipitate. Solution can be used immediately.

6.5 Sodium chloride (NaCl), reagent, crystal.

6.6 Antifoam agent, slipicone release spray, Dow Chemical Corp. Alternatively, mix equal parts of mineral oil and n-octyl alcohol.

6.7 Boric acid, 4% (w:v), with bromcresol green-methyl red indicator (0.075 % bromcresol green and 0.05% methyl red), Ricca Chemical Co.

6.8 Hydrochloric acid (HCl), 0.1 *N*, standardized. Dilute 148 mL of conc. HCl in 16 L of DDI water.

6.9 NaOH, 1 *M*. Add 500 mL of 50% NaOH solution to 8 L of DDI water. Dilute to 9 L with DDI water.

7. PROCEDURE

Extraction of Bases

7.1 Prepare sample tube by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 2.50 g of <2-mm, air-dry soil and place in sample tube. Prepare one quality control check sample per 48 samples.

7.3 Place sample tube on upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1 in) length rubber tubing and insert the plunger in the slot of the stationary disk of the extractor.

7.4 Use a squeeze bottle to fill sample tube to the 20-mL mark with NH$_4$OAc solution ($\approx$ 10 mL). Thoroughly wet the sample. Let stand for at least 20 min.

7.5 Put reservoir tube on top of the sample tube. Rapidly extract the NH$_4$OAc solution to a 0.5- to 1.0-cm height above sample. Turn off extractor. Add $\approx$ 45 mL of NH$_4$OAc solution to the reservoir tube. Set extractor for an overnight (12 to 16 h) extraction.

7.6 Next morning turn off the extractor. Pull the plunger of the syringe down. Do not pull plunger from the barrel of the syringe. Carefully remove the syringe containing the extract. Leave the rubber tubing on the sample tube. Weigh each syringe containing the NH$_4$OAc extract to the nearest 0.01 g.

7.7 Mix the extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. The solution in the polycon is reserved for analyses of extracted cations (procedures 6N2e, 6O2d, 6P2b, and 6Q2b).

Removal of Excess Ammonium Acetate

7.8 Return the extractor to starting position. Attach syringe to the sample tube and rinse the sides of the sample tube with ethanol from a wash bottle. Fill the sample tube to the 20-mL mark with ethanol and let stand for 15 to 20 min.

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH$_4$OAc, pH 7.0 (5A8)
AUTOMATIC EXTRACTOR (CEC-7)
STEAM DISTILLATION (5A8b)

7.9 Place reservoir tube on the sample tube. Rapidly extract the ethanol level to a 0.5- to 1.0-cm height above the sample. Turn off the extractor and add 55 to 60 mL of ethanol to the reservoir. Extract at a 45-min rate.

7.10 After the extractor has stopped, turn off the switch. Pull the plunger of the syringe down. Do not pull the plunger from the syringe barrel. Remove the syringe and discard the ethanol.

7.11 Repeat the ethanol wash.

7.12 After the second wash, collect a few drops of ethanol extract from the sample tube on a spot plate. Test for NH$_4^+$ by using Nessler's reagent. A yellow, red to reddish brown precipitate is a positive test. If the test is positive, repeat the ethanol wash and retest with Nessler's reagent. Repeat until a negative test is obtained.

Steam Distillation: Samples and Reagent Blanks
7.13 Remove the sample tube and transfer the sample with filter pulp to a 250-mL digestion tube. Add 6 to 7 g of NaCl to the digestion tube. Use a gentle flow of compressed air to blow the filter pulp and sample out of the syringe. Wash the tube with DDI water and use a rubber policeman to complete transfer. The amount of distilled water that is added depends on the amount that is required to complete the transfer of tube contents.

7.14 Perform the same transfer and addition of reagents for blanks as for samples.

7.15 Spray silicone antifoam agent (or 2 drops of octyl alcohol) into the digestion tubes for each of the samples and reagent blanks.

7.16 When using new reagents, e.g., boric acid, reagent blanks are distilled in 2 sets of 6, one set per Kjeltec machine. Each set of 6 is averaged and recorded on bench worksheet and manually set on each machine. During the steam distillation, the mean reagent blank titer is automatically subtracted from the sample titer.

7.17 On bench worksheet, record the normality of standardized acid, i.e., ≈ 0.1 N HCl.

7.18 Connect the tube to the distillation unit. Close the safety door. Distillation and titration are performed automatically. Record the titer in mL of titrant.

8. CALCULATIONS

```
CEC (meq/100g) =  Titer x N x 100 x AD/OD
                 _____

                           Weight
```

```
where
Titer   = Titer of sample (mL)
N       = Normality of HCl titrant
Weight  = Sample weight (g)
100     = Conversion factor to 100 g basis
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)
```

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH$_4$OAc, pH 7.0 (5A8)
AUTOMATIC EXTRACTOR (CEC-7)
STEAM DISTILLATION (5A8b)

9. REPORT

Report CEC-7 in units of meq/100 g of oven-dry soil to the nearest 0.1 meq/100 g.

10. PRECISION

Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples. With 113 observations of the quality control check sample, the mean, standard deviation, and C.V. for the CEC are 27.1, 0.57, and 2.1%, respectively.

11. REFERENCES

Holmgren, George G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.

Peech, M., L.T. Alexander, L.A. Dean, and J.F. Reed. 1947. Methods of soil analysis for soil fertility inv.s474A. EMge L.Apt L.g AmCirc. 7, 0.25 pp1208.in J.Fp. arvi1 EMge LGovt. Piint. Off de, Wasleacto mean,

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH$_4$Cl, pH 7.0 (5A9)
AUTOMATIC EXTRACTOR
STEAM DISTILLATION (5A9b)

1. APPLICATION
The CEC determined with a neutral unbuffered salt, e.g., 1 *N* NH$_4$Cl, is an estimate of the "effective" CEC (ECEC) of the soil (Peech et al., 1947). For a soil with a pH of <7.0, the ECEC value should be < CEC measured with a buffered solution at pH 7.0. The NH$_4$Cl CEC is $\approx$ equal to the NH$_4$OAc extractable bases plus the KCl extractable Al for noncalcareous soils.

2. SUMMARY OF METHOD
Displacement after washing is the basis for this procedure. The CEC is determined by saturating the exchange sites with an index cation (NH4$^+$); washing the soil free of excess saturated salt; displacing the index cation (NH4$^+$) adsorbed by the soil; and measuring the amount of the index cation (NH4$^+$). A sample is leached using 1 *N* NH$_4$Cl and a mechanical vacuum extractor (Holmgren et al., 1977). The extract is weighed and saved for analyses of the cations. The NH$_4^+$ saturated soil is rinsed with ethanol to remove the NH$_4^+$ that was not adsorbed. Steam distillation and titration are used to determine the NH$_4^+$ adsorbed on the soil exchange complex. The CEC by NH$_4$Cl is reported in meq/100 g oven-dry soil in procedure 5A9b (Soil Conservation Service, 1984).

3. INTERFERENCES
Incomplete saturation of the soil with NH$_4^+$ and insufficient removal of NH$_4^+$ are the greatest interferences to this method. Ethanol removes some adsorbed NH$_4^+$ from the exchange sites of some soils. Isopropanol rinses has been used for some soils in which ethanol removes adsorbed NH$_4^+$. Soils that contain large amounts of vermiculite can irreversibly "fix" NH$_4^+$. Soils that contain large amounts of soluble carbonates can change the extractant pH and/or can contribute to erroneously high cation levels in the extract.

4. SAFETY
Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses) when preparing reagents, especially concentrated acids and bases. Dispense concentrated acids and bases in a fume hood. Thoroughly wash hands after handling reagents. Use the safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.
Ethanol is flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the vacuum extractor and the Kjeltec Auto 1030 Analyzer.

5. EQUIPMENT
5.1 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE
5.2 Syringes, polypropylene, disposable, 60 mL, for sample tube, extractant reservoir, and tared extraction syringe.
5.3 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (1/8 ID x 1/4 OD x 1 in), for connecting syringe barrels.
5.4 Polycons, Richards Mfg. Co.
5.5 Kjeltec Auto 1030 Analyzer, Tecator, Fisher Scientific Inc.
5.6 Digestion tubes, straight neck, 250 mL
5.7 Analytical filter pulp, Schleicher and Schuell, no. 289
5.8 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.
5.9 Electronic balance, ±1-mg sensitivity

6. REAGENTS
6.1 Distilled deionized (DDI) water

ION EXCHANGE ANALYSES
CATION EXCHANGE CAPACITY (5A)
NH$_4$Cl, pH 7.0 (5A9)
AUTOMATIC EXTRACTOR
STEAM DISTILLATION (5A9b)

6.2 Ammonium chloride solution (NH$_4$Cl), 1 *N*. Dissolve 535 g of NH$_4$Cl reagent in DDI water and dilute to 10 L.

6.3 Ethanol (CH$_3$CH$_2$OH), 95%, U.S.P.

6.4 Nessler's reagent. Add 4.56 g of potassium iodide (KI) to 30 mL DDI water. Add 5.68 g of mercuric iodide (HgI$_2$). Stir until dissolved. Dissolve 10 g of sodium hydroxide (NaOH) in 200 mL DDI water. Transfer NaOH solution to a 250-mL volumetric flask and slowly add K-Hg-I solution. Dilute to volume with DDI water and thoroughly mix. Solution should not contain a precipitate. Solution can be used immediately.

6.5 Sodium chloride (NaCl), reagent, crystal.

6.6 Antifoam agent, slipicone release spray, Dow Chemical Corp. Alternatively, mix equal parts of mineral oil and n-octyl alcohol.

6.7 Boric acid, 4% (w:v), with bromcresol green-methyl red indicator (0.075 % bromcresol green and 0.05% methyl red), Ricca Chemical Co.

6.8 Hydrochloric acid (HCl), 0.1 *N*, standardized. Dilute 148 mL of conc. HCl in 16 L of DDI water.

6.9 NaOH, 1 *M*. Add 500 mL of 50% NaOH solution to 8 L of DDI water. Dilute to 9 L with DDI water.

7. PROCEDURE

Extraction of Bases

7.1 Prepare sample tube by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 2.50 g of <2-mm, air-dry soil and place in sample tube. Prepare one quality control check sample per 48 samples.

7.3 Place sample tube on upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1 in) length rubber tubing and insert the plunger in the slot of the stationary disk of the extractor.

7.4 Use a squeeze bottle to fill sample tube to the 20-mL mark with NH$_4$Cl solution (~ 10 mL). Thoroughly wet the sample. Let stand for at least 20 min.

7.5 Put reservoir tube on top of the sample tube. Rapidly extract the NH$_4$Cl solution to a 0.5- to 1.0-cm height above sample. Turn off extractor. Add ≈ 45 mL of NH$_4$Cl solution to the reservoir tube. Set extractor for an overnight (12 to 16 h) extraction.

7.6 Next morning turn off the extractor. Pull the plunger of the syringe down. Do not pull plunger from the barrel of the syringe. Carefully remove the syringe containing the extract. Leave the rubber tubing on the sample tube. Weigh each syringe containing the NH$_4$Cl extract to the nearest 0.01 g.

7.7 Mix the extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. The solution in the polycon is reserved for analyses of extracted cations (procedures 6N2e, 6O2d, 6P2b, and 6Q2b).

Removal of Excess Ammonium Chloride

7.8 Return the extractor to starting position. Attach syringe to the sample tube and rinse the sides of the sample tube with ethanol from a wash bottle. Fill the sample tube to the 20-mL mark with ethanol and let stand for 15 to 20 min.

7.9 Place reservoir tube on the sample tube. Rapidly extract the ethanol level to a 0.5- to 1.0-cm height above the sample. Turn off the extractor and add 55 to 60 mL of ethanol to the reservoir. Extract at a 45-min rate.

7.10 After the extractor has stopped, turn off the switch. Pull the plunger of the syringe down. Do not pull the plunger from the syringe barrel. Remove the syringe and discard the ethanol.

7.11 Repeat the ethanol wash.

7.12 After the second wash, collect a few drops of ethanol extract from the sample tube on a spot plate. Test for NH_4^+ by using Nessler's reagent. A yellow, red to reddish brown precipitate is a positive test. If the test is positive, repeat the ethanol wash and retest with Nessler's reagent. Repeat until a negative test is obtained.

Steam Distillation: Samples and Reagent Blanks
7.13 Remove the sample tube and transfer the sample with filter pulp to a 250-mL digestion tube. Add 6 to 7 g of NaCl to the sample. Use a gentle flow of compressed air to blow the filter pulp and sample out of the syringe. Wash the tube with DDI water and use a rubber policeman to complete transfer. The amount of distilled water that is added depends on the amount that is required to complete the transfer of tube contents.

7.14 Perform the same transfer and addition of reagents for blanks as for samples.

7.15 Spray silicone antifoam agent (or 2 drops of octyl alcohol) into the digestion tubes for each of the samples and reagent blanks.

7.16 When using new reagents, e.g., boric acid, reagent blanks are distilled in 2 sets of 6, one set per Kjeltec machine. Each set of 6 is averaged and recorded on bench worksheet and manually set on each machine. During the steam distillation, the mean reagent blank titer is automatically subtracted from the sample titer.

7.17 On bench worksheet, record the normality of standardized acid, i.e., $\approx$ 0.1 *N* HCl.

7.18 Connect the tube to the distillation unit. Close the safety door. Distillation and titration are performed automatically. Record the titer in mL of titrant.

8. CALCULATIONS

```
CEC (meq/100g)  = Titer x N x 100 x AD/OD
                  _____

                          Weight
```

```
where
Titer   = Titer of sample (mL)
N       = Normality of HCl titrant
Weight  = Sample weight (g)
100     = Conversion factor to 100 g basis
AD/OD   = Air-dry/oven-dry ratio (procedure 4B5)
```

9. REPORT

Report neutral salts CEC in units of meq/100 g of oven-dry soil to the nearest 0.1 meq/100 g.

10. PRECISION

Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples. With 19 observations of the quality control check sample, the mean, standard deviation, and C.V. for the CEC are 26.0, 0.37, and 1.4%, respectively.

11. REFERENCES

Holmgren, George G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.

Peech, M., L.T. Alexander, L.A. Dean, and J.F. Reed. 1947. Methods of soil analysis for soil fertility investigations. U.S. Dept. Agr. Circ. 757, 25 pp.

CHEMICAL ANALYSES
TOTAL CARBON (6A)
DRY COMBUSTION (6A2)
LECO CR-12 CARBON ANALYZER (6A2d)

1. APPLICATION

Total C in soils is the sum of organic and inorganic C. Most of the organic C is associated with the organic matter fraction, and the inorganic C is generally found with carbonate minerals. The organic C in mineral soils generally ranges from 0 to 12%.

Total C is quantified by two basic methods, i.e., wet or dry combustion. The SSL uses dry combustion. In total C determinations, all forms of C in a soil are converted to CO_2 followed by a quantification of the evolved CO_2. Total C can be used to estimate the organic C content of a soil. The difference between total and inorganic C is an estimate of the organic C. Organic C also can be determined directly (procedure 6A1c). The inorganic C should be equivalent to carbonate values measured by CO_2 evolution with strong acid (Nelson and Sommers, 1982).

Organic C defines mineral and organic soils. In *Soil Taxonomy*, organic C is also used at lower taxonomic levels, e.g., ustollic and fluventic subgroups (Soil Survey Staff, 1975).

2. SUMMARY OF METHOD

An 80-mesh soil sample is oxidized at high temperatures. The released gases are scrubbed, and the CO_2 in the combustion gases is measured by using an infrared detector. Percent total C is reported on an oven-dry soil basis.

3. INTERFERENCES

This procedure simultaneously measures inorganic and organic C.

4. SAFETY

Wear protective clothing and safety glasses. Magnesium perchlorate may form explosive mixtures. Magnesium perchlorate may contain traces of perchloric acid, which remain from manufacturer's operations. This acid is anhydrous because of the strong desiccating capability of the salt. Avoid prolonged contact with oxidizable material or material capable of forming unstable perchlorate esters or salts. Remove magnesium perchlorate by using an excess of water to thoroughly dilute the material.

The use of high temperatures in the oxidation of samples requires that extreme caution be used to prevent burns and fires. Follow standard laboratory procedures when handling compressed gases. Oxygen is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the carbon analyzer.

5. EQUIPMENT
5.1 Carbon analyzer, Leco Model CR-12 781-600 Carbon System, Leco Corp., St. Joseph, MI
5.2 Data transmit card, part no. 772-573, Leco Corp., St. Joseph, MI
5.3 Combustion boats, part no. 529-203, Leco Corp., St. Joseph, MI
5.4 Single-stage regulator, oxygen service, part no. E11-W-N115Box, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105
5.5 Electronic balance, ±1-mg sensitivity

6. REAGENTS
6.1 Anhydrone, anhydrous magnesium perchlorate, granular
6.2 Glass wool
6.3 Compressed oxygen, >99.5% @ 30 psi
6.4 Calcium carbonate, $CaCO_3$, reagent grade.

CHEMICAL ANALYSES
TOTAL CARBON (6A)
DRY COMBUSTION (6A2)
LECO CR-12 CARBON ANALYZER (6A2d)

7. PROCEDURE

7.1 Use a fine-ground 80-mesh, air-dry soil

7.2 Weigh sample in a tared combustion boat. The sample size is dependent upon the C content. The product of sample weight (g) multiplied by C percentage should not be >10%. In most cases, the sample size is 1.00 g, unless the C content is >10%.

7.3 Refer to the Appendix V, Carbon Analyzer, and the manufacturer's manual for operation of carbon analyzer.

7.4 Combust sample in an O_2 atmosphere in which the C is oxidized to CO_2. Moisture and dust are removed by the instrument, and the CO_2 gas is then measured by a solid state infrared detector. The microprocessor formulates the analytical results (C_i) by combining the outputs of the infrared detector and the system ambient sensors with pre-programmed calibration, linearization and weight compensation factors. Analytical results are displayed and printed on the control console.

8. CALCULATIONS

C (%) = C_i x AD/OD

where:
C (%)   = C (%), oven-dry basis
C_i = C (%) instrument
AD/OD   = air-dry/oven-dry ratio (procedure 4B5)

9. REPORT
Report total C percentage on an oven-dry basis to the nearest 0.1%.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is included in every batch of ten samples. For 41 observations of the quality control check sample, the mean, standard deviation, and C.V. for total carbon are 11.38, 0.062, and 5.5%, respectively.

11. REFERENCES
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Soil Survey Staff. 1975. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. USDA-SCS Agric. Handb. 436. U.S. Govt. Print. Office, Washington, DC.

CHEMICAL ANALYSES
NITROGEN (6B)
KJELDAHL DIGESTION II (6B3)
AMMONIA STEAM DISTILLATION, AUTOMATIC TITRATOR (6B3a)

1. APPLICATION

The total N content of the soil may range from <0.02% in subsoils, 2.5% in peats, and 0.06 to 0.5% in surface layers of many cultivated soils (Bremmer and Mulvaney, 1982). The total N data may be used to determine the soil C:N ratio, the soil potential to supply N for plant growth, and the N distribution in the soil profile. The C:N ratio generally ranges between 10 to 12. Variations in the C:N ratio may serve as an indicator of the amount of soil inorganic N. Uncultivated soils usually have higher C:N ratios than do cultivated soils.

Soils with large amounts of illites or vermiculites can "fix" significant amounts of N compared to those soils dominated by smectites or kaolinites (Young and Aldag, 1982; Nommik and Vahtras, 1982). Since the organic C of many soils diminishes with depth while the level of "fixed" N remains constant or increases, the C:N ratio narrows (Young and Aldag, 1982). The potential to "fix" N has important fertility implications as the "fixed" N is slowly available for plant growth.

2. SUMMARY OF METHOD

A soil sample is digested using the Kjeldahl technique. The digest is made alkaline, the steam is distilled to release NH_4^+-N, and the NH_4^+-N is complexed with boric acid. The complexed NH_4^+-N is titrated with HCl, and the total N is calculated against a reagent blank (Soil Conservation Service, 1984).

3. INTERFERENCES

The total N that is measured by the Kjeldahl method does not distinguish among the types of N that are present in the soil. Practically all of the N is measured, but some forms of N are not recovered. Generally, soils have small amounts of N in the nonrecoverable forms, i.e., NO_3^- and NO_2^-. Soils with significant amounts of NO_3^- or NO_2^- are usually saline. The anion analysis of the saturated paste extracts measures NO_3^- and NO_2^- (procedures 6M1c and 6W1a, respectively).

The most significant error in the Kjeldahl method is the heating of the digestion mixture over 400°C. Loss of N occurs when the temperature of the digestion is >400°C (Bremmer and Mulvaney, 1982).

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards and gloves) and eye protection (face shields, goggles, or safety glasses) when handling acids and bases. Use heat resistant gloves when handling hot digestion tubes during digestion and steam distillation. Use the provided safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids. Digestion blocks are used at high temperatures, i.e., 250 and 400°C. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Use the fume hood and fume aspiration devices to control and dispose of the acid fumes when digesting samples.

Boric acid is toxic and must not be ingested. Hengar granules contain Se which is toxic. Concentrated H_2SO_4 reacts violently with water and must be handled with caution. The 50% NaOH solution is very corrosive. Follow prudent laboratory safety precautions when handling these chemicals. Follow the manufacturer's safety precautions when using the Kjeltec Auto 1030 Analyzer.

5. EQUIPMENT

5.1 Electronic balance, ±0.001-g sensitivity
5.2 Digestion tubes, 250 mL, with constricted neck, Ace Glass Co., Inc.
5.3 Digestion blocks, 250 and 400°C
5.4 Dispenser, Zippette, 30 mL or equivalent, for conc. sulfuric acid (H_2SO_4), Brinkmann Instruments Inc.
5.5 Kjeltec Auto 1030 Analyzer, Tecator, Fisher Scientific Inc.

6. REAGENTS

6.1 Distilled water

6.2 Distilled deionized (DDI) water

6.3 Hydrochloric acid (HCl), conc., 12 *N*

6.4 Sodium hydroxide (NaOH), 50% (w:v), reagent

6.5 Hengar granules (selenized)

6.6 Digestion salt mixture. Mix 1000 g of potassium sulfate powder, 55 g of ferrous sulfate powder (anhydrous), and 32 g of copper II sulfate powder (anhydrous) in a tumbling mill for at least 30 min.

6.7 Antifoam, silicone spray bottle, Slipicone release spray, Dow Chemical Corp.

6.8 Boric acid, 4% (w:v), with bromcresol green-methyl red (0.075% bromcresol green and 0.05% methyl red) indicator, Ricca Chemical Co.

6.9 HCl, 0.1 *N*, standardized. Dilute 148 mL of conc. HCl in 16 L of DDI water.

6.10 Sucrose

7. PROCEDURE

Kjeldahl Digestion of Sample

7.1 Weigh 3.000 g of <2-mm, air-dry soil into a 250-mL digestion tube. Refer to Table 1 for sample size.

7.2 Prepare 3 to 5 reagent blanks in every batch of 20 analyses. Reagent blanks contain 0.5 g of sucrose plus all reagents used in sample analysis, i.e., 12 mL of H_2SO_4, 4.5 g of digestion salt mixture, and 1 or 2 Hengar granules. Samples do not receive the 0.5 g of sucrose. Reagent blanks are run as samples and are not automatically subtracted during distillation procedure.

7.3 Use a dispenser to add 5 mL of distilled water to sample tube. Shake the tube to wet the sample.

7.4 Use a dispenser to add 12 mL of conc. H_2SO_4 to sample.

7.5 Allow sample to stand overnight.

7.6 Use a calibrated scoop to add 4.5 g of digestion salt mixture to sample.

7.7 Add 1 or 2 Hengar granules to sample.

7.8 Preheat one digestion heating block to 250°C and the other to 400°C.

7.9 Place the tube in the 250°C block, attach a fume aspirator, and digest for at least 30 min.

7.10 Remove the tube, place in the 400°C block, and digest sample for 1 h.

7.11 Remove the tube, place on a cooling board, and allow sample to cool for at least 15 min.

7.12 Remove the aspirator. Add 50 mL of distilled water.

CHEMICAL ANALYSES
NITROGEN (6B)
KJELDAHL DIGESTION II (6B3)
AMMONIA STEAM DISTILLATION, AUTOMATIC TITRATOR (6B3a)

Table 1. Sample size for total N based on volume of titrant (FeSO$_4$) used in organic C analysis (procedure 6A1c).

```
FeSO₄                      Sample size
(mL)                           (g)
───────                    ────────
>6.00                          3.0
4.00 to 5.00                   2.0
3.00 to 4.00                   1.5
<2.00                          1.0
```

If >10.00 mL of $K_2Cr_2O_7$ (procedure 6A1c) is used and/or sample size is <1.00 g, then divide the volume of FeSO$_4$ by 2 and then use Table 1. To obtain a representative sample, do not use a sample size <0.5 g for total N analysis.

Ammonia Steam Distillation, Automatic Titrator

7.13 Spray silicone antifoam solution (or 2 drops of octyl alcohol) into the digestion tube and connect to the distillation unit.

7.14 Close the safety door.

7.15 Distillation and titration are performed automatically.

7.16 On bench worksheet, record the mL that are titrated for samples and reagent blanks. On bench worksheet, also record the normality of standardized HCl.

8. CALCULATIONS

$$N\ (\%) = \frac{(Titer_{sample} - Titer_{blank})\ \mathrm{x}\ N\ \mathrm{X}\ 1.4\ \mathrm{X}\ AD/OD}{Sample\ Weight}$$

```
where
Titer_sample = Titer of sample (mL)
Titer_blank  = Average titer of reagent blank (mL)
N            = Normality of HCl titrant solution
1.4          = Conversion factor
AD/OD        = Air-dry/oven-dry ratio (procedure 4B5)
```

9. REPORT
Report total N as a dimensionless value to the nearest 0.001 unit on an oven-dry basis.

10. PRECISION
Precision data are not available for this procedure. For 105 observations of the quality control check sample, the mean, standard deviation, and C.V. for total N are 0.143, 0.004, and 2.7%, respectively.

CHEMICAL ANALYSES
NITROGEN (6B)
KJELDAHL DIGESTION II (6B3)
AMMONIA STEAM DISTILLATION, AUTOMATIC TITRATOR (6B3a)

11. REFERENCES

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Nommik, H., and K. Vahtras. 1982. Retention and fixation of ammonium and ammonia in soils. *In* F.J. Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22:123-171.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA-SCS Soil Surv. Invest. Rep. no. 1. U.S. Govt. Print. Office, Washington, DC.

Young, J.L., and R.W. Aldag. 1982. Inorganic forms of nitrogen in soil. *In* F.J. Stevenson (ed.) Nitrogen in agricultural soils. Agronomy 22:43-66.

CHEMICAL ANALYSES
IRON, ALUMINUM, AND POTASSIUM (6C, 6G, and 6Q)
HF DISSOLUTION (6C7, 6G11, and 6Q3)
ATOMIC ABSORPTION (6C7a, 6G11a and 6Q3a)

1. APPLICATION

Historically, elemental analysis was developed for the analysis of rocks and minerals (Washington, 1930). The elemental analysis of soils, sediments, and rocks necessitates their decomposition into soluble forms. Hydrofluoric acid (HF) is efficient in the digestion and dissolution of silicate minerals for elemental decomposition. Elemental concentrations of Fe, Al, and K are determined by atomic absorption using 100 mg of clay suspension contained in a closed vessel with boric acid (H_3BO_3) to neutralize excess acid (Berdanier, Lynn, and Threlkeld, 1978; Soil Conservation Service, 1984).

2. SUMMARY OF METHOD

To 100 mg of clay suspension (procedure 7A2i), 5 mL of HF acid are added. The solution is heated, cooled, and 2 to 3 g of H_3BO_3 are added to neutralize excess acid. The solution is diluted to 100 mL, allowed to stand overnight, and 20 mL are decanted (procedure 7C3). The concentrations of Fe, Al, and K are determined by atomic absorption (AA) in procedures 6C7a, 6G11a, and 6Q3a, respectively. Data are reported in procedure 7C3.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in AA analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

The stable matrix system (HBF_4-H_3BO_3-ionic constituents of silicates) provides a suitable salt-free single matrix that greatly diminishes the chemical ionization, matrix, and instrumental interferences for AA determinations. One of the principal advantages of this technique is that all elements may be determined from a single sample solution (Lim and Jackson, 1982).

4. SAFETY

There are no significant hazards to analyst by this procedure. Wear protective clothing, e.g., coats and aprons. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Follow the manufacturer's safety precautions when using the AA.

5. EQUIPMENT

5.1 Atomic Absorption spectrophotometer (AA), Perkin-Elmer Corp., Norwalk, CT
5.2 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT
5.3 Microcomputer, 7500 Professional Computer, Perkin-Elmer Corp., Norwalk, CT
5.4 Dot matrix printer, P-132, Interdigital Data Systems, Inc.
5.5 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. box 10030, Reno, NV, 89510
5.6 Syringes, 10000 and 1000 μL, 1001 DX an 10110-TEL LL gastight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510
5.7 Centrifuge tubes, polystyrene, 15 mL, conical bottom, graduated, part no. 2087, for sample dilution and sample changer, Becton Dickinson Labware, Becton Dickinson and Co., 2 Bridgewater Lane, Lincoln, Park, NJ 07035
5.8 Containers, polypropylene or teflon

6. REAGENTS

6.1 Distilled Deionized (DDI) water
6.2 Sodium chloride (NaCl) solution, 1143 ppm Na. Dissolve 5.81 g of NaCl in 2 L of DDI water.
6.3 Boric acid, H_2BO_3

6.4 Hydrofluoric acid (HF) solution, 2.47 *N*. Fill a polyethylene volumetric flask 1/3 full with DDI water. In hood, slowly and carefully add 49.36 g of HF. Slowly and carefully add 20 g of H_2BO_3. Hot reaction. May not completely dissolve. Make to 1-L volume with DDI water. Store HF solution in refrigerator. Use HF solution as reagent blank.

6.5 Fe stock solution, 1000 ppm. Commercial. Weigh 1.0000 g of Fe wire, dissolve in HCl, and make to 1-L volume with DDI water. Store in polypropylene container.

6.6 Al stock solution, 1000 ppm. Commercial. Weigh 1.0000 g of Al wire, dissolve in HCl, and make to 1-L volume with DDI water. Store in polypropylene container.

6.7 K stock solution, 50 meq L^{-1}. Dissolve 3.7279 g of KCl in 1 L of DDI. Store in polypropylene container.

6.8 Fe standard, 200 ppm. To 50 ml of Fe stock solution, add 12.34 ml of HF solution and 5 g of H_2BO_3. Make to 250-ml volume with DDI water. Store in polypropylene container.

6.9 Al standard, 200 ppm. To 50 ml of Al stock solution add 12.34 ml of HF solution and 5 g of H_2BO_3. Store in polypropylene container.

6.10 K standard, 1 meq L^{-1}. Add 12.34 ml of HF solution and 5 g of H_2BO_3 to 10 ml of K stock solution. Store in polypropylene container.

6.11 NaCl solution (1143 ppm Na). Dissolve 2.54 g of NaCl in DDI and make to 1-L volume.

7. PROCEDURE

Dilution of Sample Extracts and Standards
7.1 Set the digital settings at 60 for the diluent (NaCl solution) and 99 for the HF sample, calibration reagent blanks, and calibration standards.

7.2 Dilute 1 part HF sample with 7 parts of NaCl solution (1:7 dilution).

7.3 Dilute 1 part calibration reagent blank (HF solution) with 7 parts NaCl solution (1:7 dilution).

7.4 Dilute 1 part of each calibration standard (200 ppm Fe, 200 ppm Al, and 1 meq^{-1} K) with 7 parts of NaCl solution (1:7 dilution).

7.5 Dispense the diluted solutions into 15-mL conical polystyrene centrifuge tubes. Place tubes in carousels of the sample changer.

AA Calibration
7.6 Use calibration reagent blank (HF solution) and calibration standards to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. During AA determinations, perform one calibration, i.e., blank plus standard, for every 8 samples.

AA Operation
7.7 The following parameters are only very general guidelines for instrument conditions for the analyte.

Element	Wavelength	Angle	Fuel/Oxidant
Fe	302.1	Parallel	C_2H_2/Air 20/25
Al	308.2	Parallel	C_2H_2/N$_2$O 30/17
K	766.5	30°	C_2H_2/Air 20/25

7.8 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.9 If a sample exceeds the calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record the dilution. Remember to keep the matrix the same after dilution.

8. CALCULATIONS
Calculations are reported in procedure 7C3.

9. REPORT
Report concentrations of Fe, Al, and K by atomic absorption. Elemental concentrations are converted to percent oxides. Data are reported in procedure 7C3.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Berdanier, C.R., W.C. Lynn, and G.W. Threlkeld. 1978. Illitic mineralogy in Soil Taxonomy: X-ray vs. total potassium. Agron. Absts. 1978 Annual Mtgs.
Lim, C.H., and M.L. Jackson. 1982. Dissolution for total elemental analysis. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:1-12.
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CHEMICAL ANALYSES
IRON, ALUMINUM, AND SILICON (6C, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (6C9a, 6G12a, 6V2a)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

1. APPLICATION

Oxalic acid-ammonium oxalate (acid oxalate) is used as a selective dissolution extractant for organically complexed Fe and Al, noncrystalline hydrous oxides of Fe and Al, allophane, and amorphous aluminosilicates (Wada, 1989). Acid oxalate is a poor extractant of imogolite and layer silicates and does not extract crystalline hydrous oxides of Fe and Al, opal, or crystalline silicate (Wada, 1989). A more reliable and accurate estimation of soil properties and a better understanding of soil exchange complex is provided when acid oxalate extraction is used in conjunction with other selective dissolution procedures, thermal techniques, and chemical tests. In Soil Taxonomy, acid oxalate extractable Fe and Al are criteria for andic soil properties (Soil Survey Staff, 1990).

2. SUMMARY OF METHOD

A soil sample is extracted with a mechanical vacuum extractor (Holmgren et al., 1977) in a 0.2 *M* acid oxalate solution buffered at pH 3.0 under darkness. The acid oxalate extract is weighed. The acid oxalate extract is diluted with 0.1 *N* HCl. The diluted extract is vaporized and atomized by a inductively coupled plasma emission spectrophotometer (ICP). The atoms or ions of the analyte are energized in high temperatures, resulting in the movement of valence electrons to higher orbits from the nucleus. As the electrons fall back to a lower orbit, electromagnetic energy at a specific wavelength for a given atom is emitted in measurable amounts (Soltanpour et al., 1982). Data are automatically recorded by a microcomputer and printer. The percent acid oxalate extractable Fe, Al, and Si are reported in procedures 6C9a, 6G12a, and 6V2a, respectively (Soil Conservation Service, 1984). On a less routine basis, Mn is also measured. To date, however, a National Soil Survey Laboratory (NSSL) method code has not been assigned to the Mn determination by acid oxalate extraction. In procedure 8J, the optical density of the extract is measured with a UV spectrophotometer at 430 nm.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the ICP analyses of these elements. These interferences vary in importance, depending upon the particular analyte chosen.

The acid oxalate buffer extraction is sensitive to light, especially UV light. The exclusion of light reduces the dissolution effect of cystalline oxides and clay minerals. If the sample contains large amounts of amorphous material (>2% Al), an alternate method should be used, i.e., shaking with 0.275 *M* acid oxalate, pH 3.25, 1:100 soil:extractant.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Follow the manufacturer's safety precautions when using the UV spectrophotometer and ICP.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity
5.2 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE
5.3 Syringes, polypropylene, disposable, 60 mL, for sample tube, extractant reservoir, and tared extraction syringe
5.4 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (1/8 ID x 1/4 OD x 1 in) for connecting syringe barrels
5.5 Polycons, Richards Mfg. Co.
5.6 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.
5.7 UV-visible spectrophotometer, DU-7, Beckmann Instruments, Inc.
5.8 Cuvettes, disposable, polystrene, 1-cm light path

CHEMICAL ANALYSES
IRON, ALUMINUM, AND SILICON (6C, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (6C9a, 6G12a, 6V2a)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

5.9 Inductively coupled plasma spectrophotometer (ICP), Perkin-Elmer model 6000

5.10 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT

5.11 Microcomputer, 7500 Professional Computer, Perkin-Elmer Corp., Norwalk, CT

5.12 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

5.13 Single-stage regulator, high-purity, high-flow, argon, product no. E11-X-N145DHF, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105

5.14 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.15 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gastight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.16 Centrifuge tubes, polystyrene, 15 mL, conical, graduated, part no. 2087, for sample dilution and sample changer, Becton Dickinson Labware, Becton Dickinson and Co., 2 Bridgewater Lane, Lincoln Park, NJ 07035

5.17 Containers, polyproylene

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), conc. 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of conc. HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of conc. HCl to 1 L with DDI water.

6.5 HCl, 0.1 *N*. Add 8.33 mL of conc. HCl to DDI water and make to 1-L volume.

6.6 Acid oxalate buffer solution, 0.2 *M*, pH 3.0. *Solution A* (base): Dissolve 284 g of $(NH_4)_2C_2O_4 \cdot H_2O$ in 10 L of DDI water. *Solution B* (acid): Dissolve 252 g of $H_2C_2O_4 \cdot H_2O$ in 10 L of DDI water. Mix 4 parts solution A with 3 parts solution B. Adjust acid oxalate solution pH by adding either acid or base solution. Store in a polypropylene bottle.

6.7 pH buffers, pH 4.00 and 7.00, for electrode calibration.

6.8 Primary Fe standard, 1000 ppm. Dissolve 1.000 g of Fe wire in a minimum volume of 1:1 HCl:DDI. Dilute to 1-L volume in a volumetric flask using 1% HCl. Store in a polypropylene bottle.

6.9 Primary Al standard, 1000 ppm. Dissolve 1.000 g of Al wire in a minimum volume of 1:1 HCl:DDI. Dilute to 1-L volume in a volumetric flask using 1% HCl water. Store in a polypropylene bottle.

6.10 Primary Si standard, 1000 ppm. Fuse 0.2139 g of SiO_2 with 2 g of Na_2CO_3 in a platinum crucible. Dissolve the melt with DDI water and transfer to a 100-mL volumetric flask. Dilute to 1-L volume with DDI water. Store in a polypropylene bottle.

6.11 Primary Mn standard, 1000 ppm. Dissolve 1.000 g of Mn wire in a minimum volume of 1:1 HCl:DDI. Dilute to 1-L volume in a volumetric flask using 1:1 HCl:DDI. Store in a polypropylene bottle.

6.12 High calibration standard. Mix 30 mL of each primary standard (Al, Fe, and Si) with 5 mL of primary Mn standard. Add 50 mL of 0.4 *M* acid oxalate solution, 20 mL of conc. HCl, and make to 1-L volume with DDI water. Resulting solution contains 5 ppm Mn and 30 ppm each of Al, Fe, and Si. Store in a polypropylene bottle.

6.13 Low calibration standard. Mix 10 mL of each primary standard (Al, Fe, and Si) with 2 mL of primary Mn standard. Add 30 mL of 0.4 *M* acid oxalate solution, 20 mL of conc. HCl, and make to 1-L volume with DDI water. Resulting solution contains 2 ppm Mn and 10 ppm each of Al, Fe, and Si. Store in a polypropylene bottle.

6.14 Calibration reagent blank solution. Add 30 mL of 0.4 *M* acid oxalate solution, 20 mL of conc. HCl, and make to 1-L volume with DDI water.

6.15 Argon gas, purity 99.9%

CHEMICAL ANALYSES
IRON, ALUMINUM, AND SILICON (6C, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (6C9a, 6G12a, 6V2a)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

7. PROCEDURE

Extraction of Fe, Al, Si, and Mn

7.1 Prepare sample tube by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh 0.500 g of <2-mm, air-dry soil and place in sample tube. Prepare two reagent blanks (no sample in tube) per set of 48 samples.

7.3 Place the sample tube on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a dispenser to add 15.00 mL of acid oxalate buffer to the sample tube. Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Set extractor for 30-min extraction rate and extract until the acid oxalate buffer solution is at a 0.5 to 1.0-cm height above sample. Turn off extractor.

7.6 Put reservoir tube on top of the sample tube.

7.7 Add 35 mL of acid oxalate buffer to the reservoir tube.

7.8 Cover the extractor with a black plastic bag to exclude light. Adjust the extraction rate for a 12-h extraction.

7.9 After the extraction, shut off the extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the sample tube.

7.10 Weigh each syringe containing acid oxalate extract to the nearest 0.01 g.

7.11 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution. This solution is reserved for determinations of Fe, Mn, Al, and Si. If optical density is to be measured, fill a disposable cuvette with extract solution. Discard excess solution.

Determination of Optical Density of Extract

7.12 Place 4 mL of acid oxalate extract in disposable cuvette.

7.13 Place 4 mL of acid oxalate reagent blank in disposable cuvette.

7.14 On DU-7 spectrophotometer, select a 430-nm wavelength. Select normal slit width and height.

7.15 Use the acid oxalate extract reagent blank to set spectrophotometer.

7.16 Record optical density of acid oxalate extract to nearest 0.000.

CHEMICAL ANALYSES
IRON, ALUMINUM, AND SILICON (6C, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (6C9a, 6G12a, 6V2a)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

Dilution of Sample Extracts and Standards

7.17 For better nebulization, add one drop of DDBSA solution to each tube (sample extracts, calibration standards, and reagent blanks) to reduce surface tensions. Add DDBSA to tube before the addition of diluted solution.

7.18 Set the digital settings of the Hamilton diluter at 63 for the diluent (0.1 *N* HCl) and 70 for the acid oxalate extracts for a 1:10 dilution. Calibration reagent blanks and calibration standards are not diluted.

7.19 Dilute 1 part acid oxalate sample extract with 10 parts of 0.1 *N* HCl (1:10 dilution).

7.20 Dispense the diluted solutions into 15-mL conical polystyrene centrifuge tubes which have been placed in carousels of the sample changer.

ICP Calibration

7.21 Use high calibration standard and calibration reagent blank to calibrate ICP. The ICP requires a standard and a blank, in that order, for calibration. During ICP determinations, perform one calibration, i.e., standard plus blank, for every 6 samples.

7.22 Use the low calibration standard as a check sample.

ICP Set-up and Operation

7.23 The following parameters are only very general guidelines for instrument conditions for the various analytes.

Parameter	Value
ICP power	1250 W
Plasma gas flow	Ar 12 L min^{-1}
Nebulizer gas flow	Ar 0.5 L min^{-1}
Auxiliary gas flow	Ar 0.05 to 1 L min^{-1}

Use a high solids nebulizer instead of the cross flow nebulizer.

7.24 Analyte data for some elements are reported at 2 wavelengths which serve as data checks.

Analyte	Wavelength		Standards Low (ppm)	High (ppm)
	(nm)			
Fe	238.204	239.562	30.00	10.00
Al	394.400	396.150	30.00	10.00
Si	212.412	251.611	30.00	10.00
Mn	257.610		5.00	2.00

7.25 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings. The instrument readings are usually programmed in ppm.

CHEMICAL ANALYSES
IRON, ALUMINUM, AND SILICON (6C, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (6C9a, 6G12a, 6V2a)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

7.26 If sample exceeds calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with 0.1 *N* HCl at the 1:1 ratio.

8. CALCULATIONS

```
Analyte (%) =
```

$$\frac{ICP \times (Syr_{fin} - Syr_{init}) \times Dil. \ Rat. \times AD/OD}{Sample \times 10000 \times Density}$$

```
where
ICP        = ICP analyte concentration (ppm)
Syr_fin    = Weight of syringe + extract (g)
Syr_init   = Tare weight of syringe (g)
Dil. Rat. = Dilution ratio of samples over calibration range
Sample     = Weight of sample (g)
Density    = Density of acid oxalate solution (1.007)
AD/OD      = Air-dry/oven-dry ratio (procedure 4B5)
```

9. REPORT

Report the percent acid oxalate extractable Fe, Al, and Si to the nearest 0.01%. Percent acid oxalate extractable is also reported. To date, however, no method code has been assigned to Mn determination by acid oxalate extraction. Report the optical density of the acid oxalate extract to the nearest 0.001 unit.

10. PRECISION

Precision data are not available for this procedure. The mean, standard deviation, and CV for Fe, Al, Si, and optical density for both the low and high standards are as follows:

High Standard	n	Mean	Std. Dev.	C.V.
Optical Density	18	0.18	0.03	14.2
Fe	17	0.94	0.17	18.2
Al	17	2.6	0.19	7.6
Si	17	1.2	0.09	7.3

Low Standard	n	Mean	Std. Dev.	C.V.
Optical Density	25	0.06	0.00	7.5
Fe	24	0.26	0.03	9.7
Al	25	0.17	0.01	8.4
Si	26	0.02	0.01	53.2

CHEMICAL ANALYSES
IRON, ALUMINUM, AND SILICON (6C, 6G, and 6V)
AMMONIUM OXALATE EXTRACTION (6C6, 6G12, and 6V2)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (6C9a, 6G12a, 6V2a)
OPTICAL DENSITY (8J)
(of ammonium oxalate extract)

11. REFERENCES

Holmgren, G.G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA-SCS Soil Surv. Invest. Rep. no. 1. U.S. Govt. Print. Office, Washington, DC.

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Soltanpour, P.N., J.B. Jones Jr., and S.M. Workman. 1982. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:29-65.

Wada, K. 1989. Allophane and imogolite. *In* J.B. Dixon and S.B. Weed (eds.). Minerals in soil environment. 2nd ed. Soil Sci. Soc. Amer. No. 1. p. 1051-1087.

CHEMICAL ANALYSES
MANGANESE AND ALUMINUM (6D and 6G)
1 *N* KCl EXTRACTABLE, AUTOMATIC EXTRACTOR (6D3 and 6G9)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (6D3 and 6G9b)

1. APPLICATION

The Al extracted by 1 *N* KCl approximates exchangeable Al and is a measure of the "active" acidity present in soils with a 1:1 water pH <5.5. Above pH 5.5, precipitation of Al occurs during analysis. This method does not measure the acidity component of hydronium ions (H_3O^+). If Al is present in measurable amounts, the hydronium is a minor component of the active acidity. Because the 1 *N* KCl extractant is an unbuffered salt and usually affects the soil pH one unit or less, the extraction is determined at or near the soil pH. The KCl extractable Al is related to the immediate lime requirement and existing CEC of the soil. The "potential" acidity is better measured by the $BaCl_2$-TEA method (procedure 6H5a) (Thomas, 1982).

2. SUMMARY OF METHOD

A soil sample is leached with 1 *N* KCl using the mechanical vacuum extractor (Holmgren et al., 1977). The leachate is weighed. The KCl extracted solution is diluted with 0.5 *N* HCl. The diluted extract is vaporized and atomized by a inductively coupled plasma emission spectrophotometer (ICP). The atoms or ions of the analyte are energized in high temperatures, resulting in the movement of valence electrons to higher orbits from the nucleus. As the electrons fall back to a lower orbit, electromagnetic energy at a specific wavelength for a given atom is emitted in measurable amounts (Soltanpour et al., 1982). Data are automatically recorded by a microcomputer and printer. The Mn and Al are reported in meq/100 g ovendry soil in procedures 6D3 and 6G9b (Soil Conservation Service, 1984).

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the ICP analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

The soil:extractant ratio must remain constant. A soil:extractant ratio of 1:10 (w:v) for batch procedures is most commonly used. Using a leaching technique, a 1:20 (w:v) ratio gives comparable results. If the sample size is changed, the amount of extractable Al is changed. No other significant interferences have been identified for this procedure.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Follow the manufacturer's safety precautions when using the ICP.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity
5.2 Analytical filter pulp, Schleicher and Schuell, no. 289
5.3 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE
5.4 Syringes, polypropylene, disposable, 60 mL, for sample tube, extractant reservoir, and tared extraction syringe.
5.5 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (1/8 ID x 1/4 OD x 1 in), for connecting syringe barrels
5.6 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.
5.7 Wash bottle, 20 mL, to dispense KCl.
5.8 Polycons, Richards Mfg. Co.
5.9 Inductively coupled plasma (ICP) atomic emission spectrophotometer, Perkin-Elmer model 6000
5.10 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT
5.11 Microcomputer, 7500 Professional Computer, Perkin-Elmer Corp., Norwalk, CT
5.12 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

CHEMICAL ANALYSES
MANGANESE AND ALUMINUM (6D and 6G)
1 *N* KCl EXTRACTABLE, AUTOMATIC EXTRACTOR (6D3 and 6G9)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (6D3 and 6G9b)

5.13 High-purity, high-flow, single-stage regulator, argon, product no. E11-X-N145DHF, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105

5.14 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.15 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), conc., 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of conc. HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of conc. HCl to 1 L with DDI water.

6.5 HCl, 0.5 *N*. Add 1 part of conc. HCl to 24 parts DDI water (1:25 dilution).

6.6 Potassium chloride solution (KCl), 1.0 *N*. Dissolve 1342 g of KCl reagent in 16 L DD water. Allow solution to equilibrate to room temperature. Dilute to 18 L with DDI water. Use 1.0 *N* KCl for Al and Mn extraction.

6.7 Potassium chloride solution (KCl), 2.0 *N*. Dissolve 298.24 g of KCl reagent in 1.5 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 2 L with DDI water. Use 2.0 *N* KCl for standards.

6.8 Primary Al standard, 2248.5 ppm (250 meq L^{-1}). Dissolve 2.2485 g of Al wire in a minimum volume of 1:1 HCl:DDI. This is a very slow reaction. Dilute to 1 L in a volumetric flask using 1% HCl solution. Store in polypropylene container.

6.9 Primary Mn standard, 1000 ppm (36 meq L^{-1}). Commercial. Dissolve 1.000 g of Mn metal in a minimum volume of 1:1 HCl:DDI. When dissolved, dilute to 1 L in a volumetric flask using 1% HCl solution. Store in a polypropylene container.

6.10 Mn standard, 250 ppm (9 meq L^{-1}). Mix 25 mL of primary Mn standard (1000 ppm) with 10 mL of 1:1 HCl:DDI and dilute to 100-mL volume with DDI water. Store in polypropylene bottle.

6.11 Calibration Al and Mn standard, 10 meq L^{-1} Al and 5 ppm Mn. Mix 10 mL of primary Al standard (250 meq L^{-1}) with 125 mL 2.0 *N* KCl solution. Add 5 mL of Mn standard (250 ppm). Make to 250-mL volume with DDI water. Store in polypropylene container.

6.12 Calibration Al and Mn check standard, 5 meq L^{-1} Al and 2 ppm Mn. Mix 5 mL of primary Al standard (250 meq L^{-1}) with 125 mL 2.0 *N* KCl solution. Add 2 mL of Mn standard (250 ppm). Store in polypropylene container.

6.13 Calibration reagent blank solution, 1.0 *N* KCl. Add 125 mL of 2.0 *N* KCl to a volumetric flask and make to 250-mL volume with DDI water. Store in polypropylene container.

6.14 Dodecylbenzenesulfonic acid (DDBSA), tech 97%. Working stock is 0.1 *M*. Dilute 25 mL of 0.1 *M* DDBSA to 1-L volume with DDI water.

6.15 Argon gas, purity 99.9%

7. PROCEDURE

Extraction of Al and Mn

7.1 Prepare sample tube by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh exactly 2.50 g of <2-mm, air-dry soil and place in sample tube. Prepare one quality control check sample per 48 samples.

7.3 Place the sample tube on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

7.4 Use a squeeze bottle and fill sample tube to the 20-mL mark with 1.0 *N* KCl solution ($\approx$ 10 mL). Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Put reservoir tube on top of the sample tube. Set extractor for fast extraction rate and extract until the KCl solution is at a 0.5- to 1.0-cm height above sample. Turn off extractor.

7.6 Add 45 mL KCl solution to reservoir tube. Set extractor for 45-min extraction.

7.7 After the extraction, shut off extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the sample tube.

7.8 Weigh each syringe containing KCl extract to the nearest 0.01 g.

7.9 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. This solution is reserved for extractable Al and Mn analyses.

Dilution of Extracts and Standards
7.10 For better neubilization, add one drop of DDBSA solution to KCl sample extracts, calibration reagent blanks and calibration standards to reduce surface tensions. Add DDBSA to tube before adding diluted solution.

7.11 Set the digital settings at 40 for the diluent (0.5 *N* HCl) and 99 for the KCl sample extracts, calibration reagent blanks, calibration standards, and calibration check standards for a 1:5 dilution as follows:

7.12 Dilute 1 part KCl sample extract with 4 parts of 0.5 *N* HCl (1:5 dilution).

7.13 Dilute 1 part calibration reagent blank with 4 parts of 0.5 *N* HCl (1:5 dilution).

7.14 Dilute 1 part calibration standard (10 meq L^{-1} Al and 5 ppm Mn) with 4 parts of 0.5 *N* HCl (1:5 dilution).

7.15 Dilute 1 part calibration check standard (5 meq L^{-1} Al and 2 ppm Mn) with 4 parts of 0.5 *N* HCl (1:5 dilution).

7.16 Dispense the diluted solutions into 15-mL conical polystyrene centrifuge tubes which have been placed in carousels of the sample changer.

ICP Calibration
7.17 Use calibration standard (10.00 meq L^{-1} Al and 5.00 ppm Mn,) and calibration reagent blank (1.0 *N* KCl) to calibrate ICP. The ICP requires a standard and a blank, in that order, for calibration. During ICP determinations, perform one calibration, i.e., standard plus blank, for every 6 samples.

CHEMICAL ANALYSES
MANGANESE AND ALUMINUM (6D and 6G)
1 *N* KCl EXTRACTABLE, AUTOMATIC EXTRACTOR (6D3 and 6G9)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (6D3 and 6G9b)

7.18 Use the calibration check standard (5.00 meq L^{-1} Al and 2.00 ppm Mn) as a check sample.

ICP Set-up and Operation

7.19 The following parameters are only very general guidelines for instrument conditions for the analytes.

```
Parameter                         Al        Mn
Plasma flow (1 Ar min⁻¹)        12.0      12.0
Nebulizer flow (1 Ar min⁻¹)      0.5       0.5
Auxiliary flow (1 Ar min⁻¹)      0.5       0.5
Viewing height (nm)             15.0      15.0

                   Wavelength 1
Wavelength (nm)       394.400           259.373
Scan speed (s)          2.0               1.0
Background
  Correction (nm)  -0.069,+0.055         0.0


                   Wavelength 2
Wavelength (nm)    396.152            294.920
Scan speed (s)       2.0                2.0
Background
  Correction (nm)  -0.069,+0.055   -0.046, +0.049
```

High solids nebulizer has a 20 s read delay.

7.20 Load sample tubes in the carousel so that the calibration standard, reagent blank, calibration check standard, and 6 unknown samples are determined in order. Determine a set of 24 unknown samples with each carousel.

7.21 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.22 If a sample exceeds the calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with the 0.5 *N* HCl solution (1:5 dilution).

7.23 Analyze one quality control check sample for every 48 samples.

8. CALCULATIONS

8.1 The instrument readings are the analyte concentration (meq L^{-1} Al and ppm Mn) in undiluted extract. Use these values to calculate the analyte concentration on an oven-dry soil basis (meq/100 g).

CHEMICAL ANALYSES
MANGANESE AND ALUMINUM (6D and 6G)
1 *N* KCl EXTRACTABLE, AUTOMATIC EXTRACTOR (6D3 and 6G9)
INDUCTIVELY COUPLED PLASMA SPECTROMETRY (6D3 and 6G9b)

```
Analyte (meq/100 g) =

ICP x (Wt_syr+ext - Wt_syr) x Dil. x 100 x AD/OD
————————————————————————————————————————————
          Smp.Wt. x 1.0412 x 1000

where
ICP      = ICP analyte reading
Wt_syr+ext = Weight of extraction syringe & extract (g)
Wt_syr   = Weight of tared extraction syringe (g)
Dil.     = Dilution ratio of samples over calibration range
Smp. Wt.= Sample weight (g)
1.0412   = Density of 1 N KCl @ 20°C
1000     = g L⁻¹
100      = Conversion factor (100-g basis)
AD/OD    = Air-dry/oven-dry ratio (procedure 4B5)
```

9. REPORT

Report KCl extractable Al and Mn in units of meq/100 g of oven-dry soil to the nearest 0.01 meq/100 g.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

Holmgren, George G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.

Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA-SCS Soil Surv. Invest. Rep. no. 1. U.S. Govt. Print. Office, Washington, DC.

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Thomas, G.W. 1982. Exchangeable cations. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:159-165.

CHEMICAL ANALYSES
ALUMINUM (6G)
KCl, AUTOMATIC EXTRACTOR (6G9)
ATOMIC ABSORPTION (6G9a)

1. APPLICATION

The Al extracted by 1 N KCl approximates exchangeable Al and is a measure of the "active" acidity present in soils with a 1:1 water pH <5.5. Above pH 5.5, precipitation of Al occurs during analysis. This method does not measure the acidity component of hydronium ions (H_3O^+). If Al is present in measurable amounts, the hydronium is a minor component of the active acidity. Because the 1 N KCl extractant is an unbuffered salt and usually affects the soil pH one unit or less, the extraction is determined at or near the soil pH. The KCl extractable Al is related to the immediate lime requirement and existing CEC of the soil. The "potential" acidity is better measured by the $BaCl_2$-TEA method (procedure 6H5a) (Thomas, 1982).

2. SUMMARY OF METHOD

A soil sample is leached with 1 N KCl using the mechanical vacuum extractor (Holmgren et al., 1977). The leachate is weighed. The KCl extract is diluted with distilled deionized (DDI) water. The diluted extract is aspirated into an atomic absorption spectrophotometer (AA). The analyte is measured by absorption of the light from a hollow cathode lamp. An automatic sample changer is used to aspirate a series of samples. The AA converts absorption to analyte concentration. The data are automatically recorded by a microcomputer and printer. The Al is reported in meq/100 g ovendry soil in procedure 6G9a.

3. INTERFERENCES

There are four types of interferences (matrix, spectral, chemical, and ionization) in the AA analyses of these cations. These interferences vary in importance, depending upon the particular analyte selected.

The soil:extractant ratio must remain constant. A soil:extractant ratio of 1:10 (w:v) for batch procedures is most commonly used. Using a leaching technique, a 1:20 (w:v) ratio gives comparable results. If the sample is changed, the amount of extractable Al is changed. No other significant interferences have been identified for this procedure.

4. SAFETY

Wear protective clothing and eye protection. When preparing reagents, exercise special care. Restrict the use of concentrated HCl to a fume hood. Many metal salts are extremely toxic and may be fatal if ingested. Follow standard laboratory practices when handling compressed gases. Gas cylinders should be chained or bolted in an upright position. Acetylene gas is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the AA.

5. EQUIPMENT

5.1 Electronic balance, ±1-mg sensitivity
5.2 Mechanical vacuum extractor, 24 place, Centurion International, Inc., Lincoln, NE
5.3 Syringes, polypropylene, disposable, 60 mL, for sample tube, extractant reservoir, and tared extraction syringe.
5.4 Rubber tubing, 3.2 ID x 6.4 OD x 25.4 mm (1/8 ID x 1/4 OD x 1 in) for connecting syringe barrels
5.5 Wash bottle, 20 mL, to dispense KCl.
5.6 Plunger, modified. Remove rubber and cut plastic protrusion from plunger end.
5.7 Polycons, Richards Mfg. Co.
5.8 Atomic absorption spectrophotometer (AA), Perkin-Elmer model 5000
5.9 Autosampler, AS-50, Perkin-Elmer Corp., Norwalk, CT
5.10 Microcomputer, 7500 Professional Computer, Perkin-Elmer Corp., Norwalk, CT
5.11 Dot matrix printer, P-132, Interdigital Data Systems, Inc.

5.12 Single-stage regulator, acetylene service, part number E11-0-N511A, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105

5.13 Heated regulator, single-stage, nitrous oxide, stock number 808 8039, Airco Welding Products, P.O. Box 486, Union, NJ 07083

5.14 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.15 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510

5.16 Centrifuge tubes, polystyrene, 15 mL, conical bottom, graduated, part no. 2087, for sample dilution and sample changer, Becton Dickinson Labware, Becton Dickinson and Co., 2 Bridgewater Lane, Lincoln Park, NJ 07035

5.17 Containers, polyproylene or teflon

6. REAGENTS

6.1 Distilled deionized (DDI) water

6.2 Hydrochloric acid (HCl), conc., 12 *N*

6.3 HCl, 1:1 HCl:DDI, 6 *N*. Carefully mix 1 part of conc. HCl to 1 part DDI water.

6.4 HCl, 1% wt. Carefully dilute 25 mL of conc. HCl to 1 L with DDI water.

6.5 Potassium chloride solution (KCl), 1.0 *N*. Dissolve 1342 g of KCl reagent in 16 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 18 L with DDI water. Use 1.0 *N* KCl solution for Al extraction.

6.6 Potassium chloride solution (KCl), 2.0 *N*. Dissolve 298.24 g of KCl reagent in 1.5 L DDI water. Allow solution to equilibrate to room temperature. Dilute to 2 L with DDI water. Use 2.0 *N* KCl solution for standards.

6.7 Primary Al standard, 2248.5 ppm (250 meq L^{-1}). Dissolve 2.2485 g of Al wire in a minimum volume of 1:1 HCl:DDI. This is a very slow reaction. Dilute to 1 L in a volumetric flask using 1% HCl solution. Store in polypropylene bottle.

6.8 Calibration Al standard, 10 meq L^{-1}. Mix 10 mL of primary Al standard (250 meq L^{-1}) with 125 mL of 2.0 *N* KCl solution. Make to 250-mL volume with DDI water. Store in polypropylene bottle.

6.9 Calibration Al check standard, 5 meq L^{-1}. Mix 5 mL of primary Al standard (250 meq L^{-1}) with 125 mL of 2.0 *N* KCl solution. Make to 250-mL volume with DDI water. Store in polypropylene bottle.

6.10 Calibration reagent blank solution, 1.0 *N* KCl. Add 125 mL of 2.0 *N* KCl to a volumetric flask and make to 50-mL volume with DDI water. Store in polypropylene bottle.

6.11 Nitrous oxide gas, compressed

6.12 Acetylene gas, compressed, purity 99.6%

6.13 Compressed air with water and oil traps

7. PROCEDURE

Extraction of Al

7.1 Prepare sample tube by tightly compressing a 1-g ball of filter pulp into the bottom of a syringe barrel with a modified plunger.

7.2 Weigh exactly 2.50 g of <2-mm, air-dry soil and place in sample tube. Prepare one quality control check sample per 48 samples.

7.3 Place the sample tube on the upper disk of the extractor and connect a tared extraction syringe. Use 25.4-mm (1-in) length rubber tubing to insert the handle of the plunger in the slot of the stationary extractor disk.

CHEMICAL ANALYSES
ALUMINUM (6G)
KCl, AUTOMATIC EXTRACTOR (6G9)
ATOMIC ABSORPTION (6G9a)

7.4 Use a squeeze bottle and fill sample tube to the 20-mL mark with 1.0 *N* KCl solution (~ 10 mL). Make sure that the sample is thoroughly wetted. During the addition, wash sides of the tube and wet the sample. Shaking, swirling, or stirring may be required to wet organic samples. Allow sample to stand for at least 30 min.

7.5 Put reservoir tube on top of the sample tube. Set extractor for fast extraction rate and extract until the KCl solution is at a 0.5- to 1.0-cm height above sample. Turn off extractor.

7.6 Add 45 mL KCl solution to reservoir tube. Set extractor for 45-min extraction.

7.7 After the extraction, shut off extractor and pull plunger of syringe down. Do not remove the plunger from syringe barrel. Carefully remove the syringe with extract leaving the rubber tubing on the sample tube.

7.8 Weigh each syringe containing KCl extract to the nearest 0.01 g.

7.9 Mix extract in each syringe by manually shaking. Fill a polycon with extract solution and discard the excess. This solution is reserved for extractable Al analysis.

Dilution of Sample Extracts and Standards

7.10 No ionization suppressant is required as the K in the extractant is present in sufficient quantity. Set the digital settings at 40 for the diluent (DDI water) and 99 for the KCl sample extracts, calibration reagent blanks, calibration standards, and calibration check standards for a 1:5 dilution as follows:

7.11 Dilute 1 part KCl sample extract with 4 parts of DDI water (1:5 dilution).

7.12 Dilute 1 part calibration reagent blank with 4 parts of DDI water (1:5 dilution).

7.13 Dilute 1 part calibration standard (10 meq L^{-1} Al) with 4 parts of DDI water (1:5 dilution).
7.14 Dilute 1 part calibration check standard (5 meq L^{-1} Al) with 4 parts of DDI water (1:5 dilution).

7.15 Dispense the diluted solutions into 15-mL conical polystyrene centrifuge tubes which are placed in carousels of the sample changer.

AA Calibration

7.16 Use calibration reagent blank (1.0 *N* KCl) and calibration standard (10 meq L^{-1} Al) to calibrate the AA. The AA program requires a blank and a standard, in that order, to establish a single point calibration curve for element determination. During AA determinations, perform one calibration, i.e., blank plus standard, for every 12 samples.

7.17 Use the calibration check standard (5 meq L^{-1} Al) as a check sample.

AA Set-up and Operation

7.18 The following parameters are only very general guidelines for instrument conditions for the analyte.

Element Head = Al
Wavelength (nm) = 309.3
Burner head & angle = 5 cm Parallel
Fuel/Oxidant (C_2H_2/N_2O) = 30/17
Typical read delay is 6 s, and integration by peak area is 8 s.

CHEMICAL ANALYSES
ALUMINUM (6G)
KCl, AUTOMATIC EXTRACTOR (6G9)
ATOMIC ABSORPTION (6G9a)

7.19 Use the microcomputer and printer to set instrument parameters and to collect and record instrument readings.

7.20 If a sample exceeds the calibration standard, dilute the sample (dilution ratio in calculation) with appropriate matrix and record dilution. Remember to keep the matrix the same after dilution by diluting with DDI water (1:5 dilution).

7.21 Analyze one quality control check sample for every 48 samples.

8. CALCULATIONS

8.1 The instrument readings are the analyte concentration (meq L^{-1} Al) in undiluted extract. Use these values to calculate the analyte concentration on an oven-dry soil basis (meq/100 g).

```
Al (meq/100 g) =

AA   x (Wt      - Wt  ) x D.R. x 100 x AD/OD
  Al      syr+ext    syr
_____

          Smp. Wt. x 1.0412 x 1000
```

```
where
AA         = AA Al reading (meq L⁻¹)
  Al
Wt       = Weight of extraction syringe and extract (g)
  syr+ext
Wt         = Weight of tared extraction syringe (g)
  syr
D.R        = Dilution ratio for samples over calibration range
Smp. Wt.   = Sample weight (g)
1.0412     = Density of 1 N KCl @ 20°C
1000       = g L⁻¹
100        = Conversion factor (100-g basis)
AD/OD      = Air-dry/oven-dry ratio (procedure 4B5)
```

9. REPORT
    Report KCl extractable Al in units of meq/100 g of oven-dry soil to the nearest 0.1 meq/100 g.

10. PRECISION
    Precision data are not available for this procedure. A quality control check sample is run with every batch of 48 samples. For 21 observations of the quality control sample, the mean, standard deviation, and C.V. for extractable Al are 3.1, 0.18, and 5.7 %, respectively.

11. REFERENCES
Holmgren, George G.S., R.L. Juve, and R.C. Geschwender. 1977. A mechanically controlled variable rate leaching device. Soil Sci. Amer. J. 41:1207-1208.
Thomas, G.W. 1982. Exchangeable cations. *In* A. Klute (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:159-165.

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH
(6K1c, 6L1c, 6M1c, 6U1a, and 6W1a)

1. APPLICATION

The soluble anions that are commonly determined in saline and alkali soils are carbonate, bicarbonate, sulfate, chloride, nitrate, nitrite, fluoride, phosphate, silicate, and borate (Khym, 1974; U.S. Salinity Laboratory Staff, 1954). Carbonate and bicarbonate are determined by titration in procedures 6I1b and 6J1b, respectively (Soil Conservation Service, 1984). Phosphate, silicate, and borate usually are not determined because they are found only occasionally in measurable amounts in soils. Chloride, sulfate, nitrate, fluoride, and nitrite are measured in solution in procedures 6K1c, 6L1c, 6M1c, 6U1a, and 6W1a, respectively (Soil Conservation Service, 1984). In saline and alkali soils, carbonate, bicarbonate, sulfate, and chloride are the anions that are found in the greatest abundance. In general, soluble sulfate is usually more abundant than soluble chloride.

2. SUMMARY OF METHOD

The saturation extract is diluted according to its electrical conductivity (EC_s). The diluted sample is injected into the ion chromatograph, and the anions are separated. A conductivity detector is used to determine the anion. A chart recording is made of the chromatograph. Standard anions are used to calibrate the system. A calibration curve is determined, and the anion concentrations are calculated. The saturated extract anions, Cl^-, SO_4^{2-}, NO_3^-, F^-, and NO_2^- are reported in meq L^{-1} in procedures 6k1c, 6L1c, 6M1c, 6U1a, and 6W1a, respectively (Soil Conservation Service, 1984).

3. INTERFERENCES

Some saturation extracts contain suspended solids. Filtering after dilution removes the particles. Saturation extracts of acid soils that contain Fe and/or Al may precipitate and clog the separator column. Saturation extracts of very high pH may contain organic material which may clog or poison the column. Low molecular weight organic anions will co-elute with inorganic anions from the column.

4. SAFETY

Wear protective clothing and safety glasses. When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Follow the manufacturer's safety precautions when using the chromatograph.

5. EQUIPMENT

5.1 Ion chromatograph, Series 2110i, with conductivity detector, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.2 HPIC AS3 analytical column, P/N 030985, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.3 HPIC AG3 analytical guard column, P/N 030986, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.4 Anion micro membrane suppressor, P/N 037072, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.5 Automated sampler, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.6 Poly-vials, 5 mL, P/N 038008, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.7 Poly-vials, filtercaps, 5 mL, P/N 038009, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086

5.8 Chart recorder, Honeywell Corp., chart speed 0.5 cm min^{-1}, span 1000 mV F.S.

5.9 Digital diluter/dispenser, product number 100004, with hand probe and actuator, product number 230700, Hamilton Co., P.O. Box 10030, Reno, NV 89510

5.10 Syringes, gas tight, Hamilton 1001 DX and 1010-TEF LL, Hamilton Co., P.O. Box 10030, Reno, NV 89510

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH
(6K1c, 6L1c, 6M1c, 6U1a, and 6W1a)

5.11 Syringes, disposable, polypropylene, 12 mL

5.12 Disposable 0.2-μm pore size, 25-mm filter assembly, Gelman Sciences, Inc., 674 South Wagner Road, Ann Arbor, MI 48106. Use for saturation extracts and standards.

5.13 Disposable 0.2-μm pore size, Ultipor N$_{66}$ DFA3001NAEY, Pall Trinity Micro Corp., Cortland, NY 13045. Use for filtering distilled deionized (DDI) water.

6. REAGENTS

6.1 Distilled deionized (DDI) filtered water

6.2 Sulfuric acid (H_2SO_4), conc., reagent

6.3 Toluene

6.4 Isopropanol to de-gas column

6.5 Regenerant solution for membrane suppressor columns, 0.025 N H_2SO_4. Carefully mix 22.92 g of conc. H_2SO_4 with filtered DDI water and dilute to 18-L volume. Store in a clean glass carboy with a solid stopper. Cover the carboy top with aluminum foil to protect the contents from dust.

6.6 Stock NaHCO$_3$ solution, 0.480 M. Mix 40.34 g of dried NaHCO$_3$ with filtered DDI water and dilute to 1-L volume.

6.7 Stock Na$_2$CO$_3$ solution, 0.3838 M. Mix 40.68 g of dried Na$_2$CO$_3$ with filtered DDI water and dilute to 1-L volume.

6.8 Working eluent solution. Mix 112.5 mL of 0.480 M NaHCO$_3$ and 112.5 mL of 0.3838 M Na$_2$CO$_3$ with filtered DDI water and dilute to 18-L volume. Add 3 drops of toluene to retard microbial growth.

6.9 Primary SO$_4^{2-}$ standard, 0.5 M (1.0 N). Mix 17.7560 g of Na$_2$SO$_4$ with filtered DDI water and dilute to 250-mL volume.

6.10 Primary Cl$^-$ standard, 1.0 M (1.0 N). Add 18.6392 g of KCl with filtered DDI water and dilute to 250-mL volume.

6.11 Primary F$^-$ standard, 0.125 M (0.125 N). Add
1.3122 g of NaF with filtered DDI water and dilute to 250-mL volume.

6.12 Primary NO$_3^-$ standard, 1.0 M (1.0 N). Add 25.2770 g of KNO$_3$ with filtered DDI water and dilute to 250-mL volume.

6.13 Primary mixed standard. Prepare 1 primary mixed standard by taking aliquots of each of the proceeding primary standards and diluting the combined aliquots to a 1-L volume with working eluent as follows:

Primary Standards	Aliquot	Final Volume w/Eluent	Concentration
	mL	mL	meq L^{-1}
Na$_2$SO$_4$	50	1000	50
KCl	10	1000	10
NaF	100	1000	12.5
KNO$_3$	30	1000	30

Add eight drops of toluene to primary mixed standard to retard microbial growth and store in a glass container.

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH
(6K1c, 6L1c, 6M1c, 6U1a, and 6W1a)

6.14 Mixed calibration standards. Prepare 4 mixed calibration standards (0.5, 1.0, 3.0, and 7.0 readings) by taking aliquots of primary mixed standard and diluting each aliquot to 100-mL volume with working eluent as follows:

Primary Mixed Standards	Final Volume w/Eluent	Concentration			
		SO_4^{2-}	Cl^-	F^-	NO_3^-
mL	mL	meq L^{-1}			
0.5	100	0.25	0.05	0.0625	0.15
1.0	100	0.50	0.10	0.125	0.30
3.0	100	1.5	0.30	0.375	0.90
7.0	100	3.5	0.70	0.875	2.1

6.15 $NaNO_2$, Baker reagent grade, 99.5% purity

6.16 Primary NO_2^- standard, 1 N (1000 meq L^{-1}). Mix 69.3568 g of reagent grade $NaNO_2$ with filtered DDI water and dilute to 1-L volume. Take 5 mL aliquot of primary NO_2^- standard and dilute with 500 mL of filtered DDI water (10 meq L^{-1}). Add eight drops of toluene to primary NO_2^- standard to retard microbial growth and store in a glass container.

6.17 NO_2^- calibration standards. Prepare 4 NO_2^- calibration standards (0.5, 1.0, 3.0, and 7.0 readings) by taking aliquots of primary NO_2^- standard (10 meq L^{-1}) and diluting each aliquot to 100-mL volume with working eluent as follows:

Primary Standard (meq L^{-1})	Final Volume w/Eluent	NO_2 Concentration
mL	mL	meq L^{-1}
0.5	100	0.5
1.0	100	1.0
3.0	100	3.0
7.0	100	7.0

7. PROCEDURE

Dilution of extracts

7.1 To estimate the total soluble anion concentration (meq L^{-1}), multiply the EC_s (procedure 8A3a) by 10. Subtract the CO_3^{2-} and HCO_3^- concentrations (procedures 6I1b and 6J1b) from the total anion concentration. The remainder is the $\approx$ concentration (meq L^{-1}) of anions to be separated by ion chromatography.

Anion concentration (meq L^{-1}) = EC_s x 10 - (HCO_3^- + CO_3^{2-})

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH
(6K1c, 6L1c, 6M1c, 6U1a, and 6W1a)

7.2 Dilute the saturation extract with the working eluent. Some typical dilutions are as follows:

EC_s (mmhos cm^{-1})	Dilution Factor
0.0 to 0.4	1: 3
0.4 to 0.7	1. 5
0.8 to 1.2	1: 9
1.2 to 1.8	1: 17
1.8 to 2.9	1: 39
3.0 to 5.5	1: 80
5.5 to 7.5	1: 150
7.7 to 9.7	1: 200
9.7 to 13.5	1: 290
13.5 to 15.5	1: 350
15.5 to 25.0	1: 660
25.0 to 40.0	1: 1 100
40.0 to 55.0	1: 2 100
55.0 to 75.0	1: 4 800
+75.0	1:15 500

7.3 Place the diluted samples in 12-mL syringes. Cap syringes to prevent evaporation or contamination.

7.4 Place the mixed calibration standards in 12-mL syringes.

Set-up and Operation of Ion Chromatograph (IC)

7.5 Because any number of factors may cause a change in IC operating conditions, only a general set-up of the Dionex 2110i ion chromatograph is presented. Individual analysts may modify some or all of the operating conditions to achieve satisfactory results. The uS cm^{-1} units are equivalent to mmhos cm^{-1}. Typical operation parameters are as follows:

Parameter	Range
Conductivity cell range	3 uS cm^{-1} full scale to 100 uS cm^{-1}
Auto offset	"On"
Analytical pump flow rate	2.0 to 2.5 mL min^{-1}
Low pressure limit	200 psi
High pressure limit	1000 psi
Regenerant flow rate	3 to 4 mL min^{-1}
Injector loop	0.50 mL
Air pressure	3 to 6 psi
Chart recorder speed	0.5 cm min^{-1}
Chart recorder span	1000 mV full scale

CHEMICAL ANALYSES
CHLORIDE, SULFATE, NITRATE, FLUORIDE, AND NITRITE
(6K, 6L, 6M, 6U, and 6W)
SATURATION EXTRACT
(6K1, 6L1, 6M1, 6U1, and 6W1)
CHROMATOGRAPH
(6K1c, 6L1c, 6M1c, 6U1a, and 6W1a)

7.6 Initial IC operation should be long enough to establish a stable baseline.

7.7 Inject the most concentrated standard. The IC adjustment may be necessary to obtain adequate stability, resolution, and reproducibility.

7.8 Inject standards in random order to detect if memory effects are evident.

7.9 Analyze blanks at frequent intervals.

7.10 The injection loop requires complete flushing, i.e., 3 to 5x the loop volume.

7.11 Inject samples, standards, and blanks in the IC after achievement of stability. The analyst may change the detector range to suit the sample.

7.12 The analyst records the detector range and peak height for each detected anion. The anion identity may be determined by comparison to standards. Peak height is determined from the baseline to the peak.

8. CALCULATIONS

Calibration Calculations
8.1 Use the peak height of each anion standard to either construct a calibrated curve to plot anion concentration or use a least squares analysis to calculate anion concentration. The analytes are reported in meq L^{-1}.

8.2 *Calibration Curve*: Plot the peak height against the meq L^{-1} of each anion standard on graph paper. Construct the calibration curve by finding the "best" line that fits the plotted standards.

8.3 *Linear Squares Analysis*: Use a least squares criterion,
i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. An example for the anion Cl^- is as follows:

```
Cl⁻ (meq L⁻¹)  =   Y =    0.1      1.5       4.0

Peak height    =  X =    8.43   170.0     441.5

Number of standards =   n =   3

ΣYᵢ  = 5.6                ΣXᵢ  = 619.93

ΣYᵢ/n = Y = 1.866     ΣXᵢ/n = X = 206.6433

ΣXᵢYᵢ   = 2021.843     ΣXᵢ²   = 223893.31

ΣXᵢΣYᵢ = 3471.608
```

CHEMICAL ANALYSES
TOTAL SULFUR (6R)
SO$_2$ EVOLUTION, INFRARED (6R3)
LECO SC-132 SULFUR ANALYZER (6R3b)

1. APPLICATION

Organic and inorganic S forms are found in soils, with the organic S fraction accounting for >95% of the total S in most soils from humid and semi-humid (Tabatabai, 1982). Mineralization of organic S and its conversion to sulfate by chemical and biological activity may serve as a source of plant available S. Total S typically ranges from 0.01 to 0.05% in most mineral soils. In organic soils, total S may be >0.05%.

In well-drained, well-aerated soils, most of the inorganic S normally occurs as sulfate. In marine tidal flats, other anaerobic marine sediments, and mine spoils, there are usually large amounts of reduced S compounds which oxidize to sulfuric acid upon exposure to the air. In arid regions, significant amounts of inorganic S are found as sulfates such gypsum and barite.

The typical use of total S is as an index of the total reserves of this element, which may be converted to plant available S. The SSL uses the combustion technique (LECO sulfur analyzer) for analysis of total S (procedure 6R3b). Extractable sulfate S (SO$_4^{2}$-S) is an index of readily plant-available S. Reagents that have been used for measuring SO$_4^{2}$-S include water, hot water, ammonium acetate, sodium carbonate and other carbonates, ammonium chloride and other chlorides, potassium phosphate and other phosphates, and ammonium fluoride (Bray-1). Extractable SO$_4^{2}$-S does not include the labile fraction of soil organic S that is mineralized during the growing season (Tabatabai, 1982). Extraction reagents for organic S include hydrogen peroxide, sodium bicarbonate, sodium hydroxide, sodium oxalate, sodium peroxide, and sodium pyrophosphate. There other methods available for determination of soil S, especially for total S and SO$_4^{2}$-S. The investigator may refer to the review by Beaton et al. (1968).

2. SUMMARY OF METHOD

A fine-ground (<80-mesh) soil sample is oxidized at high temperature. The gases released are scrubbed, and the SO$_2$ in the combustion gases are measured using an infrared detector. Percent S is reported on an oven-dry soil basis.

3. INTERFERENCES

No significant interferences are known to affect the oxidizable S measurement.

4. SAFETY

Wear protective clothing and safety glasses. Magnesium perchlorate may form explosive mixtures. Magnesium perchlorate may contain traces of perchloric acid, which remain from manufacturer's operations. This acid is anhydrous because of the strong desiccating capability of the salt. Avoid prolonged contact with oxidizable material or material capable of forming unstable perchlorate esters or salts. Remove magnesium perchlorate by using an excess of water to thoroughly dilute the material.

The use of high temperatures in the oxidation of samples requires that extreme caution be used to prevent burns and fires. Follow standard laboratory procedures when handling compressed gases. Oxygen is highly flammable. Avoid open flames and sparks. Standard laboratory equipment includes fire blankets and extinguishers for use when necessary. Follow the manufacturer's safety precautions when using the sulfur analyzer.

5. EQUIPMENT

5.1 Sulfur analyzer, Leco Model SC-132 781-400 Sulfur System, Leco Corp., St. Joseph, MI
5.2 Data transmit card, part no. 772-573, Leco Corp., St. Joseph, MI
5.3 Combustion boats, part no. 529-203, Leco Corp., St. Joseph, MI
5.4 Single-stage regulator, Oxygen Service, Part No. E11-W-N115BOX, Air Products and Chemicals, Inc., Box 538, Allentown, PA 18105
5.5 Electronic balance, ±1-mg sensitivity

CHEMICAL ANALYSES
TOTAL SULFUR (6R)
SO$_2$ EVOLUTION, INFRARED (6R3)
LECO SC-132 SULFUR ANALYZER (6R3b)

6. REAGENTS

6.1 Anhydrone, anhydrous magnesium perchlorate, granular

6.2 Glass wool

6.3 Compressed oxygen, >99.5% @ 30 psi

7. PROCEDURE

7.1 Weigh an air-dry, fine-ground (<80-mesh) soil sample in a tared combustion boat. Sample size depends upon S content. The product of sample weight in g multiplied by the S percent must not be >2. In most cases, the sample size is 1.00 g, unless the S content is >2%.

7.2 Refer to the Appendix XVII, Sulfur Analyzer, and manufacturer's manual for operation of sulfur analyzer. An overview of the sulfur analyzer is as follows:

a. Samples are combusted in an O$_2$ atmosphere in which the S is oxidized to SO$_2$.

b. Moisture and dust are removed, and the SO$_2$ gas is then measured by a solid state infrared detector.

c. The microprocessor formulates the analysis results. The control console displays and prints results by combining the outputs of the infrared detector and system ambient sensors with pre-programmed calibration, linearization, and weight compensation factors.

8. CALCULATIONS

S (%) = S$_i$ x AD/OD

where:
S (%)   = S (%) on oven-dry basis
S$_i$ = S (%) instrument
AD/OD   = air-dry/oven-dry ratio (procedure 4B5)

9. REPORT
    Report total S as a percentage of oven-dry weight to the nearest 0.1%.

10. PRECISION
    Precision data are not available for this procedure. A quality control check sample is run in every batch of 12
samples. A blank (crucible only) and a rerun of one of the 12 samples (unknowns) also are run in every batch. For 27 observations of the quality control check sample, the mean, standard deviation, and C.V. for total S are 0.57, 0.02, and 4.3%, respectively.

11. REFERENCES
    Beaton, James D., G.R. Burns, and J. Platou. 1968. Determination of sulfur in soils and plant
            material. Tech. Bull. No. 14. The Sulfur Inst., 1725 K Street, N.W., Washington, D.C. 20006
    Tabatabai, M.A. 1982. Sulfur. *In* A.L. Page, R.H. Miller, and D.R. Keeney (eds.) Methods of soil
            analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agronomy 9:501-538.

CHEMICAL ANALYSES
PHOSPHORUS (6S)
NEW ZEALAND P RETENTION (6S4)

1. APPLICATION

In *Soil Taxonomy*, the P retention of soil material is a criterion for andic soil properties (Soil Survey Staff, 1990). Andisols and other soils that contain large amounts of allophane and other amorphous minerals have capacities for binding P (Gebhardt and Coleman, 1984). The factors that affect soil P retention are not well understood. However, allophane and imogolite have been considered as major materials that contribute to P retention in Andisols (Wada, 1985). Phosphate retention is also called P absorption, sorption, or fixation.

2. SUMMARY OF METHOD

A 5-g soil sample is shaken in a 1000-ppm P solution for 24 h. The mixture is centrifuged at 2000 rpm for 15 min. An aliquot of the supernatant is transferred to a colorimetric tube to which nitric vanadomolybdate acid reagent (NVAR) is added. The percent transmittance of the solution is read using a colorimeter. The New Zealand P retention is reported as percent P retained.

3. INTERFERENCES

No significant problems are known to affect the P retention measurement.

4. SAFETY

Wear protective clothing (coats, aprons, sleeve guards, and gloves) and eye protection (face shields, goggles, or safety glasses). When preparing reagents, exercise special care. Many metal salts are extremely toxic and may be fatal if ingested. Thoroughly wash hands after handling these metal salts. Restrict the use of concentrated HNO_3 to a fume hood. Use safety showers and eyewash stations to dilute spilled acids and bases. Use sodium bicarbonate and water to neutralize and dilute spilled acids.

5. EQUIPMENT

5.1 Electronic balance, ±0.01-g sensitivity
5.2 Shaker, Eberbach 6000 power unit, reciprocating speed of 60 to 260 epm, with 6040 utility box carrier and 6110 floor stand, Eberbach Corp., Ann Arbor, MI
5.3 Digital diluter/dispenser, product no. 100004, with hand probe and actuator, product no. 230700, Hamilton Co., P.O. Box 10030, Reno, NV, 89510
5.4 Syringes, 10000 and 1000 μL, 1001 DX and 1010-TEL LL gas tight, Hamilton Co., P.O. Box 10030, Reno, NV, 89510
5.5 Diluter/dispenser, 25 mL
5.6 Calorimeter, Baush and Laumb
5.7 Calorimeter tubes, glass, 10 mL, 1-cm light path, Baush and Laumb
5.8 Centrifuge, International no. 2, Model V, with no. 250 A head, International Equip. Co., Boston, MA
5.9 Trunions, International no. 320, International Equip. Co., Boston, MA
5.10 Centrifuge tubes, 50 mL, Oak-Ridge, polyallomer, Nalgene 3119, Nalge Co., Box 20365, Rochester, NY 14602.
5.11 Plastic cups, 2 fl. oz.
5.12 Pipets, volumetric, class A, glass, various sizes of 1 to 20 mL

6. REAGENTS

6.1 Distilled deionized (DDI) water
6.2 Nitric acid (HNO_3), conc.
6.3 P retention solution, 1000 ppm P. Dissolve 8.80 g of KH_2PO_4 and 32.8 g of sodium acetate (CH_3COONa) in DDI water. Add 23 mL of glacial acetic acid. Dilute to 2 L with DDI water in a volumetric flask. The solution pH should range between 4.55 and 4.65.
6.4 Molybdate solution. Dissolve 16 g of ammonium molybdate (VI) $[(NH_4)_6MO_7O_{24}\cdot 4H_2O]$ in 50°C DDI water. Allow the solution to cool to room temperature and dilute to 1 L with DDI water.

CHEMICAL ANALYSES
PHOSPHORUS (6S)
NEW ZEALAND P RETENTION (6S4)

6.5 Nitric acid solution. Carefully and slowly dilute 100 mL of conc. HNO_3 to 1 L of DDI water. Add the acid to the water.
6.6 Nitric vanadomolybdate acid reagent (NVAR), vanadate solution. Dissolve 0.8 g of NH_4VO_3 in 500 mL of boiling DDI water. Allow the solution to cool to room temperature. Carefully and slowly add 6 mL of conc. HNO_3. Dilute to 1 L with DDI water. Mix the nitric acid solution with the vanadate solution and then add the molybdate solution. Mix well.
6.7 Stock P standard solution (SPSS), 4000 ppm P. Dissolve 17.6 g K_2HPO_4 in DDI water. Dilute to 1 L with DDI water.
6.8 Standard P calibration P solutions (SPCS), 100, 80, 60, 40, 20, and 0% P retained. Dilute the SPSS with a solution that contains 32.8 g of sodium acetate (CH_3COONa) and 23 mL of glacial acetic acid diluted to 2 L with DDI water as follows: 100% = DDI water (0 ppm); 80% = 1:20 (200 ppm); 60% = 1:10 (400 ppm); 40% = 3:20 (600 ppm); 20% = 1:5 (800 ppm); and 0% = 1:4 (1000 ppm). The percent amount refers to percent P retention.

7. PROCEDURE
7.1 Weigh 5.00 g of air-dry soil into a 50-mL centrifuge tube.

7.2 Use the dispenser to add 25.0 mL of P-retention solution to centrifuge tube.

7.3 Cap centrifuge tube and place in shaker and shake for 24 h at room temperature (20°C).

7.4 Add 2 to 3 drops of Superfloc, 0.02% w/v to each tube.

7.5 Centrifuge sample at 2000 rpm for 15 min.

7.6 Pour sample supernatant into plastic cup.

7.7 Use the digital diluter to add the nitric vanadomolybdate acid reagent (NVAR) to each sample supernatant and to each SPCS. To fill a 10-mL Calorimeter tube, the diluter setting is 66 for diluent (NVAR) and 35 for sample (1:20 dilution).

7.8 The color reaction requires a minimum of 30 min before the analyst records readings.

7.9 Set the Calorimeter (blue bulb) to read at 466 nm. Set the zero against DDI water (blank). A blank has all reagents contained in the sample extract except the soil.

7.10 Record the percent transmittance to the nearest 0.01 unit for the sample extract and each SPCS.

8. CALCULATIONS

8.1 Transmittance of a solution is the fraction of incident radiation transmitted by the solution, i.e., $T = P/P_o$ and is often expressed as a percentage, i.e., $T = P/P_o \times 100$. The absorbance of a solution is directly proportional to concentration and is defined by the equation, $A = -\log_{10} T$. These relationships are derived from Beer's law.

Calibration Calculations
8.2 Use the transmittance of each SPCS to either construct a calibrated curve to plot P or use a least squares analysis to calculate P. The P is reported in percent retained.

8.3 *Calibration Curve*: Plot the transmittances against the ppm P of each SPCS on semilog graph paper or convert to absorbances and plot on linear graph paper. Construct the calibration curve by finding the "best" line that fits the plotted SPCS.

8.4 *Least Squares Analysis*: Use a least squares criterion, i.e. best moving average. Refer to a statistical analysis book for additional information on least squares analysis. To facilitate data manipulation in a least squares analysis, the following standard curve is developed using the concentration of SPCS as a f[ln(%T]. Final calculated analyte concentration with either $\log_{10}$ or ln base would be the same. Refer to procedure 6S3b for an example of least squares analysis.

Analyte Calculation

8.5 *Calibration Curve*: Read the percent P directly from the calibration curve.

8.6 *Least Squares Analysis*: Refer to procedure 6S3 for an example of least squares analysis.

9. REPORT

Report the percent New Zealand P retention to the nearest whole number.

10. PRECISION

Precision data are not available for this procedure.

11. REFERENCES

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MINERALOGY
INSTRUMENTAL ANALYSES (7A)
THERMAL GRAVIMETRIC ANALYSIS (7A4)
PERKIN-ELMER 7 SERIES (7A4b)

1. APPLICATION

Thermal analysis defines a group of analyses that determine some physical parameter, e.g., energy, weight, or evolved substances, as a dynamic function of temperature (Tan et al., 1986). Thermogravimetric analysis (TGA) is a technique for determining weight loss of a sample as it is being heated at a controlled rate. The weight changes are recorded as a function of temperature, i.e., a thermogravimetric curve, and provide quantitative information about substances under investigation, e.g., gibbsite ($Al(OH)_3$), kaolinite ($Al_2Si_2O_5(OH)_4$), and 2:1 expandable minerals (smectite and vermiculite).

2. SUMMARY OF METHOD

A 5- to 10-mg sample of soil clay is weighed into a platinum sample pan and placed in the TGA balance. The instrument records the initial sample weight. The analyst zeros the balance. The sample is then heated from a temperature of 30 to $900°C$ at a rate of $20°C$ min^{-1} in a flowing N_2 atmosphere. The computer collects weight changes as a function of temperature and records a thermogravimetric curve. Gibbsite and kaolinite are quantified by noting the weight loss between 250 to $350°C$ and 450 to $550°C$, respectively, and then relating these data to the theoretical weight loss of pure gibbsite or kaolinite (Soil Conservation Service, 1984). The weight loss is due to dehydroxylation, i.e., loss of crystal lattice water. Though not presently performed by the National Soil Survey Laboratory (NSSL), quantification of the 2:1 expandable minerals (smectite + vermiculite) is related to weight loss at $<250°C$, i.e., loss of adsorbed water (Karanthasis and Hajek, 1982; Tan et al., 1986). At this low temperature, adsorbed water is proportional to the specific area of the sample (Jackson, 1956; Karathanasis and Hajek, 1982; Mackenzie, 1970; Tan and Hajek, 1977).

3. INTERFERENCES

Organic matter is objectionable because it has a weight loss by dehydrogenation and by oxidation to CO_2 between 300 to $900°C$ (Tan, et al., 1986). Analysis in an inert N_2 atmosphere alleviates this problem. Mineral salts that contain water of crystallization also may be interferences. Samples should be washed free of any soluble salts.

A representative soil sample is important as sample size is small (<10 mg). Avoid large aggregates in sample, the presence of which may cause thermal interferences, i.e., differential kinetics of gas diffusion through the sample and physical movement of sample in a reaction.

In general, the same reactions that interfere with DSC/DTA also interfere with TGA determinations of kaolinite, gibbsite, and 2:1 expandable minerals. However, TGA is more sensitive to small water losses at slow rates, whereas DSC/DTA is more sensitive to large water losses at rapid rates (Tan, et al., 1986). This sensitivity difference may help to explain why kaolinite and gibbsite quantifications in TGA vs. DSC/DTA often are not equivalent, i.e., TGA estimates tend to be greater than the corresponding DSC/DTA estimates. In TGA, there is a greater probability of measuring water losses in specific temperature regimes that are not specifically associated with dehydroxylation reactions of interest. This problem is particularly apparent with illitic samples, which characteristically contain more "structural" water than ideal structural formulae would indicate (Rouston, et al., 1972; Weaver and Pollard, 1973).

Even though it is well established that various minerals lose the major portion of their crystal lattice water at different temperature ranges (Tan et al., 1986), there are overlaps in these weight loss regions (WLR) of minerals which interfere in the identification and measurement of the minerals of interest. The goethite WLR (250 to $400°C$) overlaps the gibbsite WLR (250 to $350°C$) (Mackenzie and Berggen, 1970). The illite WLR (550 to $600°C$) overlaps the high end of the kaolinite WLR (450 to $550°C$) (Mackenzie and Caillere, 1975). The WLR of hydroxy-Al interlayers in hydroxy-Al interlayered vermiculite (HIV) (400 to $450°C$) overlaps theslow end of the kaolinite WLR (450 t (550)Tjι˝/F8 1 Tfι2 5.129 0 TDι˝0 Tcι˝(°)
450 t (600)Tjι˝/F8 1 Tfι24. 4327 0 TDι˝(°)Tjι˝/F7 1 Tfι˝0.6024 0 TDι˝-0.001 Tcι˝(C) may interf

4. SAFETY

Secure high pressure N_2 tanks and handle with care. When changing the tanks, protect valves with covers. Do not program the analyzer for >950°C because it may present a safety hazard during sample analysis and cleaning cycles. Do not heat aluminum sample pans >600°C. Aluminum melts at 660°C, and the pans alloy with and destroy the sample holders. Always use high quality purge gases with the TGA. Minimum purity of 99.9% is recommended.

5. EQUIPMENT
5.1 Thermal analysis system, Perkin-Elmer 7 series, 7500 computer, TAC7 instrument controllers
5.2 Thermogravimetric analyzer module, TGA7, Hewlett-Packard digital plotter
5.3 Pressure tanks (2), N_2, purity 99.99%
5.4 Two-stage gas regulators (2), 50 psi outlet pressure
5.5 One-stage gas regulator for compressed air
5.6 Electronic balance, ±0.1-mg sensitivity, Mettler AE160
5.7 Forceps, flat-tipped
5.8 Weighing spatula
5.9 Desiccator, glass
5.10 Mortar and pestle
5.11 Sieves, 100 mesh or 80 mesh
5.12 Kaolinite, standard, poorly crystalline, Georgia Kaolinite, Clay Minerals Society, Source Clay Minerals Project, sample KGa-2.
5.13 Gibbsite, standard, Surinam Gibbsite, National
Soil Survey Laboratory (NSSL), 67L022.

6. REAGENTS
6.1 Magnesium nitrate saturated solution $[\,Mg(NO_3)_2 \cdot 6H_2O\,]$
6.2 Ethanol

7. PROCEDURE

Derive <2μm Clay Fractions
7.1 Prepare Na-saturated clay as in procedure 7A2i, preparation of clay suspension, 7.8 to 7.19.

7.2 Dry the clay suspension and transfer to mortar. Moisten sample with ethanol and grind with pestle to make a homogeneous slurry.

7.3 Air-dry sample using flowing air in hood. Lightly grind sample with pestle to make a homogeneous powder.

7.4 Sieve sample with 80-mesh screen. Equilibrate sample overnight over a saturated magnesium nitrate solution (55% rh) in a glass desiccator.

TGA Operation
7.5 Set-up the instrument and calibrate.

7.6 Turn on the N_2 purge gases and set to 6 and 3.5 psi for balance and sample purge, respectively. The balance purge pressure should always be greater than the sample purge pressure.

7.7 Turn on compressed air and set to 25 psi.

7.8 Place the platinum sample pan in the balance stirrup. Use the computer to raise the furnace tube and to zero the balance. Lower the furnace tube.

7.9 Remove the sample pan from the stirrup. Weigh ≈ 5 mg of sample, i.e., <100-mesh whole soil or derived <2-µm clay fraction, into tared sample pan. Refer to section on derived <2-µm clay fractions, 7.1 to 7.4.

7.10 Use flat-tipped forceps to remove the sample pan from the analytical balance. Tap the sample pan against a hard surface several times to uniformly distribute the sample.

7.11 Carefully place sample pan in the stirrup of the TGA microbalance.

7.12 The standard sample run heating program has a heating rate of 20°C min^{-1}, a starting temperature of 30°C, and an ending temperature of 900°C.

7.13 Raise the furnace tube and allow it to seat. Press "Read Weight" key (usually twice) until a relative weight percentage of 100.0% is displayed. The computer then reads the weight.

7.14 Immediately start the "Run" program.

7.15 At the end of the sample run (≈ 45 min), remove the sample pan from the microbalance stirrup. The furnace tube is lowered automatically at the end of run.

7.16 To store data, enter the appropriate file name on the computer for the completed run. If data are not stored by appropriate file name, data are stored under a default file name of "gsav". Only four of these files can be saved at any one time, after which files are overwritten. Once a file is named, it cannot be changed.

8. CALCULATIONS

8.1 The thermogravimetric curve is displayed on the computer monitor. The ordinate (Y) is expressed in a relative weight percentage, i.e., the initial sample weight is 100.0%. Use the computer to calculate the total change in sample weight (Δ Y), within the predetermined temperature range, as a 8 sample weight percent.

```
% Kaolinite  =
```

$$\frac{(\Delta \text{ sample weight \% }_{450-550}{}^{\circ}{}_{C})}{14} \times 100$$

where
Δ sample weight = total Δ in sample weight expressed as relative percent
14 = percent weight of hydroxyl water Lost from pure kaolinite

% Gibbsite =

$$\frac{(\Delta \text{ sample weight \% }_{250-350}{}^{\circ}{}_{C})}{34.6} \times 100$$

where

Δ sample weight = total Δ in sample weight expressed as relative percent

34.6 = percent weight of hydroxyl water lost from pure gibbsite

The percent weights of hydroxyl water lost from kaolinite and gibbsite are derived from the following assumed dehydroxylation reactions.

$Si_2Al_2O_5(OH)_4 ---> 2SiO_2 + Al_2O_3 + 2H_2O$
   (kaolinite)

$2Al(OH)_3 ---> Al_2O_3 + 3H_2O$
   (gibbsite)

Using kaolinite as an example, percent weight of hydroxyl water lost is calculated from the following formula weights.

$Si_2Al_2O_5(OH)_4 = 258$ g mol^{-1}

$2H_2O = 36$ g mol^{-1}

Percent weight of hydroxyl water lost = (36/258) x 100 = 34.6%

9. REPORT
Report percent gibbsite and/or kaolinite to nearest whole number.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
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MINERALOGY
INSTRUMENTAL ANALYSES (7A)
DIFFERENTIAL SCANNING CALORIMETRY (7A6)

1. APPLICATION

Calorimetry measures specific heat or thermal capacity of a substance. Differential scanning calorimetry (DSC) is a calorimetric technique in which the rate of heat flow between a sample and a reference material is measured as materials are held isothermal to one another. The DSC directly measures the magnitude of an energy change (H, enthalpy or heat content) in a material undergoing an exothermic or endothermic reaction. DSC is commonly used to quantify gibbsite ($Al(OH)_3$) and kaolinite ($Al_2Si_2O_5(OH)_4$) in soils and clays by measuring the magnitude of their dehydroxylation endotherms which are between 250 to 350°C and 450 to 550°C, respectively (Karathanasis and Hajek, 1982; Jackson, 1956; Mackenzie and Berggen, 1970; Mackenzie, 1970).

2. SUMMARY OF METHOD

An 8 mg sample of soil clay is weighed into an aluminum sample pan and placed in the DSC sample holder. The sample and reference are heated under flowing N_2 atmosphere from a temperature of 30 to 600°C at a rate of 10°C min^{-1}. Data are collected by the computer and a thermogram is plotted. Gibbsite and kaolinite are quantified by measuring the peak area of any endothermic reactions between 250 to 350°C and 450 to 550°C, respectively, and by calculating the H of the reaction. These values are related to the values for the respective known quantities of the two minerals (gibbsite and kaolinite).

3. INTERFERENCES

Organic matter is objectionable because it produces irregular exothermic peaks in air or O_2, commonly between 300 to 500°C, which may obscure important reactions from the inorganic components of interest (Schnitzer and Kodama, 1977). Analysis in an inert N_2 atmosphere alleviates this problem. Mineral salts that contain water of crystallization also may be interferences. Samples should be washed free of any soluble salts.

Use a representative soil sample as sample size is small (<10 mg). Avoid large aggregates in sample, the presence of which may cause thermal interferences because of differential kinetics of gas diffusion through the sample and physical movement of sample in a reaction.

The dehydroxylation of goethite is between 250 to 400°C and may interfere with the identification and integration of the gibbsite endotherm (250 to 350°C) (Mackenzie and Berggen, 1970). The dehydroxylation of illite is between 550 to 600°C and partially overlaps the high end of the kaolinite endotherm (450 to 550°C), resulting in possible peak integrations (Mackenzie and Caillere, 1975). The dehydroxylation of hydroxy-Al interlayers in hydroxy-Al interlayered vermiculite (HIV) is between 400 to 450°C and may interfere with the low end of the kaolinite endotherm (450 to 550°C), especially in the poorly crystalline kaolinites (Mackenzie and Caillere, 1976). Similarly, the dehydroxylation of nontronites, Fe-rich dioctahedral smectites is between 450 to 500°C and may interfere with kaolinite identification and measurement (Mackenzie and Caillere, 1975).

4. SAFETY

Secure high pressure N_2 tanks and handle with care. When changing the tanks, valves should be protected with covers. Do not program the analyzer for >950°C because it may present a safety hazard during sample analysis and cleaning cycles. Do not heat aluminum sample pans >600°C. Aluminum melts at 660°C, and the sample pans alloy with an destroy the sample holders. Always use high quality purge gases with the DSC. Minimum purity of 99.9% is recommended.

5. EQUIPMENT
5.1 Thermal analysis system, Perkin-Elmer 7 series, 7500 computer, TAC7 instrument controllers
5.2 Differential scanning calorimeter module, DSC7, Hewlett-Packard digital plotter
5.3 Pressure tanks (2), N_2, purity 99.99%
5.4 Two-stage gas regulators (2), 50 psi outlet pressure
5.5 Electronic balance, ±0.1-mg sensitivity, Mettler AE160
5.6 Forceps, flat-tipped

5.7 Weighing spatula
5.8 Desiccator, glass
5.9 Mortar and pestle
5.10 Sieves, 100 mesh or 80 mesh
5.11 Kaolinite, standard, poorly crystalline, Georgia Kaolinite, Clay Minerals Society, Source Clay Minerals Project, sample KGa-2.
5.12 Gibbsite, standard, Surinam Gibbsite, National Soil Survey Laboratory (NSSL), 67L022.

6. REAGENTS
6.1 Magnesium nitrate saturated solution $[Mg(NO_3)_2 \cdot 6H_2O]$
6.2 Ethanol

7. PROCEDURE

Derive <2μm Clay Fractions
7.1 Prepare Na-saturated clay as in procedure 7A2i, preparation of clay suspension, 7.8 to 7.19.

7.2 Dry the clay suspension and transfer to mortar. Moisten sample with ethanol and grind with pestle to make a homogeneous slurry.

7.3 Air-dry sample using flowing air in hood. Lightly grind sample with pestle to make a homogeneous powder. Transfer to original container for storage until use.

7.4 Prior to TGA analysis, sieve sample with 80-mesh screen. Equilibrate sample overnight over a saturated magnesium nitrate solution (55% rh) in a glass desiccator.

DSC Operation
7.5 Set-up the instrument and calibrate.

7.6 Weigh ≈ 8 mg of sample, i.e., <100-mesh whole soil or derived <2-μm clay fraction, into tared aluminum sample pan. Refer to section on derived <2-μm clay fractions, 7.1 to 7.4.

7.7 Use flat-tipped forceps to remove aluminum sample pan from balance. Drop sample from a 4- to 5-mm height to uniformly distribute sample in pan. Return the sample pan with sample to the balance and record weight to nearest ±0.1 mg. This weight is entered into computer in appropriate menu.

7.8 Carefully place aluminum sample pan in the center of DSC platinum sample side (left side) of sample holder. Place platinum two-hole lid on holder that covers the sample pan. Align lid holes with purge gas exit hole in DSC head.

7.9 Place empty aluminum sample pan in reference side (right side) of sample holder. Place remaining platinum two-hole lid on holder that covers the sample pan. Align lid holes as in previous step.

7.10 Close DSC head cover and lock.

7.11 The standard sample run heating program has a heating rate of $10°C$ min^{-1}, 5.3 min data delay, 5.0 min N_2 purge.

7.12 Start the "Run" program.

7.13 Observe the milliwatts (mW) readout on the computer display terminal and when reading stabilizes ($\approx$ 5 to 10 s), remove the sample pan and sample from the sample side of sample holder. Do not disturb the reference side.

7.14 To store data, enter the appropriate file name on the computer for the completed run. If data are not stored by appropriate file name, data are stored under a default file name of "gsav". Only four of these files can be saved at any one time, after which files are overwritten. Once a file is named, it cannot be changed.

8. CALCULATIONS
The thermogram is displayed on the computer monitor. The area under the DSC curve is proportional to the enthalpy (H). Use the computer to calculate the H or enthalpy of reaction per g of kaolinite and/or gibbsite (joules g^{-1}) as appropriate.

8.1 % Kaolinite weight = $\dfrac{H}{12.62}$

where:
12.62 = factor obtained from standard curve of kaolinite mixtures using China clay of undetermined purity

8.2 % Gibbsite weight = $\dfrac{H}{15.03}$

where:
15.03 = factor obtained from standard curve of gibbsite values using deferrated Surinam gibbsite of undetermined purity

9. REPORT
Report percent kaolinite and/or gibbsite to the nearest whole number.

10. PRECISION
Precision data are not available for this procedure.

11. REFERENCES
Karathanasis, A.D., and B.F. Hajek. 1982. Revised methods for rapid quantitative determination of minerals in soil clays. Soil Sci. Soc. Am. J. 46:419-425.
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Mackenzie, R.C., and S. Caillere. 1975. The thermal characteristics of soil minerals and the use of these characteristics in the qualitative and quantitative determination of clay minerals in soils. p. 529-571. *In* J.E. Gieseking (ed.) Soil components. Vol. 2. Inorganic components. Springer-Verlag, NY.
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MINERALOGY
TOTAL ANALYSIS (7C)
HF DISSOLUTION (7C3)

1. APPLICATION

Historically, elemental analysis was developed for the analysis of rocks and minerals (Washington, 1930). The elemental analysis of soils, sediments, and rocks necessitates their decomposition into soluble forms. Hydrofluoric acid (HF) is efficient in the digestion and dissolution of silicate minerals for elemental decomposition. Procedure 7C3 is an HF acid digestion. Elemental concentration is determined by atomic absorption using 100 mg of clay suspension contained in a closed vessel with boric acid (H_3BO_3) to neutralize excess acid (Berdanier, Lynn, and Threlkeld, 1978; Soil Conservation Service, 1984).

2. SUMMARY OF METHOD

To 100 mg of clay suspension (procedure 7A2i), 5 mL of HF acid are added. The solution is heated, cooled, and 2 to 3 g of H_3BO_3 are added to neutralize excess acid. The solution is diluted to 100 mL, allowed to stand overnight, and 20 mL are decanted. The concentrations of Fe, Al, and K are determined by atomic absorption in procedures 6C7a, 6G11a, and 6Q3a, respectively. Data are reported in procedure 7C3.

3. INTERFERENCES

Organic material may remain as a residue with this method.

4. SAFETY

Perform procedure in hood. Keep HF acid refrigerated and avoid contact with skin.

5. EQUIPMENT

5.1 Pipet, 5 mL,
5.2 Volumetric flask, nalgene, 100 mL
5.3 Polyethylene container, 25 mL, with cover
5.4 Electronic balance, ±0.1-mg sensitivity

6. REAGENTS

6.1 Distilled water
6.2 Hydrofluoric acid (HF), 48%,
6.3 Boric acid, (H_3BO_3), granular

7. PROCEDURE

HF Dissolution

7.1 Prepare Na-saturated clay as in procedure 7A2i, preparation of clay suspension, 7.8 to 7.19.

7.2 Pipet 2 mL of clay suspension into a 25-mL Teflon cup and add 5 mL of HF. A 100 mg of 100-mesh whole soil sample may be substituted for the clay suspension.

7.3 Pipet a duplicate sample into a weighing dish, dry at 105°C, and weigh. Use this sample for calculations.

7.4 Place covered Teflon cup in stainless steel retainer and tighten Teflon cap. Place sample in oven at 105°C for ≈ 4 h.

7.5 Turn off oven, open door and let stand overnight to cool.

7.6 Remove sample from oven.

MINERALOGY
TOTAL ANALYSIS (7C)
HF DISSOLUTION (7C3)

7.7 Under a hood, remove Teflon cup from steel retainer vessel and add 2 to 3 g of H_3BO_3 acid.

7.8 Rinse contents of Teflon cup into a 100-mL nalgene volumetric flask and adjust to volume with distilled water. Allow to stand overnight.

7.9 Decant ≈ 20 mL into a 25-mL polyethylene container for elemental analysis by atomic absorption. Refer to procedures 7C7a, 6G11a, and 6Q3a.

8. CALCULATIONS

Use the MR 2.0 to perform calculations. Inputs are as follows: project number; sample number; tare value; tare + sample value; Al and Fe readings (mg L^{-1}); and K readings (meq L^{-1}). Review data for internal consistency. Request a rerun, if necessary, at this time. Store data on a data disk.

The following example illustrates the conversion calculations of atomic absorption readings or element concentrations of Fe, Al, and K to appropriate oxide forms. The concentrations of Fe and Al (mg L^{-1}), and K (meq L^{-1}) are converted to percent Fe_2O_3, Al_2O_3, and K_2O, respectively. Refer to procedure 4A5 for air-dry/oven-dry ratio (AD/OD).

```
Sample weight              =    S         =         0.1071 g
Fe reading                 =    [Fe]      =         34.2 mg L⁻¹
Fe₂O₃ molecular weight     =    Fe₂O₃     =         159.70
Fe atomic weight           =    Fe        =         55.85
Al reading                 =    [Al]      =         72.8 mg L⁻¹
Al₂O₃ molecular weight     =    Al₂O₃     =         101.94
Al atomic weight           =    Al        =         26.98
K reading weight           =    [K]       =         0.61 meq L⁻¹
K₂O molecular weight       =    K₂O       =         94.19
K atomic weight            =    K         =         39.10
K equivalent weight        =    39        =         39
AD/OD=1.024                =    AD/OD
100 mL/1000 mL             =    dil. factor  =      100/1000
1/1000 mg g⁻¹              =    conv. factor =      1/1000
100/1 P/100 pts.           =    conv. factor =      100/1
```

% Fe_2O_3 =

[Fe] x 1/S x 100/1000 x 1/1000 x 100/1 x AD/OD x Fe_2O_3/Fe =

34.2 x 1/0.1071 x 0.1 x 0.001 x 100 x 1.024 x 159.7/111.70

% Fe_2O_3 = 4.68

% Al$_2$O$_3$ =

[Al] x 1/S x 100/1000 x 1/1000 x 100/1 x AD/OD x Al$_2$O$_3$/Al =
72.8 x 1/0.1071 x 0.1 x 0.001 x 100 x 1.024 x 101.94/53.96

% Al$_2$O$_3$ = 13.15%

% K$_2$O =

[K] x 1/S x 100/1000 x 1/1000 x 100/1 x AD/OD x K$_2$O/K x 39 =

0.61 x 1/0.1071 x 0.1 x 0.001 x 100 x 1.024 x 94.19/78.2 x 39 =

% K$_2$O = 2.74

9. REPORT
Report data to nearest whole percent.

10. PRECISION
Precision data are not available for this procedure. A quality control check sample is routinely run in HF analyses. For 38 observations of the quality control check sample, the mean, standard deviation, and C.V. for percent Fe, Al$_2$O$_3$, and K$_2$O are as follows:

Analyte	Mean	Std Dev	C.V.
% Fe	2.8	0.40	14
% Al$_2$O$_3$	12.1	1.04	9
% K$_2$O	2.4	0.38	16

11. REFERENCES
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Soil Conservation Service. 1984. Procedures for collecting soil samples and methods of analysis for soil survey. USDA-SCS Soil Surv. Invest. Rep. no. 1. U.S. Govt. Print. Office, Washington, DC.
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SOIL SURVEY LABORATORY METHODS
(methods no longer used and in old method format)

Carbonate-Containing Material (1B3)

Procedure

Prepare dialysis membrane sacks from 5 1/2-inch cellulose casing (Visking Company), using large rubber bands to tie the bottoms. Place the sample (as much as 6 kg if very gravelly and highly calcareous) in a dialysis membrane and add about 1 L pH 5, N NaOAc buffer. Tie the top of the dialysis membrane around a glass breather tube 4 in long and hang the assembly in a 60-L reservoir of buffer held in a 20-gal plastic garbage can. If carbonate is dissolving, knead the membrane to release bubbles of CO_2. When bubbles of CO_2 no longer form on kneading, open the dialysis membrane and use strong acid to check the coarser material for carbonate coatings (carbonate remains longer in the coarser material). When sample is free of carbonate, desalt it by dialysis against tap water flowing continuously through a large plastic garbage can. Check the ionic concentration inside the membrane by measuring conductivity of a small volume of the supernatant liquid poured out through the breather tube. Continue dialysis until the salt concentration is less than 10 meq/L.

The procedure used to dry the sample depends on whether the particles larger than 2 mm have been removed before buffer treatment. If they have been removed, withdraw excess water from the sample in the membrane with filter candles. Knead the membrane to mix the sample and place it in contact with ethanol to desiccate further. Remove the sample from the membrane and air-dry.

If the buffer-treated sample contains particles larger than 2 mm, wet sieve the sample through a 2-mm sieve. Then dry sieve the material remaining on the sieve (>2 mm) and add the <2-mm fraction from this sieving to the <2-mm fraction separated by the wet sieving. Remove most of the water from the <2-mm fraction with filter candles. Use ethanol to transfer the samples to shallow pans and dry. Ethanol prevents aggregation of clay into durable flakes during drying.

Discussion

The time required for carbonate removal varies greatly, depending on particle size, percentage and type of carbonate, and sample size. Samples from horizons strongly cemented by carbonate have required as long as 2 months. The concentration of alkaline-earth ions in the buffer greatly affects the rate of carbonate removal. Changing the buffer in the reservoir well before the buffer capacity has been exhausted, thereby keeping the alkaline-earth ion concentration low, increases the rate markedly. Desalting usually takes about 4 days.

For carbonate-cemented horizons, the whole sample, not just the <2-mm material, must be buffer treated. Furthermore, for horizons without carbonate cementation, buffer treatment of the whole sample has the advantage of washing the >2-mm skeletal material free of adhering fines and organic material. This problem is considered further in 1B4.

For very gravelly horizons, large samples (several kilograms) are necessary for buffer treatment because of the small amount of <2-mm material. Using large samples also increases precision of the >2-mm percentage.

References
Grossman and Millet (1961).

Carbonate-Indurated Material Containing Coarse Fragments (1B4)

Break the field sample to get several representative subsamples. Remove the carbonate from one subsample by acid treatment and separate the coarse fragments from the fine earth (1B3). Weigh the two fractions. Use the noncarbonate fine earth for the standard characterization and mineralogical measurements (sections 6-7).

Grind another subsample of the whole field sample to pass 80-mesh sieve. Determine the carbonate content (weight) of this whole ground subsample (6E).

These weights can be used to calculate the $CaCO_3$ percentage of the fine earth. Any analytical value based on the noncarbonate fine earth can be converted to the whole-soil basis as well as to the basis of the carbonate-containing fine earth.

PARTICLE-SIZE ANALYSIS (3)
PARTICLES <2 mm (Pipet Method) (3A)

An automated balance system, consisting of a Radio Shack Model II microcomputer interfaced to a Mettler PL2000 electronic balance (for sand) and a Mettler AE160 electronic balance (for silt and clay), is used for determining, storing, and processing sample weights.

Air-Dry Samples (3A1)

Apparatus
Fleaker, 300 ml (tare to 1 mg).

Pasteur-Chamberlain filter candles, fineness "F".

Shaker, horizontal, 120 oscillations per minute.

Cylinders, 1000 ml.

Stirrer, motor-driven
Stirrer, hand. Fasten a circular piece of perforated plastic to one end of a brass rod.

Shaw pipet rack.

Pipets, 25 ml automatic (Lowy with overflow bulb).

Polyurethane foam, pipe-insulating cover.

Shaker with 1/2-in vertical and lateral movements and 500 oscillations per minute. Accommodates a nest of sieves.

Wide-mouth glass pill bottles with screw caps, 90 ml (tare to 1 mg).

Electronic balance (0.1-mg sensitivity).

Set of sieves. Square mesh woven phosphor bronze wire cloth. U.S. Series and Tyler Screen Scale equivalent designations as follows:

Sand Size	Opening (mm)	U.S. No.	Tyler Mesh Size
VCS	1.0	18	16
CS	0.5	35	32
MS	0.25	60	60
FS	0.105	140	150
VFS	0.047	300	300

Reagents

Hydrogen peroxide (H_2O_2), 30 to 35 percent.

Sodium hexametaphosphate $(NaPO_3)_6$. Dissolve 35.7 grams of $(NaPO_3)_6$ and 7.94 grams of Na_2CO_3 per liter of water.

Demineralized water.

Procedure

Removing organic matter.--Place about 10 air-dry soil containing no particles larger than 2 mm in a tared Fleaker. Add about 50-ml of demineralized water (referred to subsequently as water) and then add 5 ml of H_2O_2. Cover the fleaker with a watchglass. If a violent reaction occurs, repeat the cold H_2O_2 treatment periodically until no more frothing occurs. Heat the Fleaker to about 90°C on an electric hot plate. Add H_2O_2 in 5-ml quantities at 45-min intervals until the organic matter is destroyed, as determined visually. Continue heating for about 30 min to remove any excess H_2O_2.

Removing cementing agents (optional).--Treat the sample with about 200 ml of 1 *N* sodium acetate buffered at pH 5 to remove carbonates. When CO_2 bubbles are no longer evident, wash free of salts with a filter candle system. Highly calcareous samples may need a second treatment.

Remove siliceous cementing agents by soaking the sample overnight in 0.1 *N* NaOH. Iron oxide cementing agents are removed by shaking overnight in sodium dithionite (6C2). Wash free of salts with filter candle system before proceeding.

Removing dissolved mineral and organic components.--After the H_2O_2 treatment, place the Fleaker in a rack and add about 150 ml of water in a jet strong enough a short Pasteur-Chamberlain filter of "F" fineness. Five such washings and filterings are usually enough except for soils containing much coarse gypsum. Remove soil adhering to the filter by gentle back pressure; use finger as policeman. Dry the sample overnight in an oven at 105°C, cool in a desiccator, and weigh to the nearest milligram. Use the weight of the ovendry, H_2O_2-treated sample as the base weight for calculating percentages of the various fractions.

Dispersing the sample.--Add 10 ml of sodium hexametaphosphate dispersing agent to the Fleaker containing ovendry treated sample. Make the volume to approximately 200 ml. Stopper and shake overnight on a horizontal reciprocating shaker at 120 oscillations per minute.

Separating sands from silt and clay.--Wash the dispersed sample with water on a 300-mesh sieve. Silt and clay pass through the sieve into a 1-L cylinder. Use a clamp and stand to hold the sieve above the cylinder. Avoid using jets of water in washing the sample. Gently tap the sieve clamp with the side of the hand to facilitate sieving. Continue washing until the suspension volume in the cylinder is about 800 ml. Sand and some coarse silt remain on the sieve. It is important to wash all particles of less than 20μ diameter through the sieve. Remove the sieve from the holder, wash the sands into an evaporating dish with water, and dry at 105 to 110°C. Bring the silt and clay suspension in the cylinder to 1 L with water and cover with a watchglass.

Pipeting.--First pipet the <20μ fraction at a 10-cm depth. Vary sedimentation times according to temperature. Next, pipet the <2μ fraction after a predetermined setting time (usually 4 1/2 to 6 1/2 hr). Vary depth according to time and temperature. Use a Lowy 25-ml automatic pipet and regulate filling time to about 12 s. Before each pipeting, stir material in the sedimentation cylinder, and stir the suspension for 30 s with a hand stirrer, using an up-and-down motion. Note the time at completion of stirring. About 1 min before sedimentation is complete, lower the tip of the pipet slowly into the suspension to the proper depth with a Shaw pipet rack. At the appropriate time, fill the pipet and empty into a 90-ml, wide-mouth bottle. Rinse the pipet into the bottle once. Dry in an oven overnight at 105°C. Cool in a desiccator containing phosphorus pentoxide (P_2O_5). Weigh.

Sieving and weighing the sand fractions.--Transfer the dried sands to a nest of sieves. Shake for 3 min on a shaker that has 1/2-in vertical and lateral movements and oscillates at 500 strokes per minute. Record the weights of the individual sand fractions.

Calculations

Pipetted fractions:

Percentage of pipetted fractions = (A - B)KD

where
A = Weight (g) of pipetted fraction
B = Weight correction for dispersing agent (g)
K = 1000/(ml in pipet)
D = 100/(g of H_2O_2-treated ovendry total sample)

The <20-μ fraction minus the <2-μ fraction equals fine silt.

Sand fractions:
Percentage of sieved fractions = weight (g) of fraction on sieve times D.

Coarse silt fraction:
Obtain by difference. Subtract the sum of the percentages of sand plus the <20-μ fraction from 100.

References
Kilmer and Alexander (1949), Kilmer and Mullins (1954), Tyner (1939), and Grossman and Millet (1961).

Carbonate and Noncarbonate Clay I (3A1a)

Apparatus
Warburg manometer.
1/4-oz (5-ml) gelatin capsules.

30-ml plastic cups.

Reagents
Hydrochloric acid (HCl), 6 *N.*

Procedure
        If carbonate is present, use the glass
bottle containing clay residue from regular pipet analysis and determine carbonate as in 6E1b. Use
Warburg manometer.

Calculations

Cc = { [(A - B - C) x Factor]/D } x 100

where
Cc   = Carbonate clay (pct <2 mm)
A   = Upper reading
B   = Lower reading
C   = Blank
Factor   = Factor derived from standard curve and includes pipette volume factor
D   = Total sample weight (3A1)

Nc = Total clay - Cc

where:
Nc = Noncarbonate clay (pct <2mm)
Cc = Carbonate clay (pct <2mm)

References
Shields and Meyer (1964).

Moist Samples (3A2)

If drying affects dispersion of treated sample, ovendrying may be avoided by removal of a pipet sample to estimate the total weight of the sample. Pipet 50 ml at a depth of 20 cm at time zero while the suspension is still turbulent. Use the ovendry weight of the aliquot to calculate the total weight of the <0.05-mm fraction. Add this weight to the total weight of the sands to obtain the total weight of the sample.

An optional procedure is to carefully weigh out two identical samples and pretreat to remove organic matter and dissolved mineral matter. The first sample is continued through the standard procedure, excluding ovendrying. The second sample is ovendried, weighed, and discarded. The ovendry weight of the second sample is substituted in the calculations for the first sample.

Carbonate and Noncarbonate Clay (3A2a)

Proceed as in 3A1a except use field-moist sample.

<h2 style="text-align:center">FABRIC-RELATED ANALYSES (4)
BULK DENSITY (4A)</h2>

Density is defined as mass per unit volume. Soil density as commonly used differs from most density measurements in that the volume of interparticle space is included but the mass of the liquid phase is excluded. Therefore, soil density has been called bulk density, Db, to distinguish it from the more usual density that is based on intraparticle volume only. Since the volume of a shrinking-swelling soil changes with a change in its water content, subscripts are added to designate the moisture condition when the measurement was made. Thus, Db_m is the bulk density of a moist sample, $Db_{1/3}$ is the bulk density of a clod sample equilibrated at 1/3-bar tension, and Db_d is the
bulk density of a dry sample.

Saran-Coated Clods (4A1)

Reagents
Methyl ethyl ketone.

Dow Saran F310.--The saran resin dissolves readily in acetone or methyl ethyl ketone. In this method, methyl ethyl ketone is used as a solvent because it is less soluble in water than is acetone and there is less penetration of the Saran-solvent solution into a moist clod. However, acetone is adequate for a first (field) coat and is more readily available. Saran-solvent ratios of 1:4 to 1:7 are used, depending on the porosity of the soil to be coated.

Coating solution.--To prepare the solution, fill a weighted container with a solvent to about three-fourths its volume. From the weight of the solvent, calculate the weight of resin required to obtain a predetermined resin-solvent ratio and add to the solvent. Since the solvent is flammable and its vapors form explosive mixtures with air, mix the components with an air-powered or nonsparking electric stirrer under an exhaust hood. Information on the safe handling and use of methyl ethyl ketone is available in Chemical Safety Data Sheet SD-83, Manufacturing Chemists' Association, Inc., 1825 Connecticut Avenue NW, Washington, D.C. The threshold limits of methyl ethyl ketone are 200 ppm as given in OSHA standards, Part 2, Section 1910.93, table G1.

If a high-speed stirrer is used, the resin dissolves in about 1 hr. In the field, mix with a wooden stick. Metal cans (1 gal) are satisfactory containers for mixing and storing the plastic. Keep the containers tightly closed to prevent evaporation of the solvent.

Procedure

Collect natural clods (three per horizon) of about 100 to 200 cm^3 in volume (fist-sized). Remove a piece of soil larger than the clod from the face of a sampling pit with a spade. From this piece prepare a clod by directly cutting or breaking off protruding peaks and material sheared by the spade. If roots are present, they can be cut conveniently with scissors or side cutters. In some soils, clods can be removed directly from the face of a pit with a knife or spatula. No procedure for taking clod samples fits all soils; the procedure must be adjusted to meet the conditions in the field at the time of sampling.

The clods are tied with the fine copper wire or placed in hairnets and suspended from a rope or string, hung out like a clothesline. Moisten dry clods with a fine mist spray. The suspended clods are dipped by raising a container of the dipping mixture upward around each clod, so it is immersed momentarily. The saran-coated clods should be allowed to dry for 30 min or longer. Clods coated in this way can be transported to the laboratory and examined microscopically in an undisturbed state. For convenience, either of two concentrations of plastic solution is usually used--a 1:7 solution for most soil samples or a 1:4 solution for clods that have larger pores. If bulk density at field-moisture content is desired, store the clods in waterproof plastic bags as soon as the coating dries since the coating is permeable to water vapor. Although the coating keeps the clods intact, they may be crushed in transport unless they are packed in rigid containers.

In the laboratory, additional coatings of plastic are applied to make the clod waterproof and to prevent its disruption during wetting. Then weigh the clod, either in its natural moisture condition or in an adjusted moisture condition (e.g., 1/3-bar tension) in air and in water to obtain its volume by Archimedes' principle. Subsequent changes in moisture condition and volume of the soil sample can be followed by reweighing the coated clod in air and in water. Finally, weigh the ovendry clod in air and in water.

Be careful not to lose any soil material because the weight of material lost is calculated as soil moisture, and calculated bulk densities depend on the final ovendry weight of the clod.

Bulk-density values determined by this method are reported on the basis of fine-earth fabric. Weight and volume measurements are made on clod samples that may contain particles >2 mm; however, after the measurements are made, the weight and volume of the coarse fraction are subtracted. The remainder consists of the weight of <2-mm material and the volume of these fine-earth particles and the pore space associated with them.

Sometimes it is necessary to correct bulk density for weight and volume of the plastic coating. The coating has a density of about 1.3 g/cm^3 and it loses 10 to 20 percent of its air-dry weight on ovendrying at 105°C. Thus, the amount of correction becomes smaller as bulk density of the soil approaches the density of the coating and as moisture content of the soil approaches the weight loss of the coating.

Calculations

$$Db_{1/3} = \frac{wtclod_{od} - wt>2mm - wtcoat_{od}}{volclod_{1/3} - vol>2mm - vol\ coat}$$

$$Db_{od} = \frac{wtclod_{od} - wt{>}2mm - wtcoat_{od}}{volclod_{od} - vol{>}2mm - vol\ coat}$$

$$W_{1/3} =$$

$$\frac{wtclod_{1/3} - wtclod_{od} - (wtclod_{ad} - wtcoat_{od}) \times 100}{wtclod_{od} - wt{>}2mm - wtcoat_{od}}$$

where
$Db_{1/3}$ = bulk density of <2-mm fabric at 1/3-bar tension in grams per cubic centimeter

Db_{od} = bulk density of <2-mm fabric at ovendryness in grams per cubic centimeter

$W_{1/3}$ = the weight percentage of water retained at 1/3-bar tension

wt clod$_{od}$ = weight of ovendry coated clod

wt clod$_{1/3}$ = weight of coated clod equilibrated at 1/3-bar tension

vol clod$_{od}$ = volume of ovendry coated clod

vol clod$_{1/3}$ = volume of coated clod equilibrated at 1/3-bar tension

vol >2 mm = volume of material >2 mm separated from clod after ovendrying

wt > 2 mm = weight of material > 2mm separated from after ovendrying

wt coat$_{ad}$ = weight of Saran coating before ovendrying

wt coat$_{od}$ = weight of Saran coating after ovendrying

vol coat = volume of Saran coating (estimated)

The field coat (initial coat) of plastic penetrates the clod to some extent. Weight of the field coat, estimated to 1.5 times the weight of each additional coat, is computed by:

$$Wtcoat_{init} = \frac{(Wtclod_B - Wtclod_A) \times 1.5}{3}$$

where
$Wtcoat_{init}$ = Weight of field (initial) coat

$Wtclod_A$ = Weight of clod with one coat of plastic

$Wtclod_B$ = Weight of clod with three additional coats of plastic

References
Brasher et al. (1966).

Air-Dry (Db$_d$) (4A1b)

After measuring field-state volume, place clods in a drying room kept at 90° F. Weigh a few clods each day until they reach a constant weight. Assume then that all the clods are airdry. Coat them again with Saran and measure "airdry" volume as described in 4A1a. Determine ovendry weight and calculate bulk density as described in 4A1.

30-cm Absorption (Db$_{30}$) (4A1c)

After measuring airdry volume, remove a patch of the Saran coating from one side of each clod. Next place the clods on a sand tension table with the exposed side in contact with very fine sand that has been equilibrated to 30-cm water tension. Again weigh a few clods each day until they reach constant weight and assume that all the clods are at 30-cm water tension. Most clods reach equilibrium in 7 to 10 days. Remove the clods from the tension table and coat with Saran until waterproof. Measure volume of the clods and calculate bulk density as described in 4A1.

1/3-Bar Desorption II (Db$_{1/3}$) (4A1e)

Cut a flat surface on the coated field-moist clods with a sharp knife or diamond saw. Seat the clods on saturated ceramic plates with the flat surface in contact with the plates. Place the plates in pans and add water to just cover the surface of the plates. After the clods become wet by capillary movement, place the plates in a pressure cooker and equilibrate at 1/3 bar. After equilibration, carefully remove the clods from the plates and dip in Saran until waterproof. Measure volume of the clods and calculate bulk density as described in 4A1.

1/3-Bar Desorption III (Db$_{1/3}$) (4A1f)

Proceed as in 4A1e except prewet the clods at 10-cm tension on porous bricks (cheesecloth layer between clod and brick) instead of saturating them on ceramic plates.

1/10-Bar Desorption (Db$_{1/10}$) (4A1g)

Proceed as in 4A1d, e, or f except make final desorption at 1/10 bar.

Parafffin-Coated Clods (4A2)
Ovendry (Db$_d$) (4A2a)

Ovendry the clods, coat with paraffin, and weigh in water and in air. Calculate bulk density as follows:

$$Db_d \ (g/cc) \ = \ \frac{Wtair \ - \ Wt>2mm}{Wtair \ - \ WtH_2O \ - \ (Wt>2mm/2.65)}$$

where
Wtair   = Weight in air
Wt>2mm   = Weight of >2-mm fraction in clod
WtH$_2$O = Weight in water

Nonpolar-Liquid Saturated Clods (4A4)

Procedure

Place a natural clod in a nonpolar liquid of low viscosity, e.g., high-purity kerosene. Evacuate under vacuum until bubbles cease to appear and weigh the clod suspended in the nonpolar liquid. Remove the clod, place it on a sand table under 3-cm tension against the nonpolar liquid to drain off excess nonpolar liquid, and weigh it in air. The difference in weight of the clod in air and suspended in the nonpolar liquid divided by the density of the nonpolar liquid is the clod volume. Determine the ovendry weight and calculate bulk density as in 4A1. The difference between the clod's initial weight before immersion in the nonpolar liquid and its ovendry weight is the moisture content.

References
Rennie (1957).

FABRIC-RELATED ANALYSES (4)
WATER RETENTION (4B)

Pressure-Plate Extraction (4B1)

After measuring the 1/3-bar volume (4A1d), the Saran coating is removed from the flat surface of the clods. The clods are allowed to air-dry (4 to 6 days) and then placed in the drying room 2 or 3 days. They are then placed on a tension table of very fine sand and equilibrated to 5-cm tension as in 4A1d. After about 2 weeks, some of the highly organic clods that have not rewetted are placed in a pan of free water overnight to make certain that wetting is complete. The clods are again desorbed to 1/3-bar as in 4A1d and volume measurements of the clod are made and bulk density is calculated as described in 4A1.

Soil Pieces (4B1b)

Procedure

Make desorption measurements of soil pieces concurrently with the sieved-sample measurements. Cover the sieved samples in retainer rings with small squares of industrial tissues (Kimwipes). Place the soil pieces (about 2.5 cm in diameter) on the tissues before adding water to the plate. Proceed as in 4B1a. If the soil pieces contain >2-mm material, wet sieve and weigh the ovendry >2-mm material. Report moisture content as percentage of ovendry weight of <2mm material.

References
Young (1962).

Sand-Table Absorption (4B3)

Saran-coated clods that have been equilibrated on a sand table to determine bulk density (4A) can also be used to determine water content at these tensions.

FABRIC-RELATED ANALYSES (4)
MICROMORPHOLOGY (4E)

Thin Sections (4E1)
Moved-Clay Percentage (4E1c)

Apparatus
Diamond tile saw.

Thin-section equipment.

Point-counting eyepiece.

Reagents
Aroclor 5460 (Monsanto).

Polyester resin.

Styrene.

Procedure
      Impregnate an undisturbed field sample with Aroclor (4E1b). With a diamond saw cut the clods into pieces about 3 by 1 by 1 cm. Mount about 10 pieces side by side with polyester resin (use a little styrene) to form a block. Cut this assembly to form slices 3 by 1 by 1 cm. Slice all the field sample, composite, and withdraw subsamples of 10 to 15 slices. Stack these slices, tape them together, and mount in plastic (polyester resin plus styrene). Cut a section through the stack parallel to the direction of stacking and along the longer of the two remaining axes. Mount one such section from each stack on a glass slide and prepare a thin section.
      To estimate the moved-clay volume insert a point-counting eyepiece into the microscope and run a transect along each strip. Keep the transect length and the number of fields in a transect constant. Count the number of points that fall on moved clay. Divide this number by the total number of points to get an estimate of the proportion of moved clay. To convert these volume estimates to weight estimates, multiply by the ratio of the bulk density of the moved clay to the bulk density of the appropriate dry fabric. Assume that the moved clay has a bulk density of 2.00 g per cubic centimeter.

References
Grossman (1964).

Scanning Electron Microscopy (4E2)

      Electronically reproduced images of fabric surfaces can be obtained at magnifications ranging from 50 to 30,000 diameters. Depth of focus by this technique is large compared to that by light microscope. Stereoscopic pictures can be taken to give three-dimensional viewing.

Procedure
      Take a sample of fabric up to 10 mm in diameter and 2 to 3 mm thick. Coat with a thin metallic layer and insert in the instrument. The image is displayed on a cathode ray tube.

ION EXCHANGE ANALYSES (5)
CATION EXCHANGE CAPACITY (CEC) (5A)

NH$_4$OAc, pH 7.0 (Buchner funnel) (5A1)

Reagents

Ammonium acetate (NH$_4$OAc), 1 *N*, pH 7.0. Mix 68 ml ammonium hydroxide (NH$_4$OH), specific gravity 0.90, and 57 ml 99.5-percent acetic acid (CH$_3$COOH) per liter of solution desired. Cool, dilute to volume with water, and adjust to pH 7.0 with CH$_3$COOH or NH$_4$OH. Optionally prepare from NH$_4$OAc reagent salt and adjust pH.

Ethanol (CH$_3$CH$_2$OH), 95-percent, U.S.P.

Nessler's reagent (optional). Prepare according to Yuen and Pollard.

Procedure

Weigh 25 g airdry <2-mm soil (some early work was done with 50-g samples) into a 250-ml Erlenmeyer flask and add 35 to 50 ml NH$_4$OAc solution. Stopper, shake the flask for several minutes, and allow to stand overnight. Transfer contents of the flask to a Buchner funnel (Coors No. 1) fitted with moist Whatman No. 42 filter paper. Filter, using gentle suction if needed. Leach with 200 ml NH$_4$OAc, adding small amounts at a time so that leaching requires no less than 1 hour. Transfer leachate from suction flask to volumetric flask and retain for analysis of NH$_4$OAc-extractable cations (methods 6N2, 6O2, 6P2, 6Q2).

Add 95-percent ethanol in small amounts to the ammonium-saturated soil remaining on the Buchner funnel until the leachate gives a negative test for ammonia with Nessler's reagent or leach with 100 ml ethanol.

References

Peech et al. (1947) and Yuen and Pollard (1952).

Direct Distillation of Adsorbed Ammonia, Kjeldahl (5A1a)

Reagents

Sodium chloride (NaCl).

Antifoam mixture. Mix equal parts of mineral oil and n-octyl alcohol.

Sodium hydroxide (NaOH),   1 *N*.

Hydrochloric acid (HCl), 0.2 *N*, standardized.

Boric acid (H$_3$BO$_3$), 4-percent.

Mixed indicator. Mix 1.250 g methyl red and 0.825 g methylene blue in 1 liter 95-percent ethanol.

Brom cresol green, 0.1-percent, aqueous solution.

Procedure

Transfer the soil plus filter paper from method 5A1 to a Kjeldahl flask. Add 400 ml water and about 10 g NaCl, 5 drops antifoam mixture, a gram or two of granular zinc, and 40 ml 1 *N* NaOH. Connect the flask with the condenser and distill 200 ml into 50 ml 4-percent H$_3$BO$_3$ solution. Titrate the distillate to the first tinge of purple with 0.2 *N* HCl, using 10 drops mixed indicator and 2 drops brom cresol green.

Calculations

$$CEC(meq/100\ g) = (A/B) \times N \times 100$$

where
A = Volume HCl (mL)
B = Sample weight (g)
N = Normality of acid

Report on ovendry basis.

References
Peech et al. (1947).

Displacement of Adsorbed Ammonia, Semimicro Kjeldahl (5A1b)

Reagents
Sodium chloride (NaCl), acidified, 10-percent. Dissolve 100 g NaCl, reagent-grade, ammonia-free, in 750 ml warm water; add 25 ml 2 N hydrochloric acid (HCl) and bring to 1000-ml volume.

Sodium hydroxide (NaOH), 1 N.

Boric acid (H_3BO_3), 2-percent.

Sulfuric acid (H_2SO_4), 0.01 N, standardized.

Ethanol, 95-percent.

Mixed indicator. Dissolve 0.1 g methyl red and 0.1 g brom cresol green in 250 ml ethanol.

Procedure
    Leach soil from method 5A1 with 240 ml 10-percent acidified NaCl solution, using small increments. Drain completely between each increment. Transfer the leachate to a 250-ml volumetric flask and adjust volume to mark. Pipet a suitable aliquot of the leachate into a micro-Kjeldahl distillation flask and attach to steam-distillation apparatus. Start steam distillation and slowly add 10 ml 1 N NaOH. Catch distillate in a 250-ml Erlenmeyer flask containing 10 ml H_3BO_3 and 10 drops of mixed indicator. Distill for 5 minutes after H_3BO_3 turns green, lower receiving flask, and rinse condenser and outlet hose into receiving flask. Titrate the ammonia with 0.01 N H_2SO_4 to a red end point, using a blank for comparison.

Calculations

$$CEC(meq/100\ g) = (A/B) \times N \times (C/D) \times 100$$

where
A = Volume H_2SO_4 (mL)
B = Sample weight (g)
N = Normality of acid
C = Volume leachate (mL)
D = Volume aliquot (mL)

Report on ovendry basis.

NaOAc, pH 8.2 (5A2)

Centrifuge Method (5A2a)

Reagents
Sodium acetate (NaOAc), 1 *N*, pH 8.2.

Ethanol, 95-percent.

Ammonium acetate (NH$_4$OAc), 1 *N*, pH 7.0. Add 57 ml concentrated acetic acid and 68 ml concentrated NH$_4$OH, specific gravity 0.90, to about 800 ml water. Cool and dilute to 1 liter and adjust to pH 7.0 by adding more NH$_4$OH or acetic acid.

Procedure
        Weigh 5-g samples to an accuracy of 1 percent and place in centrifuge tubes. Add 33 ml NaOAc, stopper the tubes, and shake for 5 minutes. Remove stopper and centrifuge until the supernatant liquid is clear (usually 5 min). Decant the supernatant liquid as completely as possible and discard. Repeat four times, discarding the supernatant liquid each time. After the last saturation, wash the rubber stoppers and use absorbent paper to remove any acetate crystals remaining on lip of centrifuge tube. Add about 30 ml ethanol to each tube, stopper, shake for 5 minutes, remove stopper, and centrifuge until the supernatant liquid is clear. Decant and discard the supernatant liquid. Continue washing until the electrical conductivity of the supernatant liquid from the last washing is between 55 and 40 µmho per centimeter. Optionally, decrease volume by about 5 ml each washing. Replace the absorbed sodium from the sample by extracting with three 30-ml portions of NH$_4$OAc solution. Dilute to 100 ml and determine the sodium concentration as described in 6P2a.

Calculations

$$CEC \text{ (meq/100 g)} = (A/B) \text{ x dilution x 10}$$

where
A   = Na from curve (meq/L)
B   = Sample weight (g)

Report on ovendry basis.

References
Richards (1954).

KOAc, pH 7.0 (5A4)

Procedure
        Proceed as in 5A1 except substitute 1 *N* KOAc, pH 7.0, for NH$_4$OAc. Determine potassium with flame photometer.

BaCl$_2$, pH 8.2 (5A5)

Apparatus
Leaching tubes.

Flame photometer.

Reagents

Buffer solution. Barium chloride ($BaCl_2$), 0.5 *N*, and triethanolamine (TEA), 0.2 *N*. Adjust to pH 8.2 with HCl. Protect from CO_2 of the air by attaching a drying tube containing soda lime (sodium calcium hydrate) to the air intake.

Replacement solution. Barium chloride ($BaCl_2$), 0.5 *N*. Add 0.4 ml buffer solution per liter and mix. Protect from CO_2 with soda-lime tube.

Magnesium nitrate ($Mg(NO_3)_2$), 1 *N.*

Procedure

Transfer a 5-g sample to a leaching tube. For field-moist samples use a sample large enough to give an ovendry weight of about 5 g. Leach with 50 ml $BaCl_2$-TEA solution, controlling the leaching rate to give at least 4 hours of soil:solution contact time. Follow with 100 ml $BaCl_2$ replacement solution, controlling the leaching rate so that the soil and $BaCl_2$ solutions are in contact for a total of 20 to 24 hours. Rinse walls of leaching tube with 15 to 20 ml H_2O, collecting this washing with leachates from $BaCl_2$ solutions. Extractable acidity can be determined by using this solution (6H1a). Place leaching tube on a clean flask and wash with methanol until free of chloride ion. For many samples 100 ml methanol is enough, but more methanol may be needed for some soils, particularly those of heavy texture and containing large amounts of hydrous oxides. Leach with 100 ml 0.001 *N* $BaCl_2$ to remove methanol.

Disconnect leaching tube and flask, rinse underside of leaching tube, place over a 250-ml volumetric flask, and leach with 100 ml 1 *N* $Mg(NO_3)_2$ solution. Control leaching rate to give a soil-solution contact time of 16 hours or more. Rinse walls of leaching tube with 15 to 20 ml H_2O; collect rinse in the $Mg(NO_3)_2$ leachate. Make to volume.

Barium by Flame Photometry (5A5a)

Make standards in 1 *N* $Mg(NO_3)_2$. Determine barium by flame photometry at 489 mμ.

Calculations

$$CEC(\text{meq/100 g}) = (A/B) \times \text{dilution} \times 25$$

where
A = Ba from curve (meq/L)
B = Sample weight (g)

NH_4OAc, pH 7.0, Leaching Tube (5A6)

Apparatus

Allihn leaching tubes or 50-ml plastic syringe barrels.

Reagents

Same as in 5A1.

Procedure

Prepare the Allihn tubes by placing either filter paper (Reeve Angel No. 934 AH, 3-cm fiber glass) or filter paper pulp on the fritted glass plate. If the syringe barrel is used as a leaching tube, compress the filter paper pulp in the barrel bottom with the syringe plunger. Place a Gooch perforated plate over the filter paper to permit stirring the soil without damage to the filter. (This plate is not necessary if an adequate pulp pad is used.) Place 5 or 10 g soil and a teaspoon of Celite into the tubes. (Optionally place a layer of Celite under the soil.) Add 25 ml *N* NH_4OAc; stir and leach. Add an additional

25 ml N NH_4OAc and let stand overnight. Stop the leaching with a pinch clamp or by stoppering the leaching tube. Add the NH_4OAc directly to the leaching tube or use a constant level device (6N3, figure 7). A volumetric flask can be substituted for the 250-ml Erlenmeyer flask and tubing.

Make the leachate to volume if a volumetric flask is used or, if tared suction flasks are used, make to the appropriate calibrated weight for 100 ml NH_4OAc. Set aside the leachate for further analysis. Add about 10 ml ethanol to the soil pad, stir, and leach. Leach with 100 ml ethanol and check for NH_4^+ in leachate. If NH_4^+ is present, leach with an additional 100 ml ethanol. Some soils, particularly those containing amorphous material, require as much as 400 ml ethanol to clear the ammonia from the leachate.

Direct Distillation (5A6a)

Transfer soil cake to Kjeldahl flask and determine ammonia as described in 5A1a.

NH_4Cl, pH 7.0, Mechanical Extraction (5A7)
Direct Distillation (5A7a)

Determine ammonia by Kjeldahl distillation as described in 5A1a.

NH_4OAc, pH 7.0, Automatic Extractor (5A8)
Direct Distillation (5A8a)

Reagents
Sodium chloride (NaCl).

Antifoam mixture. Mix equal parts of mineral oil and n-octyl alcohol.

Sodium hydroxide (NaOH), 1 N.

Hydrochloric acid (HCl), 0.2 N, standardized.

Boric acid (H_3BO_3), 4 percent.

Procedure
Transfer the soil plus filter pulp from methods 5A8 or 5A9 to a Kjeldahl flask. Add 400 ml water and about 10 g NaCl, 5 drops antifoam mixture, a gram or two of granular zinc, and 40 ml of 1 N NaOH. Connect the flask with the condenser and distill 140 ml into 50 ml of 4-percent H_3BO_3 solution in 250-ml titrator beaker. Titrate with automatic titrator to end point pH setting of 4.60.

Calculations

$$CEC(meq/100g) = (A/B) \times N \times 100$$

where
A = Volume HCl (mL)
B = Sample weight (g)
N = Normality of acid

Report on ovendry basis.

References
Peech et al. (1947).

NH₄Cl, pH 7.0, Automatic Extractor (5A9)
Direct Distillation (5A9a)

Determine ammonia by Kjeldahl distillation as described in 5A8a.

ION EXCHANGE ANALYSES (5)
EXTRACTABLE BASES (5B)

NH₄OAc, pH 7.0, Buchner Funnel (5B1)

Procedure
Analyze the NH₄OAc leachate from method 5A1 a for calcium, magnesium, sodium, and potassium (methods 6N2, 6O2, 6P2, 6Q2).

Uncorrected (extractable) (5B1a)

If a soil does not contain soluble salts, the extractable bases are presumed to equal the exchangeable bases. They are, however, reported as extractable bases.

Corrected (exchangeable) (5B1b)

If a soil contains soluble salts, estimate their amount from the saturation extract as follows. Multiply cation concentration in the saturation extract (meq/L) by the saturation percentage (divided by 1000) to convert to milliequivalents per 100 g. Subtract this quantity from the concentration of the extracted cation. This procedure is not valid for calcium and magnesium in the presence of carbonates or for calcium in the presence of gypsum because these salts are soluble in NH₄OAc.

References
Peech et al. (1947).

KCl-Triethanolamine Extraction, pH 8.2 (5B2)

Reagents
Buffer solution. Potassium chloride (KCl), 1.0 *N*, and triethanolamine (TEA), 0.2 *N*, pH 8.2.

Procedure
Proceed as in 5B1 except leach with 1 *N* KCl buffered at pH 8.2 with triethanolamine. Determine calcium by method 6N4, magnesium by 6O4.

References
North-Central Regional Research Committee (1955).

KCl-Triethanolamine Extraction, pH 8.2 (revised) (5B3)

Reagents
Buffer solution. Potassium chloride (KCl), 1.0 *N*, and triethanolamine (TEA), 0.2 *N*, pH 8.2.

Procedure
Weigh 10-g samples and transfer to 100-ml beakers. Add 40 ml buffer solution. Stir thoroughly at least three times over a period of not less than 1 hour. Filter the suspension and collect the leachate in a 100-ml volumetric flask.
Analyze the leachate for Ca and Mg by an appropriate procedure (6N4, 6O4).

Uncorrected (extractable) (5B3a)

If a soil does not contain soluble salts, the extractable bases are presumed to equal the exchangeable bases. They are, however, reported as extractable bases.

Corrected (exchangeable) (5B3b)

If a soil contains soluble salts, estimate their amounts from the saturation extract and correct as in 5B1b.

NH$_4$OAc, pH 7.0, Leaching Tube (5B4)

Analyze the NH$_4$OAc leachate from method 5A6 for Ca, Mg, Na, and K (methods 6N2, 6O2, 6P2, 6Q2).

Uncorrected (extractable) (5B4a)

If a soil does not contain soluble salts, the extractable bases are presumed to equal the exchangeable bases. They are, however, reported as extractable bases.

Corrected (exchangeable) (5B4b)

If a soil contains soluble salts, estimate their amounts from the saturation extract and correct as in 5B1b.

NH$_4$OAc, pH 7.0, Automatic Extractor (5B5)
Corrected (exchangeable) (5B5b)

If a soil contains soluble salts, estimate their amount from the saturation extract as follows. Multiply cation concentration in the saturation extract (meq/L) by the saturation percentage (divided by 1000) to convert to milliequivalents per 100 g. Subtract this quantity from the concentration of the extracted cation. This procedure is not valid for calcium and magnesium in the presence of carbonates that contain those elements, or for calcium in the presence of gypsum, because these compounds are soluble in NH$_4$OAc.

ION EXCHANGE ANALYSES (5)
BASE SATURATION (5C)

NaOAc, pH 8.2 (5C2)

Divide sum of NH_4OAc-extracted bases by the exchange capacity determined by method 5A2a.

ION EXCHANGE ANALYSES (5)
EXCHANGEABLE SODIUM PERCENTAGE (ESP) (5D)

NaOAc, pH 8.2 (5D1)

Divide exchangeable sodium (meq/100 g) by the exchange capacity determined by method 5A2a.

ION EXCHANGE ANALYSES (5)
CALCIUM SATURATION (Exchangeable-Calcium Percentage) (5F)

NH₄OAc, pH 7.0 (5F1)

Divide the NH_4OAc-extracted calcium by the exchange capacity determined by procedure 5A1 or 5A6.

CHEMICAL ANALYSES (6)
ORGANIC CARBON (6A)

Determine carbon for each horizon that may contain organic matter. Report as carbon percentage by weight of <2-mm material.

To calculate total carbon per unit area, convert these weight percentages to volume percentages. Multiply each value by the bulk density Dbm, where m is usually 1/3 bar or 30 cm, and by the thickness (inches) of that horizon. If coarse fragments are present, further multiply by Cm (4A). Sum the organic-matter percentages and multiply by 0.254 to convert to kilograms of carbon per square meter.

Acid-Dichromate Digestion (6A1)
FeSO₄ Titration (6A1a)

Reagents
Potassium dichromate ($K_2Cr_2O_7$), 1.00 N (49.04 g per liter).

Ferrous sulfate, 1.0 N. Dissolve 280 g reagent-grade $FeSO_4 \cdot 7H_2O$ in water, add 80 ml concentrated H_2SO_4, cool, and dilute to 1 liter. Standardize this reagent each day by titrating against 10 ml N $K_2Cr_2O_7$ as directed.

Barium diphenylaminesulfonate indicator, 0.16 percent   aqueous solution.

Orthophenanthroline-ferrous complex (optional), 0.025 M solution of one of the phenanthroline-ferrous complex indicators.

H_2SO_4, at least 96-percent.
Phosphoric acid (H_3PO_4), 86-percent.

Procedure

Transfer 1 g (0.5 g or less if high in organic matter) soil ground to pass an 80-mesh sieve to a 500-ml Erlenmeyer flask. Add 10 ml N $K_2Cr_2O_7$. Add 20 ml concentrated H_2SO_4 rapidly, directing the stream into the solution. Immediately swirl vigorously or place in wrist-action shaker for 1 minute. Let the flask stand on a sheet of asbestos for about 30 minutes. Add 200 ml water and 10 ml H_3PO_4. Add 0.5 ml barium diphenylaminesulfonate just before titrating. Titrate by adding $FeSO_4$ drop by drop to a light green end point. If more than 8 ml of the available 10 ml $K_2Cr_2O_7$ are reduced, repeat the determination, using less soil. If orthophenanthroline-ferrous complex is the indicator, it is not necessary to add H_3PO_4.

Calculations

Organic carbon (pct.) =

$$((A - B)/C) \times N \times (0.30/0.77)$$

where
A   = Volume $FeSO_4$ blank (mL)
B   = Volume $FeSO_4$ sample (mL)
C   = Sample weight (g)
N = Normality of $FeSO_4$
0.77   = Recovery factor proposed by Walkley (1935)

Report on ovendry basis.

References
Peech et al. (1947) and Walkley (1935).

CO_2 Evolution, Gravimetric (6A1b)

Apparatus
See figure 3.

Reagents
Digestion-acid mixture. Mix 600 ml concentrated H_2SO_4 and 400 ml 85-percent H_3PO_4.

Potassium dichromate ($K_2Cr_2O_7$), reagent grade.

Potassium iodide (KI). Dissolve 100 g KI in 100 ml water.

Silver sulfate (Ag_2SO_4), saturated aqueous solution.

Concentrated sulfuric acid (H_2SO_4).

Other reagents. Indicarb or Mikohbite, soda lime, 30-mesh zinc, and anhydrone (anhydrous magnesium perchlorate).

Procedure

Place a soil sample containing 20 to 40 mg carbon (usually 0.5 to 3 g ovendry soil) in digestion flask and add 1 to 2 g $K_2Cr_2O_7$. Wash the neck of the flask with 3 ml water and connect the flask to reflux condenser. Attach the weighed Nesbitt bulb to the system and open the valve at the top. Pour 25 ml digestion-acid mixture into funnel, let it enter the flask, and close the stopcock immediately to prevent loss of CO_2. Use digestion-acid mixture to lubricate the funnel stopcock. The tip of the air-delivery tube should extend about 0.5 cm below the surface of the acid during digestion. Adjust the "carrier stream" to

a flow rate of one or two bubbles per second and maintain this rate during digestion. Heat with a gas flame of sufficient intensity to bring the sample to boiling in 3 to 4 min. Continue gentle boiling for a total heating period of 10 min (avoid excessive frothing). Heating is too rapid if white fumes of SO_3 are visible above the second bulb of the reflux condenser during boiling. At the end of the digestion period remove the flame and aerate for 10 min at the rate of six to eight bubbles per second. Then close the stopcock on the Nesbitt bulb, disconnect the bulb from the system, and weigh.

Calculations

Organic carbon (pct.) =

$$((A - B)/C) \times 27.3$$

where
A = Final bulb weight (g)
B = Initial bulb weight (g)
C = Sample weight (g)

Report on ovendry basis.

References
Allison (1960).

Dry Combustion (6A2)
CO_2 Evolution, Gravimetric I (6A2a)

Apparatus
See figure 4.

Reagents
Powdered manganese oxide (MnO_2).

Procedure
        Place 0.5 to 1.5 g soil that has been ground to 80 mesh in an Alundum boat containing 0.25 g powdered MnO_2. Insert the boat into the quartz tube of the multiple-unit combustion furnace shown. Before inserting the soil, preheat the long part of the quartz tube to 900°C or more (1000° or 1,100°C) and clear of CO_2 by passing CO_2free oxygen through the combustion train until the weighing bottle shows a constant weight. While oxygen is passing slowly through the apparatus, heat to a temperature of 900° C or higher (15 to 30 min). Continue heating in a streaming oxygen atmosphere for 30 minutes more or until the Nesbitt absorption bulb has reached a constant weight.

Calculations
Report on ovendry basis as in 6A1b.

References
Robinson (1930)

CO_2 Evolution, Gravimetric II (6A2b)

Apparatus
Figure 5.

Procedure

      Heat tube to approximately 950°C. Sweep with oxygen until weight of Nesbitt bulb is constant. Remove rubber stopper in the oxygeninlet end of the tube and insert the boat containing 0.5 to 1.5 g soil. Reinsert the stopper and use the push rod to move the boat into the hot zone. Heat for 10 minutes, remove bulb, and record weight gain. Remove boat and repeat process with fresh sample, using the same Nesbitt bulb.

Calculations

Report on ovendry basis as in 6A1b.

References

Robinson (1930) and Post. (Post, G.J. A study of three methods for determination of organic carbon in Ohio soils of several great soil groups and the profile distribution of carbon-nitrogen ratios. M.Sc. thesis. The Ohio State University, 34 pp. 1956.)

CO_2 Evolution III (6A2c)

Apparatus

LECO 70-second carbon analyzer, model 750-100.

LECO induction furnace, model 521-000.

Reagents

Manganese dioxide.

Antimony.

1-g standard sample rings containing 0.870 percent carbon.

1-g standard sample rings containing 0.073 percent carbon.

Metal accelerator.

Iron chip accelerator.

Anhydrone.

Procedure

      For noncalcareous soils, weigh approximately 1/2 g of <2-mm soil into crucibles in duplicate. Add to the soil in the crucibles one scoop of copper accelerator and one scoop of iron chip accelerator. Mix by stirring. Add an additional scoop of iron chips to the stirred mixture. Four standard soils containing 0.8, 2.1, 3.5, and 6.5 percent organic carbon are run with each group of soils. Follow LECO instruction manuals for instrument operation. Record readings from digital voltmeter as percent carbon.

References

Tabatabai and Bremner (1970).

Peroxide Digestion (6A3)
Gravimetric Weight Loss (6A3a)

Reagents
Hydrogen peroxide (H_2O_2), 6-percent.

Procedure
    Digest soil for several hours in a covered beaker with 6-percent H_2O_2. Remove soluble material by washing three to five times with a Pasteur-Chamberlain clay filter, "F" fineness. Dry the beaker and soil, and weigh.

Calculations

$$\text{Organic matter (pct.)} = ((A + B)/C) \times 100$$

where
A   = Weight loss on heating (g)
B   = Weight of dry matter in solution (g)
C   = Sample weight (g)

Note that organic matter differs from organic carbon (see 6A1a).

References
North-Central Regional Research Committee on soils (1955).

CHEMICAL ANALYSES (6)
NITROGEN (6B)

Kjeldahl Digestion I (6B1)

Reagents
Concentrated sulfuric acid (H_2SO_4).

Salt mixture:

Potassium sulfate (K_2SO_4), 1000 g.

Ferrous sulfate (anhydrous) $FeSO_4$, 55 g.

Copper sulfate (anhydrous) $CuSO_4$, 32 g.

Hengar granules (selenized).

Procedure
    Weigh 5 g soil into 800-ml Kjeldahl flask, add 20 ml distilled water and let stand overnight. Add 10 g salt mixture, 2 or 3 Henger granules, and 30 ml H_2SO_4. Digest on Kjeldahl digestion heaters, rotating flasks frequently. Continue digestion 1 hr after mixture is clear.

References
Association of Official Agricultural Chemists (1945).

Ammonia Distillation (6B1a)

Reagents
Mixed indicator. Methyl red, 0.125-percent, and methylene blue, 0.0825-percent, in 95-percent ethanol.

Methyl red (optional), 0.25-percent.

Brom cresol green, 0.1-percent aqueous solution.

Boric acid (H_3BO_3), 4-percent.

HCl, standardized, 0.1 N or 0.05 N.

Procedure
Cool digestion flask (6B1) and dilute contents with about 400 ml water. Add 2 to 3 g mossy zinc, 5 drops antifoam mixture, and 70 ml concentrated NaOH solution. Connect flask to condenser and distill ammonia into 25 or 50 ml H_3BO_3 solution. Titrate with standard HCl to purple end point, using 10 drops mixed indicator and 2 drops brom cresol green or 3 drops brom cresol green and 1 drop methyl red.

Calculations

$$N \ (pct) = ((A - B)/C) \times N \times 1.4$$

where
A = Volume HCl sample (mL)
B = Volume HCl blank (mL)
C = Sample weight (g)
N = Normality of HCl

Report on ovendry basis.

Ammonia Distillation, Automatic Titrator (6B1b)

Reagents

Boric acid (H_3BO_3), 4 percent.

HCl, standardized, 0.1 N or 0.05 N.

Concentrated sodium hydroxide (NaOH) solution, 50 percent.

Antifoam mixture: Equal parts n-octyl alcohol and mineral oil.

Mossy zinc.

Procedure
Cool digestion flask (6B1) and dilute contents with about 400 ml water. Add 2 to 3 g mossy zinc, 5 drops antifoam mixture, and 70 ml concentrated NaOH solution. Connect flask to condenser and distill ammonia into 250-ml titrator beaker containing 50 ml H_3BO_3 solution. Titrate with standard HCl to end point pH setting of 4.60 on automatic titrator.

Calculations

$$N\ (pct.) = ((A - B)/C) \times N \times 1.4$$

where
A = Volume HCl sample (mL)
B = Volume HCl blank (mL)
C = Sample weight (g)
N = Normality of acid

Report on ovendry basis.

Semimicro Kjeldahl (6B2)

Apparatus
Aminco-Koegel semimicro rotary digestion rack and steam-distillation apparatus.

Reagents
Concentrated sulfuric acid (H_2SO_4).

H_2SO_4, 0.01 N, standardized.
Sodium hydroxide (NaOH), 50-percent.

Boric acid (H_3BO_3), 2-percent.

Mixed indicator. Mix 0.1 g methyl red and 0.1 g brom cresol green and dissolve in 250 ml ethanol.

Salt mixture. Mix 790 g potassium sulfate (K_2SO_4), 100 g ferrous sulfate ($FeSO_4$), 100 g copper sulfate ($CuSO_4$), and 10 g selenium metal.

Procedure
   Using an analytical balance, weigh on a cigarette paper either 0.500 or 1.000 g ovendry soil that has been ground to about 0.2 mm. Roll soil in cigarette paper and drop into a 100-ml digestion-distillation flask. Add 2 g salt mixture 1 ml water, and 5 ml concentrated H_2SO_4. Swirl vigorously and digest, rotating the flask frequently until fumes are emitted. Continue digestion for at least 1 hour after mixture becomes white. Cool to room temperature and add 15 ml water. Shake until the contents of the flask are thoroughly mixed.

Ammonia Distillation (6B2a)

Procedure
        Measure 10 ml 2-percent H_3BOa with an automatic pipet into a 125-ml flask and add 0.5 ml mixed indicator. Place this flask under delivery tube. Connect digestion-distillation flask containing soil digested according to method 6B2 to the distillation unit by the ground-glass connection. Start steam passing through the system and slowly add 15 ml 50-percent NaOH. Distill for 12 minutes, add 0.5 ml more mixed indicator, and titrate the absorbed ammonia with 0.01 N H_2SO_4.

Calculations

$$N\ (pct) = (A/B) \times N \times 1.4$$

where
A = Volume H_2SO_4 (mL)
B = Sample weight (g)
N = Normality of H_2SO_4

Report on ovendry basis.

CHEMICAL ANALYSES (6)
IRON (6C)

Dithionite-Extraction (6C1)

Reagents
Sodium dithionite powder ($Na_2S_2O_4$).

Hydrochloric acid (HCl), 10-percent.

Apparatus
8-oz Pyrex nursing bottles or 250-ml flat-bottomed centrifuge bottles.

Procedure
Place 4 g soil, ground to 80 mesh, in a nursing or centrifuge bottle. Add 4 g $Na_2S_2O_4$ and 75 ml water. Stopper and shake overnight or for 16 hours. Then adjust the pH to 3.5 to 4.0, if necessary, with 10-percent HCl. Let stand for no less than 1 hour, stirring four or five times. Transfer the suspension to a graduated cylinder, dilute to 200 ml with water, and mix. Centrifuge or filter a part of the suspension and transfer 50 ml of the clear solution to a 250-ml beaker.

References
Kilmer (1960).

Dichromate Titration (6C1a)

Reagents
Hydrogen peroxide (H_2O_2), 35-percent.

Ammonium hydroxide (NH_4OH), 1:1.

Hydrochloric acid (HCl), 1:1.
Stannous chloride ($SnCl_2$). Dissolve 1 g $SnCl_2$ in 2 to 4 ml concentrated HCl and dilute to 50 ml with water; prepare fresh each time.

Mercuric chloride ($HgCl_2$), saturated aqueous solution.

Phosphoric acid (H_3PO_4), 85-percent.

Potassium dichromate ($K_2Cr_2O_7$), 0.100 *N*, standard.

Barium diphenylaminesulfonate, 0.16-percent aqueous solution.

Procedure

Add 10 to 15 ml H_2O_2 (6C1) to the solution to destroy any excess reducing agent. Cover the beaker with a watchglass and warm on a hot plate until the reaction starts. Set the solution aside until the reaction subsides and then boil for 10 to 15 minutes. Add a slight excess of 1:1 NH_4OH and boil the solution for 15 to 20 minutes to insure complete removal of H_2O_2. Dissolve $Fe(OH)_3$ by adding 1:1 HCl through the lip of the beaker. Usually 10 to 15 ml are enough. Heat the solution to 90° C and reduce by adding $SnCl_2$ by drops, stirring until the yellow color just disappears. Add three to four drops more. Cool the solution to room temperature and add 15 ml $HgCl_2$ solution all at once. A light silky precipitate of Hg_2Cl_2 forms if the proper amount of $SnCl_2$ has been added. Dilute the solution to 100 to 150 ml and add 5 ml H_3PO_4. Add 10 drops of barium diphenylaminesulfonate and titrate the solution with standard $K_2Cr_2O_7$ to a violet-blue end point.

Calculations

$$Fe \ (pct.) = (A/B) \ x \ N \ x \ (C/D) \ x \ 5.58$$

where
A = Volume $K_2Cr_2O_7$ (mL)
B = Sample weight (g)
N = Normality of $K_2Cr_2O_7$
C = Volume extract (mL)
D = Volume aliquot (mL)

$$Fe_2O_3 \ (pct.) = Fe \ (pct.) \ x \ 1.43$$

Report on ovendry basis.

EDTA Titration (6C1b)

Reagents
Hydrogen peroxide (H_2O_2), 35-percent.
Ammonium persulfate (($NH_4)_2S_2O_8$).

Salicylic acid, 1-percent in 95-percent ethanol.

EDTA, standardized as g iron per ml EDTA. Prepare EDTA as described in 6N1a.

Iron standard, 0.500 g iron per liter.

Procedure

Pipet a 5- to 25-ml aliquot from the centrifuge tube of procedure 6C1 into a 250-ml beaker. Add 50 ml water to the beaker. Then add by drops 5 ml H_2O_2 and digest over low heat until bubbling from the decomposing H_2O_2 ceases. Remove immediately to avoid precipitation of Fe_2O_3 in samples high in iron. Caution: Add H_2O_2 slowly to prevent liberation of elemental sulfur from any remaining $Na_2S_2O_4$. Keep the volume in the beaker to about 50 ml during the digestion by adding water if necessary. Remove from heat and cool. Adjust the pH between 2.0 and 3.0 with a pH meter, using either concentrated acetic acid or a 20-percent NaOAc solution. Add a few milligrams ($NH_4)_2S_2O_8$ to the solution to insure total oxidation of iron. Then add 1 ml indicator (1-percent salicylic acid) and titrate with 0.02 N EDTA to a pale yellow or colorless end point.

Calculations

$$Fe \ (pct.) = (A/B) \ x \ V \ x \ (C/D) \ x \ 100$$

where
A = Volume EDTA (mL)
B = Sample weight (g)
V = Titer of EDTA in g Fe/ml EDTA
C = Volume extract (mL)
D = Volume aliquot (mL)

$$Fe_2O_2 \text{ (pct.)} = Fe \text{ (pct.)} \times 1.43$$

Report on ovendry basis.

References
Cheng, Bray, and Kurtz (1953).

Dithionite-Citrate Extraction (6C2)

Reagents
Sodium dithionite ($Na_2S_2O_4$)

Sodium citrate

Superfloc flocculating agent, 0.2 percent in water

Procedure
        Weigh 1 to 4 g of soil (approximately 0.2 g maximum extractable iron) into an 8-oz nursing bottle. Add 2 g sodium dithionite and 20 to 25 g sodium citrate. Make up to 4 oz with water, and shake overnight in a reciprocating shaker. Add 2 ml Superfloc solution to the suspension, make up to 8 oz with water, shake vigorously for 15 s and allow to settle for at least 1 hr. This extract is used for analysis of iron (6C2b), aluminum (6G7a), and manganese (6D2a).

References
Holmgren (1967).

Orthophenanthroline Colorimetry (6C2a)

Apparatus
Seligson pipet, 0.1-ml.

Reagents
Orthophenanthroline, 0.25-percent.

Iron solution, 1000 mg per liter, standard.

Sodium dithionite powder ($Na_2S_2O_4$).

Sodium citrate crystals.

Superfloc flocculating agent, 0.2-percent, in water.

Procedure

Add 5 drops Superfloc solution to the dithionite-treated soil suspension (6C2) and make to 8 oz. Shake vigorously for about 15 seconds and allow to settle. Pipet a 0.1-ml aliquot with a Seligson pipet into a 25-ml volumetric flask. Add water to about 10 ml. Using a small scoop, tap a pinch of dithionite and a pinch of sodium citrate into the flask. Add 0.5 ml 0.25-percent orthophenanthroline and make to volume. Shake and read in a colorimeter at 508 Mμ after 1 hour. To prepare the standards, pipet 5-, 10-, 25-, 50-, 100-, 150-, and 200-ml aliquots of standard iron solution (1000 mg/L) into 8-oz shaking

Potassium thiocyanate (KSCN), 20-percent.

Hydrogen peroxide (H_2O_2), 30-percent.

Procedure

Transfer suitable aliquot (0.5 to 3 ppm iron in final solution) to 50 ml-volumetric flask. Add water to 35 ml, 1 drop H_2O_2, 5 ml HCl, and 5 ml KSCN solution. Make to volume and read at 490 mμ in colorimeter.

Calculations

$$Fe \ (pct.) = (A/B) \ x \ (C/D) \ x \ 0.005$$

where
A = Fe from curve (mg)
B = Sample weight (g)
C = Volume extract (mL)
D = Volume aliquot (mL)

$$Fe_2O_3 \ (pct.) = Fe \ (pct.) \ x \ 1.43$$

Report on ovendry basis.

References
Jackson (1958).

Pyrophosphate-Dithionite Extraction (6C4)

Reagents
Pyrophosphate solution. Dissolve 89.2 g $Na_4P_2O_7 \cdot 10H_2O$ in 800 to 900 ml water. Adjust the pH of this solution to 8.0 by adding hydrogensaturated exchange resin. Decant or filter, wash the resin, and dilute the solution to 1000 ml to make 0.2 M $Na_4P_2O_7$.

Sodium dithionite ($Na_2S_2O_4$).

Digestion acid. 10 Parts concentrated HNO_3, 4 parts concentrated H_2SO_4, and 4 parts concentrated $HClO_4$.

Procedure

Mix 80 ml pyrophosphate solution and 2.0 g solid sodium dithionite in a beaker and add this solution to 4 g soil in a centrifuge tube (pH 8.0 pyrophosphate solution and dithionite combined in this ratio result in a solution having a pH of about 7.3). Continue the extraction for 30 minutes at 50°C, shaking the suspension in the tube every 5 minutes. Centrifuge the suspension 5 to 10 minutes at 2000 rpm. Dilute the extract to 100 ml (solution A).

Immediately transfer 5 ml solution A to a beaker. Add 1 to 2 ml digestion acid and heat on a hot plate until almost dry to destroy the organic and hydrolyze pyrophosphate to orthophosphate. Allow to cool, dissolve the salts in HCl, and dilute to 100 ml (solution B). Determine iron and aluminum in solution B by appropriate methods, such as 6C3a and 6G1a.

References
Franzmeier, Hajek, and Simonson (1965).

Sodium Pyrophosphate Extraction (6C5)

Reagents
Sodium pyrophosphate ($Na_4P_2O_7$), 0.1 *M*.

Superfloc solution, 0.4 percent.

Procedure
        Place 2 g soil into 250-ml centrifuge bottle (polypropylene). Add 200 ml 0.1 *M* $Na_4P_2O_7$, cap, and shake overnight. Add 5 to 10 drops 0.4-percent Superfloc, shake, and centrifuge at 2000 rpm (Int. No. II centrifuge). Transfer the supernatant liquid to a plastic or glass container and reserve for Fe and Al analyses.
        The supernatant liquid must be clear in reflected light. If fine colloids are visible, repeat the procedures. If fine colloids are still present, spin the suspension in a super centrifuge until the supernatant liquid is clear. Foam rubber can be used in the centrifuge cups as a cushion for the 250-ml flat-bottom plastic bottles.

References
Bascomb (1968).

Atomic absorption (6C5a)

Apparatus
Atomic absorption spectrophotometer.

Reagents
Standard Fe solution, 0 to 50 ppm.

Procedure
        Establish standard curve and match readings from extract to curve readings. Dilute where necessary.

Calculations

$$Fe \ (pct.) = A \times (B/C) \times (1/10000) \times dilution$$

where
A = Fe (ppm)
B = Volume extract (mL)
C = Sample weight (g)

Report on ovendry basis.

Ammonium Oxalate Extraction (6C6)

Reagents
Ammonium oxalate $(NH_4)_2C_2O_4$ 0.2 *M*, pH 3.0.

Adjust the pH of 0.2 *M* $(NH_4)_2C_2O_4$ to 3.0 with 0.2 *M* oxalic acid ($H_2C_2O_4$).

Superfloc solution, 0.4 percent.

Procedure

  Place 2 g soil into 250-ml centrifuge bottle (polypropylene). Add 200 ml 0.2 M $(NH_4)_2C_2O_4$, cap, and shake immediately in the dark for 4 hours. Add 5 to 10 drops 0.4-percent Superfloc, shake, and centrifuge at 2000 rpm (Int. No. II centrifuge). Transfer the supernatant liquid to a plastic or glass container. Store in the dark and reserve for Fe and Al analyses.

  The supernatant liquid must be clear in reflected light. If fine colloids are visible repeat the procedure. If fine colloids are still present, spin the suspension in a supercentrifuge until the supernatant liquid is clear.

References

McKeague and Day (1965).

Atomic Absorption (6C6a)

  Proceed as in 6C5a except use extract from 6C6.

CHEMICAL ANALYSES (6)
MANGANESE (6D)

Dithionite Extraction (6D1)

  Extract 4.00 g soil as described in 6C1.

Permanganate Colorimetry (6D1a)

Reagents

Concentrated nitric acid (HNO_3).

Hydrogen peroxide (H_2O_2), 30-percent.

Phosphoric acid (H_3PO_4), 85-percent.

Sodium para periodate ($Na_3H_2IO_6$) or sodium meta periodate ($NaIO_4$).

Purified water diluent. Add 100 ml 80-percent H_3PO_4 and 1 g $Na_3H_2IO_6$ to 1 liter water (Mn-free); heat to boiling and digest for 1 hour; stopper with foil-covered stopper. About 85 ml of this diluent is needed for each sample.

$KMnO_4$, standard.

Procedure

  Take a 10- to 25-ml aliquot from the dithionite extract and place in a 150-ml beaker. Add 5 ml 30-percent H_2O_2, digest on hot plate, and evaporate until dry. Cool beaker and contents and add 3 ml concentrated HNO_3 and 2 ml 30-percent H_2O_2. Digest on hot plate for 30 minutes, using a close fitting cover glass, then raise cover glass, and evaporate until dry. Take up residue with 10 ml 85-percent H_3PO_4, heat to boiling, remove, and cool to about 50°C. Dilute with 10 ml water and add 0.2 g $Na_3H_2IO_6$. Cover beaker and heat to boiling. Cool to 50°C and add 62 ml purified water diluent and 0.1 g $Na_3H_2IO_6$. Digest at 90° C for 40 minutes or until no further color develops. Transfer the hot solution to a 100-ml volumetric flask, using purified water diluent to rinse the beaker. Cool, make up to volume with the diluent, stopper, and shake. Determine percentage transmittance with a photoelectric colorimeter at 540 mμ. Interpolate concentration from a standard absorbance concentration.

Calculations

$$Mn\ (pct.) = (A/B) \times (C/D) \times 54.9$$

where
A = MnO_4^- (meq/L)
B = Sample weight (g)
C = Volume extract (mL)
D = Volume aliquot (mL)

$$MnO\ (pct.) = Mn\ (pct.) \times 1.291$$

Report on ovendry basis.

References
Jackson (1958).

CHEMICAL ANALYSES (6)
CALCIUM CARBONATE (6E)

HCl Treatment (6E1)
Gas Volumetric (semiquantitative) (6E1a)

This procedure uses a simple leveling device to measure the volume of gas released when the soil is treated with HCl. It has an inherent error caused by the solubility of CO_2 in the HCl solution. Data on file at the laboratory at Lincoln, Nebr., indicate that the results are about 10 percent (8 to 12 percent) low for $CaCO_3$ equivalents ranging from 40 percent to 6 percent (1-g basis). For 1-percent equivalents the values are about 20 percent low and for less than 1 percent, the values have doubtful significance.

References
Association of Official Agricultural Chemists (1945).

Manometric (6E1b)

Apparatus
Wide-mouth prescription bottles, 3-oz, with bakelite cap; drill 7/16-in hole in cap for serum bottle stopper. Rubber gasket, 1 3/8 in OD x 15/16 in ID.

Serum bottle stopper.

Mercury manometer and a 26-gauge hypodermic needle attached to manometer tube.

Gelatin capsule. 1/4 oz.

Reagents
Hydrochloric acid (HCl), 6 *N.*

Glycerin.

Procedure

Place 2 g of soil in prescription bottle and add 5 ml water. Moisten lip of bottle with a drop of glycerin to ensure a good seal with rubber gasket. Fill gelatin capsule with HCl, put cap in place and invert to seal cap on capsule. Place, capsule in bottle and immediately cap the bottle. In a minute or two the HCl will dissolve the capsule. After 1 hr insert hypodermic needle through serum stopper and read manometer. Compare reading with those for standards prepared by treating aliquots of standard Na_2CO_3 solution in same manner as samples.

Vary sample weight according to $CaCO_3$ content as follows: For <25 percent $CaCO_3$, use 2 g soil; for 25 to 50 percent $CaCO_3$, 1 g soil; and for >50 percent $CaCO_3$, 0.5 g soil. For trace amounts, add a few drops 6 N HCl to soil and observe under binocular microscope. Evolution of gas bubbles indicates the presence of $CaCO_3$.

References

Williams (1948).

Gravimetric (weight loss) (6E1c)

Apparatus

See figure 6.

Reagents

Hydrochloric acid (HCl), 6 N.

Anhydrone $(Mg(ClO_4)_2)$.

Procedure

Assemble apparatus as shown in figure 6. Place a sample of soil containing less than 1 g $CaCO_3$ equivalent in a 125-ml Erlenmeyer flask. Wash down the sides of the flask with 10 ml water. Place 7 ml 6N HCl into vial C and then place the vial upright in the flask without spilling any acid. Moisten stopper G with glycerin, sprinkle with a small amount of 180-mesh abrasive to overcome slipperiness, and place the apparatus with stopcocks D and E, tubes I and J, attached firmly in position in the flask. Close stopcocks D and E. Place the apparatus beside the balance. Wait 30 minutes before weighing to allow temperature of the apparatus to equilibrate with temperature of air in the balance. Do all weighing with stopcock D open since a change in temperature of the flask with the stopcock closed results in a change in weight of the apparatus. Use tongs to place apparatus on the weighing pan, open stopcock D, weigh to 0.1 mg, and then immediately close stopcock D. Check the weight 10 minutes later to be certain that the weight of the flask has stabilized. Open stopcock D and then shake apparatus to upset the vial, allowing the acid to react with the carbonates. After 10 minutes, attach the rubber tube from the airdrying vessel to stopcock E. Open stopcock E and apply suction at stopcock D to give 5 to 10 bubbles per second at the base of tube J to sweep out CO_2. Shake the flask after 10 minutes and again after 20 minutes. After 30-minutes sweeping time, stop the suction and close stopcocks D and E. Return apparatus to the balance. Delay weighing for 1 hour to allow the heat generated by absorption of water by the anhydrone to be dissipated. Weigh apparatus with stopcock D open. Check the weight after 10 minutes.

Calculations

$$\text{Carbonate as } CaCO_3 \text{ (pct.)} = ((A - B)/C) \times 228$$

where
A = Initial weight of flask (g)
B = Final weight of flask (g)
C = Sample weight (g)

Report on ovendry basis.

References
Erickson et al. (1947).

Gravimetric (weight gain) (6E1d)

Proceed as in 6E1c except add additional trap containing CO_2-absorbing Ascarite to end of gas train. Weigh Ascarite bulb before and after CO_2 evolution. Weight gain equals the CO_2 evolved from the sample. Better results are obtained if the Ascarite is size-graded so that CO_2 passes through the coarser material first. Indicarb can be used in place of Ascarite.

Titrimetric (6E1e)

Reagents
Hydrochloric acid (HCl), 0.5 *N*, standardized.

Sodium hydroxide (NaOH), 0.25 *N*, standardized.

Phenolphthalein, 1 percent in 60-percent ethanol.

Procedure
Place 5 to 25 g soil in a 150-ml beaker, add exactly 50 ml HCl, cover with a watchglass, and boil gently for 5 minutes. Cool, filter, and wash all the acid from the soil with water. Determine the amount of unused acid by adding 2 drops of phenolphthalein and back-titrating with NaOH.

Calculations

$$\text{Carbonate as } CaCO_3 \text{ (pct.)} = ((50 \text{ x } A - B \text{ x } C)/D) \text{ x } 5$$

where
A = Normality of HCl
B = Volume NaOH (mL)
C = Normality of NaOH
D = Sample weight (g)

Report on ovendry basis.

References
Richards (1954)

Warburg Method (6E1f)

Apparatus
Warburg manometer, mercury filled.

Warburg reaction vessel, 15-ml capacity, with vented stopper for sidearm.

Constant temperature bath.

Reagents
HCl, 1:1. Na_2CO_3 solution for standard curve. Dissolve 1.06 g Na_2CO_3 in water and make to 1 liter. Solution contains 1.06 mg Na_2CO_3 per ml or the equivalent of 1 mg $CaCO_3$ per ml. Obtain standard curve by measuring CO_2 pressure from 1, 2, 4, 6, 8, and 10 ml Na_2CO_3 solution.

Procedure
Weigh 100 mg sample of finely ground soil and transfer to Warburg reaction vessel. Be careful not to get any sample in center well. Pipet 1 ml water into vessel and mix well with sample. Pipet 1 ml 1:1 HCl into sidearm, insert greased stopper, and leave in vent-open position. Attach reaction vessel to manometer and fasten with rubber bands or spring supports. Place reaction vessel in constant temperature bath at 25°C for 5 to 10 minutes to bring flask contents to temperature of water bath. Remove flask from bath, close stopper vent, and fasten with rubber bands or springs. Tilt flask to allow acid to flow from sidearm into reaction vessel, mix contents, and return vessel to water bath. Let stand for at least 30 minutes before reading manometer. Use the standard curve to convert the difference between the two manometer arm readings (mm), to milligrams $CaCO_3$. Gently tap the manometer holder occasionally to
prevent low readings caused by mercury adhering to manometer walls.

Sensitive Qualitative Method (6E2)
Visual, Gas Bubbles 6E2a)

Add few drops 6 N H_2SO_4 to soil and observe under binocular microscope. Evolution of gas bubbles indicates the presence of $CaCO_3$.

H_2SO_4 Treatment (6E3)
Gravimetric (weight gain) (6E3a)

Apparatus
See figure 3, procedure 6A1b.

Reagents
Sulfuric acid (H_2SO_4). Dissolve 57 ml concentrated H_2SO_4 and 92 g of $FeSO_4 \cdot 7H_2O$ in 600 ml water, cool, and dilute to 1000 ml. This solution is approximately 2 N in acidity and contains 5-percent $FeSO_4$ as anti-oxidant. Keep well stoppered.

Procedure
Place a 1- to 5-g sample of ovendry soil in the digestion flask E and connect condenser D. Weigh the Nesbitt bulb, attach to the system, and adjust the carrier stream to a flow rate of 1 or 2 bubbles per second. Pour 25 ml of the acid solution into the funnel and let it enter the digestion flask E. Close the stopcock immediately. Apply heat slowly and bring contents of flask to a boil in about 4 minutes. Continue gentle boiling for exactly 3 minutes more for a total heating period of 7 minutes. Remove the flame, adjust the carrier stream to 6 or 8 bubbles per second, and continue aerating for 10 minutes. Disconnect the Nesbitt bulb and weigh.

Calculations

$$\text{Carbonate as } CaCO_3 \text{ (pct.)} = ((A - B)/C) \times 227$$

where
A = Final weight of bulb (g)
B = Initial weight of bulb (g)
C = Sample weight (g)

Report on ovendry basis.

References
Allison (1960).

CHEMICAL ANALYSES (6)
GYPSUM (6F)

Water Extract (6F1)
Indirect Estimate (6F1b)

Add a weighed quantity of soil to enough water to dissolve all the gypsum by overnight shaking. The concentration of sulfate in this dilute soil:water extract should be <10 meq/L. Gypsum can be estimated by method 6F2. If crystals are observed or estimated gypsum content is >5 percent, the <2-mm sample should be ground to approximately 80 mesh. Determine total sulfate in this extract by any appropriate procedure. Also determine Ca and SO_4 in a saturation extract by any appropriate procedure.

Calculations

$\text{Gypsum} = (SO_4)_{DE} - (SO_4)_{\text{non-gypsum SE}}$

but $SO_{4\ \text{non-gypsum SE}} = (SO_4)_{SE} - (SO_4)_{\text{gypsum SE}}$

@ $\text{gypsum} = (SO_4)_{DE} + (SO_4)_{\text{gypsum SE}} - (SO_4)_{SE}$

$(SO_4)_{DE} = SO_4$ in dilute water extract

$(SO_4)_{SE} = SO_4$ in saturation extract

$(SO_4)_{\text{gypsum SE}} = 30$ meq/L if SO_4 and Ca are $\geq$ 30 meq/L

$= (SO_4)_{SE}$ if $(Ca)_{SE} > (SO_4)_{SE}$

$= (Ca)_{SE}$ if $(Ca)_{SE} < (SO_4)_{SE}$

All quantities are reported in meq/100 g.

$$\text{Gypsum (pct.)} = \text{Gypsum (meq/100 g)} \times 0.0861 \text{ (g/meq)}$$

References
Lagerwerff, Akin, and Moses (1965).

Ion Chromatograph (6F1c)

Apparatus
DIONEX Model 2110i ion chromatograph

Recorder (1 volt input).

Voltage stabilizer.

Reagents
0.1 M Na$_2$CO$_3$.

0.003 M NaHCO$_3$.

0.0024 M Na2CO$_3$.

1 N H$_2$SO$_4$.

Mixed standard solutions:
Fluoride 0.0125 to 5.0 meq/L.

Chloride 0.01 to 4.0 meq/L.

Nitrate 0.025 to 10.0 meq/L.

Sulfate 0.05 to 20.0 meq/L.

All solutions are filtered through a polycarbonate membrane having 0.4μm pore size. Soil extracts are filtered with a disposable filter unit (Millix^{TM}) having 0.22μm pore size.

Procedure
The soil extract is obtained as described in 6F1a. Fill a plastic syringe (3 to 10 cc) with a solution having a concentration within the range of the sulfate standard. Baseline is established using a full-scale μmhos setting of 3 before each determination. This setting is adjusted as needed, keeping in the range used for making the determinations on the mixed standard. Peak height readings are made on the mixed standard using eight concentrations. A curve fitting linear regression equation [$y(meq/L) = a_1 (PKH) + a_0$] is established for the sulfate standards. Sulfate concentration in the soil extracts is determined by this equation.

Calculations
See 6F1b.

Weight Loss (6F2)

Apparatus
Vacuum desiccator.

Aluminum dish.

Balance, 0.001-g sensitivity.

Reagents

Phosphorus pentoxide (P_2O_5).

Procedure

Place about 10 g of soil in a tared (Wt A) aluminum dish. Saturate sample with water and let stand overnight to air-dry. Place in a vacuum desiccator with P_2O_5 desiccant. Evacuate desiccator and allow to stand 48 hr. Remove dish from desiccator and weigh (Wt B), then place in oven at 105° C for 24 hr. Allow dish to cool in desiccator and weigh (Wt C).

Calculations

$$Gypsum \ (pct.) = ((WtB - WtC) \times 100)/((WtB - WtA) \times 0.1942)$$

The theoretical crystal water content of gypsum is 20.91 percent. However, Nelson et al. have determined that, in practice, this content averages 19.42 percent.

References

Nelson, Klameth, and Nettleton (1978).

Gypsum Requirement (6F5)

The amount of gypsum needed to replace all of the sodium on the exchange complex with calcium is the gypsum requirement.

Reagents

Saturated gypsum solution. Place about 25 g gypsum ($CaSO_4$-$2H_2O$) in 5 L water in a large flask, stopper, and shake by hand periodically for 1 hr or more. Let settle and decant through a filter into storage bottle. Determine calcium concentration by titration of an aliquot with standard EDTA solution using Eriochrome black T as indicator.

EDTA solution. Dissolve 1.25 g di-sodium ethylenediamine tetraacetate in water and dilute to 1 L. Standardize against solutions containing known concentrations of Ca and Mg.

Buffer solution. Dissolve 6.75 g ammonium chloride in about 400 ml water. Add 570 ml concentrated ammonium hydroxide and dilute to 1 L with distilled water.

Eriochrome black T indicator. Dissolve 1 g Eriochrome black T in 100 ml triethanolamine.

Procedure

Weigh 5 g soil into flask, add 100 ml saturated gypsum solution, stopper, and shake for 5 min in mechanical shaker. Filter through folded filter paper, discarding the first few milliliters of filtrate, which may be cloudy. Pipet a 5-ml aliquot of filtrate into a 125-ml Erlenmeyer flask and dilute to 25 or 30 ml with distilled water. Add 10 drops of buffer solution, 2 drops Eriochrome black T indicator, and titrate with standard EDTA solution to blue end point.

Calculations

$$Gypsum \ requirement \ (meq/100 \ g) = (A - B) \times 2$$

where
A   = Ca concentration of gypsum solution (meq/L)
B   = Ca + Mg concentration of filtrate (meq/L)

References

Richards (1954).

CHEMICAL ANALYSES (6)
ALUMINUM (6G)

KCl Extraction I (30 min) (6G1)

Reagents

Potassium chloride (KCl), 1 *N*.

Procedure

      Weigh 10-g soil samples into 125-ml Erlenmeyer flasks. Add 50 ml 1 *N* KCl to each flask, mix several times, and let stand for 30 minutes. Filter through 5.5-cm Whatman No. 42 filter paper in Buchner funnel, using suction as necessary. Leach each sample as rapidly as possible with about five 9-ml portions of KCl, using the first to help transfer the remaining soil in the Erlenmeyer flasks to the Buchner funnels. Transfer the extract to 100-ml volumetric flasks and dilute to volume with the extracting solution. Or use Allihn leaching tubes and bring to standard weight in tared suction flasks.

References

Lin and Coleman (1960) and Pratt and Bair (1961).

Aluminon Colorimetry I, Hot Color Development (6G1a)

Reagents

Thioglycolic acid ($HSCH_2COOH$). Dilute 1 ml purified acid to 100 ml with water.

Aluminon reagent. Dissolve in separate containers 0.75 g

Aluminon (ammonium aurine tricarboxylate), 15 g gum acacia, and 200 g NH_4OAc crystals. To the NH_4OAc solution add 189 ml concentrated HCl, then the gum acacia, and finally the Aluminon. Mix, filter, and dilute to 1,500 ml with water. To get the gum acacia in suspension, add slowly to boiling water while stirring constantly.

Aluminum standard. Add 2.24 g $AlCl_3 \cdot 6H_2O$ per liter of water. This solution should be nearly 250 ppm aluminum. Check concentration of an aliquot containing 10 ppm aluminum by analyzing for chloride.

Procedure

      If samples contain less than 5 meq per 100 g aluminum, pipet a 1-ml aliquot of each extract into numbered and calibrated test tubes. If more aluminum is present, dilute before the aliquot is taken. Dilute to approximately 20 ml with distilled water. Add 2 ml dilute thioglycolic acid to each tube, stopper, and shake all the tubes. Pipet 10 ml Aluminon into each tube and dilute to exactly 50 ml. The pH should be between 3.7 and 4.0. Stopper and shake all tubes. Place tubes in a rack and heat in a boiling-water bath for 4 minutes. Cool in running water to room temperature. Transfer samples to reading tubes and measure light transmittance at 535 mμ and compare with a standard curve.

Calculations

$$Al\ (meg/100g) = (A/B) \times (C/D) \times (9/5)$$

where
A   = Al from curve (mg/L)
B   = Sample weight (g)
C   = Volume extract (mL)
D   = Volume aliquot (mL)

Report on ovendry basis.

References
Chenery (1948) and Yoe and Hill (1927).

Aluminon Colorimetry II, HCl Predigestion (6G1b)

Procedure
Proceed as in 6G1a but first add 3 ml N HCl to the aliquot and heat for 30 minutes at 80 to 90° C.

References
Hsu (1963).

Aluminon Colorimetry III, Overnight Color Development (6G1c)

Proceed as in 6G1a except eliminate boiling-water bath, adjust pH to 4.0, and allow color to develop overnight before reading.

Fluoride Titration (6G1d)

Reagents
Potassium fluoride (KF), 1 N. Titrate with NaOH to a phenolphthalein end point. This eliminates the need for a blank correction in the Al titration.

Sodium hydroxide (NaOH), 0.1 N, standardized.

Sulfuric acid (H_2SO,), 0.1 N, standardized.

Phenolphthalein, 0.1 percent.

Procedure
Add 6 to 8 drops phenophthalein to the leachate in the suction flask (6G1). Titrate with standard NaOH to a pink color that persists for 30 seconds or more. Correct for a KCl blank to obtain KCl extractable acidity. Then add 10 ml KF, and titrate with standard H_2SO_4 until the pink color disappears. Set aside while other samples are titrated and then complete to a lasting colorless end point. If there is a considerable amount of Al, add a few more drops of phenolphthalein.

Calculations

$$Acidity\ (meq/100\ g) = (A/B) \times N \times 100$$

where
A = Volume NaOH (mL)
B = Sample weight (g)
N = Normality of NaOH

$$Al(meq/100) = (A/B) \times N \times 100$$

where
A = Volume H_2SO_4 (mL)
B = Sample weight (g)
N = Normality of H_2SO_4

References
Yuan (1959).

Atomic absorption (6G1e)

Apparatus
Perkin-Elmer Model 290 atomic absorption spectrophotometer with nitrous oxide burner attachment.

Reagents
Standard Al solution, 0 to 5 meq per liter.

Procedure
Dilute sample to within range of standard curve. Compare absorbance with standard curve.

Calculations

$$Al \ (meq/100 \ g) = (A/B) \times dilution \times (C/10)$$

where
A = Al from curve (meq/L)
B = Sample weight (g)
C = Volume extract (mL)

KCl Extraction II, Overnight (6G2)

Weigh 10 g soil into 125-ml Erlenmeyer flask. Add 50 ml 1 *N* KCl and let stand overnight. In the morning transfer to filter funnels and leach with an additional 50 ml KCl.

Aluminon Colorimetry I (6G2a)

Follow procedure for aluminum analysis described in 6G1a.

NH$_4$OAc Extraction (6G3)

Prepare soil as described in 5A1.

Aluminon Colorimetry III (6G3a)

Follow procedure of 6G1c.

NaOAc Extraction (6G4)

Prepare soil as described in 5A2.

Aluminon Colorimetry III (6G4a)

Follow procedure of 6G1c.

Sodium Pyrophosphate Extraction (6G5)

Prepare extract as described in 6C5.

Atomic Absorption (6G5a)

Apparatus
Atomic absorption spectrophotometer.

Reagents
Standard Al solution, 0 to 50 ppm or 0 to 160 ppm.

Procedure
Establish standard curve and match readings from extract to curve readings. Dilute where necessary.

Calculations

$$\text{Al (pct.)} = A \times (B/C) \times (1/10000) \times \text{dilution}$$

where
A = Al (ppm)
B = Volume extract (mL)
C = Sample weight (g)

Report on ovendry basis.

Ammonium Oxalate Extraction (6G6)

Prepare extract as described in 6C6.

Atomic absorption (6G6a)

Analyze extract as described in 6G5a.

NH$_4$Cl, Automatic Extractor (6G8)

Prepare extract as described in 5A9.

Atomic Absorption (6G8a)

Apparatus
Atomic absorption spectrophotometer.

Reagents
Standard Al solutions, 0 to 6 meq/L

Procedure
Compare absorbance of samples from 5A9 with that of standards at 309.3 nm, diluting if necessary.

Calculations

$$Al\ (meq/100\ g) = (A/B) \times dilution \times (C/10)$$

where
A   = Al (meq/L)
B   = Sample weight (g)
C   = Volume extract (mL)

Report on ovendry basis.

CHEMICAL ANALYSES (6)
EXTRACTABLE ACIDITY (6H)

BaCl$_2$-Triethanolamine I (6H1)

Extractable acidity data are reported on some data sheets as exchange acidity and on others as extractable H$^+$.

Reagents
Buffer solution. Barium chloride, 0.5 *N*, and triethanolamine, 0.2 *N*. Add about 90 ml, 1 *N* HCl per liter to adjust pH to 8.2. Protect the buffer solution from CO$_2$ of the air by attaching a drying tube containing soda lime (sodium calcium hydrate) to the air opening at the top of the solution bottle.

Replacement solution. Barium chloride, 0.5 *N*. Add 5 ml buffer solution per liter. Protect the. replacement solution from CO$_2$ of the air by attaching a drying tube similar to that used for the buffer solution.

Procedure
Weigh 5 g soil into a 125-ml Erlenmeyer flask. Add 15 ml buffer solution and let stand for 30 minutes, swirling occasionally to mix. Use 35 ml buffer solution to transfer all the soil solution to a No. 4 Gooch crucible containing a moist Whatman No. 540 filter paper and filter into a 500-ml suction flask. The rate of filtration should be such that at least 30 minutes is needed to complete the filtering and leaching. Then leach the soil with 100 ml of the replacement solution, adding small amounts at a time. It may be necessary to use a larger amount of buffer solution to leach allophanic soils high in organic matter with extractable acidity of more than 35 meq per 100 g.

Back-Titration with HCl (6H1a)

Reagents
Hydrochloric acid (HCl), 0.2 N, standardized.

Brom cresol green, 0.1-percent aqueous solution.

Mixed indicator. Dissolve 1.250 g methyl red indicator and 0.825 g methylene blue in 1 liter 90-percent ethanol.

Procedure
    Run a blank by adding 100 ml replacement solution, 2 drops brom cresol green, and 10 drops mixed indicator to 50 ml buffer solution. Titrate with HCl to a chosen end point in the range from green to purple. Add 2 drops brom cresol green and 10 drops mixed indicator to the leachate and titrate to the same end point chosen for the blank. Calculate exchange acidity *(EA)* as follows.

Calculations

$$EA \text{ (meq/100 g)} = ((A - B)/C) \times N \times 100$$

where
A = Volume HCl blank (mL)
B = Volume HCl sample (mL)
C = Sample weight (g)
N = Normality of HCl

Report on ovendry basis.

References
Peech et al. (1947).

BaCl$_2$-Triethanolamine II (6H2)

Apparatus
Sulfur absorption tubes.

Whatman No. 41 filter paper or glass-fiber filter paper cut to fit sulfur absorption tubes.

Reagents
Buffer solution. BaCl$_2$, 0.5 N, and triethanolamine, 0.2 N as in 6H1.

Mixed indicator. Dissolve 1.250 g methyl red and 0.825 g methylene blue in 1 liter 90 percent ethanol.

Celite.

Procedure
    Stopper bottom of sulfur absorption tubes with medicine-dropper bulbs and fit to a 300-ml suction flask with a rubber stopper. Place Whatman No. 41 filter paper in bottom of absorption tube, cover with 1/4 inch of acid-washed sand, and add exactly 25 ml buffer solution. Weigh 10 g soil and mix with teaspoonful of Celite. Add to the absorption tube by means of a funnel. After 30 minutes remove the medicine-dropper bulbs, wash bulbs out with a little water, and add washings to absorption tubes. Leach with 25 ml more buffer solution and then leach with 100 ml replacement solution in small increments. If necessary, use suction to facilitate leaching.

Back-Titration with HCl (6H2a)

Reagents
Same as in 6H1a.

Procedure
Titrate with standard HC1, using either 2 drops brom cresol green and 10 drops methyl red or 10 drops mixed indicator. Use same end point as that chosen for a blank run by leaching sand and Celite with 50 ml buffer solution and 100 ml replacement solution.

Calculations
Use same calculation as in 6H1a.

KCl-Triethanolamine (6H3)

Back-titration with NaOH (6H3a)

Procedure
        Leach 10 g soil with 50 ml KCl-triethanolamine solution and follow by washing with 50 ml unbuffered 1 *N* KCL. Add a known volume of standard acid to leachate and washings and back-titrate with standard alkali (NaOH). Titrate an equal volume of acid to the same end point for a blank.

Calculations

$$EA \text{ (meq/100 g)} = ((A - B)/C) \times N \times 100$$

where
A = Volume NaOH sample (mL)
B = Volume NaOH blank (mL)
C = Sample weight (g)
N = Normality of NaOH

References
North-Central Regional Research Committee (1955).

BaCl$_2$-Triethanolamine III (6H4)

Apparatus
60-ml plastic syringe barrels.

Reagents
Buffer solution. Barium chloride, 0.5 *N*, and triethanolamine, 0.2 *N*. Add l *N* HCl (about 90 ml/L) to adjust pH to 8.2. Protect the buffer solution from CO_2 of the air by attaching a drying tube containing soda lime (sodium calcium hydrate) to the air opening at the top of the solution bottle.

Replacement solution. Barium chloride, 0.5 *N*. Add 5 ml of above buffer solution per liter. Protect the replacement solution from CO_2 of the air by attaching a drying tube similar to that used for the buffer solution.

"Celite" filter pulp.

Procedure

Prepare syringe barrels as leaching tubes by forcing a 1-g ball of filter pulp into bottom of barrel with syringe plunger. Measure 1.5 g celite and 5 g soil sample into tube. Attach pinch clamp to delivery tube of syringe barrel and add approximately 25 ml buffer solution to sample. Let stand 30 min, stirring occasionally. Remove pinch clamp and filter with low suction into titrator beaker using a total of 50 ml buffer solution followed by 100 ml replacement solution.

References
Peech (1947).

Back-Titration with HCl, Automatic Titrator (6H4a)

Reagents
Hydrochloric acid (HCl), 0.33 N, standardized.

Procedure

Titrate the leachate contained in the 250-ml beaker to an end-point pH setting of 4.60 with automatic titrator. Carry reagent blank through procedure.

Calculations

$$\text{Extractable acidity (meq/100 g)} = ((A - B)/C) \times N \times 100$$

where
A = Volume HCl blank (mL)
B = Volume HCl sample (mL)
C = Sample weight (g)
N = Normality of HCl

Report on ovendry basis.

CHEMICAL ANALYSES (6)
CARBONATE (6I)

Saturation Extract (6I1)
Acid titration (6I1a)

Reagents
Sulfuric acid (H_2SO_4), 0.05 N, standardized.

Phenolphthalein.

Procedure

Pipet an appropriate aliquot of saturation extract into a 250-ml Erlenmeyer flask or a porcelain crucible. The electrical conductivity (EC X 10_3) of the saturation extract (8A1a) can be used to determine the aliquot to be used for carbonate, bicarbonate, and chloride determinations. Where EC X 10_3 is 1.0 or less, use a 10-ml aliquot; if 1.0 to 10.0, use a 5-ml aliquot; if more than 10.0, use a 2-ml aliquot.

Make volume to 50 ml (10 ml for porcelain crucible) with water. To the 50 ml in the Erlenmeyer flask, add a drop or two of phenolphthalein. If a pink color is produced, titrate with 0.05 N H_2SO_4, adding a drop every 2 or 3 seconds until the pink color disappears. Use this solution to determine bicarbonate (6J1a).

Calculations

$$\text{Carbonate (meq/L)} = (A/B) \times N \times 2000$$

where
A = Volume H_2SO_4 (mL)
B = Volume aliquot (mL)
N = Normality of H_2SO_4

References
Association of Official Agricultural Chemists (1945) and Richards (1954).

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CHEMICAL ANALYSES (6)
BICARBONATE (6J)

</div>

Saturation Extract (6J1)
Acid Titration (6J1a)

Reagents
Sulfuric acid (H_2SO_4), 0.05 N, standardized.

Methyl orange, 0.01-percent aqueous solution.

Procedure
Use solution remaining from carbonate titration (6I1a). To the colorless solution from this titration or to the original solution if no color is produced with phenolphthalein, add 4 drops methyl orange and continue titration to the methyl orange end point without refilling the buret. Retain this solution for the chloride determination (6K1a). Make a blank correction for the methyl orange titration.

Calculations

$$\text{Bicarbonate (meq/L)} = ((A - (2 \times B))/C) \times N \times 1000$$

where
A = Total volume H_2SO_4 (mL)
B = Volume H_2SO_4 from 6I1a (mL)
C = Volume aliquot (mL)
N = Normality of H_2SO_4

References
Association of Official Agricultural Chemists (1945) and Richards (1954).

CHEMICAL ANALYSES (6)
CHLORIDE (6K)

Saturation Extract (6K1)
Mohr Titration (6K1a)

Reagents

Potassium chromate (K_2CrO_4) indicator. Dissolve 5 g K_2CrO_4 in water and add a saturated solution of $AgNO_3$ until a permanent slight red precipitate is produced, filter, and dilute to 100 ml.

Silver nitrate ($AgNO_3$), 0.05 N, standardized.

Sodium bicarbonate ($NaHCO_3$), saturated solution (optional).

Nitric acid (HNO_3), 0.1 N (optional).

Procedure

To the solution from the bicarbonate titration (6J1a) add 6 drops K_2CrO_4 indicator and titrate with $AgNO_3$ to a reddish-orange end point. Make a correction with a blank of 50 ml water containing the indicators of both titrations. The laboratory at Riverside, Calif., modifies this procedure by adding saturated $NaHCO_3$ solution to a pink end point and neutralizing to a colorless end point with HNO_3 before adding the indicator.

Calculations

$$\text{Chloride (meq/L)} = ((A - B)/C) \times N \times 1000$$

where
A = Volume $AgNO_3$ sample (mL)
B = Volume $AgNO_3$ blank (mL)
C = Volume aliquot (mL)
N = Normality of $AgNO_3$

References
Association of Official Agricultural Chemists (1945).

Potentiometric Titration (6K1b)

Apparatus
Silver Billet combination electrode, No. 39187.

Zeromatic pH meter (expanded scale).

Reagents
Standard silver nitrate ($AgNO_3$), 0.025 N.

Buffer solutions. Either potassium acid phthalate or trisodium citrate and citric acid. To prepare phthalate buffer, weigh 37.5 g potassium acid phthalate and bring to a volume of 500 ml with water; 4 ml of this buffer added to a 46-ml solution brings the pH to about 4. To prepare trisodium citrate buffer, weigh 43.8 g trisodium citrate and 43.3 g citric acid into 500-ml volumetric flask and bring to volume with water. Add a small amount of toluene to the solution for storage; 10 ml of this buffer added to a 40-ml solution brings pH to about 4.

Procedure

Standardize the pH meter by adjusting the needle to a convenient setting (about 0.8) on the expanded scale when the electrode is immersed in buffer solution (4 or 10 ml made to 50 ml) without chloride. To titrate the sample, pipet an aliquot containing as much as 2.0 meq chloride into a beaker and add 4 ml buffer. Make to 50 ml. Immerse the electrode and buret tip into the beaker and titrate with $AgNO_3$ to the end point previously established for the buffer without chloride.

Calculations

$$\text{Chloride (meq/L)} = (A/B) \times N \times 1000$$

where
A = Volume $AgNO_3$ (mL)
B = Volume aliquot (mL)
N = Normality of $AgNO_3$

CHEMICAL ANALYSES (6)
SULFATE (6L)

Saturation Extract (6L1)
Gravimetric, $BaSO_4$ Precipitation (6L1a)

Reagents
Concentrated hydrochloric acid (HCl).

Barium chloride ($BaCl_2$), 10-percent.

Methyl orange, 0.01-percent.

Procedure

Pipet an aliquot of saturation extract into a 250-ml beaker. Dilute to approximately 100 ml with water. Add 2 drops methyl orange and 0.5 ml concentrated HCl to the beaker. Heat to boiling and add $BaCl_2$ solution by drops, stirring constantly until precipitation is complete. Let stand on hot plate for several hours. Remove from heat and let samples stand overnight. Filter through Gooch crucibles, which have been ignited and weighed. Dry in 105°C oven and ignite in muffle furnace at 1,200°F (650°C) for 30 minutes. Cool in desiccator and weigh.

Calculations

$$SO_4 \text{ (meq/L)} = (A/B) \times 8.568$$

where
A = $BaSO_4$ (mg)
B = Volume aliquot (mL)

References
Richards (1954).

EDTA Titration (6L1b)

Apparatus
Repipet, automatic dilutor, pipet range 0.1 to 1.0 ml.

Titration assembly including a 10-ml buret with magnetic stirrer.

Reagents
Thymol blue indicator, 0.04-percent.

Nitric acid (HNO_3), 0.4 *N*.

Calcium nitrate ($Ca(NO_3)_2$), 0.05 *N*. Dissolve 5.90 g $Ca(NO_3)_2 \cdot 4H_2O$ in 1 liter CO_2-free water. EC is 5.15 ± 0.15 mmhos per cm at 25°C.

Acetone, reagent grade, boiling range 55.5 to 57.5°C

Ethanol, 95-percent, reagent grade.

Hydrochloric acid (HCl), 0.01 *N*.

EDTA solution, 0.02 *N*. Standardize against $CaCl_2$.

Procedure
    Pipet an aliquot containing 0.01 to 0.05 meq SO_4 from soil-water extracts and transfer to a 100-ml beaker. Bring volume to 7.5 ± 0.5 ml with water. Add 2 drops 0.04-percent thymol blue and 0.4 *N* HNO_3 drop by drop until color changes from yellow to distinct red. Add 2 ml 0.05 *N* $Ca(NO_3)_2$, 20 ml acetone, and stir. Allow 30 minutes for the precipitate to flocculate. Place a 9.0-cm Whatman No. 42 filter paper in a 5.0-cm fluted funnel and fit snugly with water. Wash the sides of filter paper with 5 ml 95-percent ethanol from a wash bottle. Transfer the precipitate and supernatant to the filter paper with alcohol. Rinse the beaker twice and wash filter paper three times, using 3 to 5 ml ethanol per rinse. Allow the alcohol in the filter paper to evaporate. Wash the funnel stem thoroughly with water. Place the beaker that contained the $CaSO_4$ precipitate under the funnel and wash the filter paper with 3 to 5 ml portions of 0.01 *N* HCl until approximately 25 ml is leached. Proceed as in 6N1a, except eliminate carbamate and add an extra drop 4 *N* NaOH to neutralize the 25 ml 0.01 *N* HCl.
    The amount of sulfate is determined from the Ca^{++} content in the $CaSO_4$ precipitate.

Calculations

$$SO_4 \text{ (meq/L)} = (A/B) \times N \times 1000$$

where
A   = Volume EDTA (mL)
B   = Volume aliquot (mL)
N = Normality of EDTA

References
Bower and Wilcox (1965), Lagerwerff, Akin, and Moses (1965), and Nelson (1970).

NH_4OAc Extraction (6L2)

    Obtain extract by procedure 5B1.

Gravimetric, BaSO₄ Precipitation (6L2a)

Proceed as in 6L1a. A greater quantity of acid will be needed to lower the pH. Otherwise the procedures are the same.

CHEMICAL ANALYSES (6)
NITRATE (6M)

Saturation Extract (6M1)

Phenoldisulfonic Acid Colorimetry (6M1a)

Reagents
Phenoldisulfonic acid. Dissolve 25 g phenol in 150 ml concentrated H_2SO_4, add 75 ml fuming H_2SO_4 (13 to 15 percent SO_3), and heat at 100°C for 2 hours.

Standard potassium nitrate (KNO_3), 0.010 N.

Silver sulfate (Ag_2SO_4), 0.020 N.

Ammonium hydroxide solution (NH_4OH), 1:1, approximately 7 N.
Calcium oxide (CaO).

Procedure
First determine the chloride concentration in an aliquot of saturation extract as directed in 6K1a. Pipet another aliquot containing 0.004 to 0.04 meq of nitrate into a 25-ml volumetric flask. Add an amount of Ag_2SO_4 equivalent to the amount of chloride present, dilute to volume, and mix. Separate the precipitate by centrifuging the suspension in a 50-ml centrifuge tube. Transfer the solution to another centrifuge tube, flocculate any suspended organic matter by adding about 0.1 g CaO, and clear by centrifuging again. Pipet a 10-ml aliquot into an 8-cm evaporating dish. Evaporate the aliquot to dryness, cool, and dissolve the residue in 2 ml phenoldisulfonic acid. After 10 minutes, add 10 ml water and transfer to a 100-ml volumetric flask. Make alkaline by adding NH_4OH, dilute to volume, and mix. Measure light transmission through a 460 mμ filter of solution in an optical cell against that of water in a similar cell.
Prepare a calibration curve by pipetting 0-, 0.2, 0.4-, 0.8-, 1.2-, and 1.6-ml aliquots of standard KNO_3 into evaporating dishes and treating as for sample except for additions of Ag_2SO_4 and CaO and the clarifying procedure.

Calculations

$$NO_3 \text{ (meq/L)} = (A/B) \times 1000$$

where
A = NO_3 from curve (meq/L)
B = Volume aliquot (mL)

References
Richards (1954).

Diphenylamine (qualitative) (6M1b)

Use this procedure to test for nitrates if there is a significant excess of cations over anions in the extract. A quantitative measurement can be made if there is a positive indication of NO_3 (6M1a).

Reagents
Diphenylamine in H_2SO_4. Dissolve 0.05 g diphenylamine in 25 ml concentrated sulfuric acid. Store in polyethylene dropper bottle.

Procedure
Place a drop of extract in a spot plate and add 3 or 4 drops diphenylamine reagent. Nitrate is present if a blue color develops.

References
Treadwell and Hall (1943).

CHEMICAL ANALYSES (6)
CALCIUM (6N)

Saturation Extract (6N1)
EDTA titration (6N1a)

Reagents
Sodium hydroxide (NaOH), approximately 4 *N*.

Calcium chloride ($CaCl_2$), 0.02 *N*. Dissolve calcite crystals in HCl and make to volume.

Murexide. Thoroughly mix 0.5 g ammonium purpurate with 100 g powdered potassium sulfate (K_2SO_4).

EDTA solution, 0.02 *N*. Standardize against $CaCl_2$

Sodium diethyldithiocarbamate, 1-percent.

Procedure
Pipet an aliquot containing 0.02 to 0.20 meq of calcium into a beaker. Add 5 drops carbamate, 1 drop NaOH for each 5-ml aliquot, and a suitable amount (15 to 20 mg for a 10-ml aliquot) of murexide, mixing after each addition. A magnetic stirrer is helpful. Titrate with EDTA to a lavender end point. A blank containing NaOH, murexide, carbamate, and a drop or two of EDTA helps to distinguish the end point. If the sample is overtitrated with EDTA, it can be back-titrated with standard $CaCl_2$. Retain solution for magnesium determination (6O1a).

Calculations

$$Ca \ (meq/L) = (A/B) \ x \ N \ x \ 1000$$

where
A = Volume EDTA (mL)
B = Volume aliquot (mL)
N = Normality of EDTA

References
Cheng and Bray (1951).

NH₄OAc Extraction (6N2)

Prepare NH₄OAc extract as described in 5A1. EDTA-alcohol extraction.

EDTA-Alcohol Separation (6N2a)

Reagents

Standard calcium chloride ($CaCl_2$), 5 mg per ml. Dissolve calcite crystals in HCl and make to volume.

Ethanol, 95-percent.

Standard EDTA. Dissolve 1.25 g disodium ethylenediaminetetraacetate in water and dilute to a volume of 1 liter. Standardize against solutions containing known amounts of calcium and magnesium. Run the standards through the separation procedure before titrating.

Sodium hydroxide (NaOH), 10-percent aqueous solution.

Calcon. Dissolve 1 g Calcon (Eriochrome Blue Black R) in 100 ml triethanolamine.

Procedure

Pipet 25-ml aliquots from the pH 7, NH₄OAc extracts obtained in the total exchange-capacity procedure (5A1) into 100-ml beakers and evaporate to dryness at moderate heat. Cool and add 3 ml N HNO₃ to dissolve the residue. Transfer the solution quantitatively to 50-ml conical centrifuge tubes with ethanol, using a wash bottle with a fine delivery tip. Add 1 ml 6 N H₂SO₄. While mixing the contents of the tube by swirling, add approximately 34 ml 95-percent ethanol. Cover the tubes and let stand overnight. The next morning remove the covers and centrifuge the tubes at about 2000 rpm (Int. No. II centrifuge) for 15 minutes. Decant the alcohol solution into 250-ml Erlenmeyer flasks and retain for the magnesium determination. Use the CaSO₄ precipitate for calcium determination.

Break up the CaSO₄ precipitate with a small steam of water from a wash bottle and transfer the precipitate and solution to 250-ml Erlenmeyer flasks. Dilute the solution to a total volume of about 100 ml. Place the sample on a magnetic stirrer, add 5 ml 10-percent NaOH, 2 drops Calcon indicator solution, and titrate with the standard EDTA solution to the blue color of a blank carried through the procedure. The pH of the solution should be about 12.5. The color change is from red to clear blue. Titrate until the color in the sample and in the blank are the same.

Calculations

$$Ca \text{ (meq/100 g)} = (A/B) \times N \times (C/D) \times 100$$

where
A = Volume EDTA (mL)
B = Sample weight (g)
N = Normality of EDTA
C = Volume extract (mL)
D = Volume aliquot (mL)

References

Barrows and Simpson (1962).

Oxalate Precipitation I, KMnO$_4$ Titration (6N2b)

Reagents
Oxalic acid (C$_2$H$_2$O$_4$), 5-percent aqueous solution.

Brom cresol green, 0.04-percent aqueous solution.

Ammonium hydroxide (NH$_4$OH), 1 *N*.

Sulfuric acid (H$_2$SO$_4$), 1 *N*.

Standard potassium permanganate (KMnO$_4$), 0.05 *N*

Wash solution, saturated calcium oxalate (CaC$_2$2O$_4$)

Asbestos. Digest asbestos in 1 *N* HNO$_3$ solution containing just enough KMnO$_4$ to give a deep purple color. Add more permanganate if the color disappears; digest for 24 hours or until the permanganate color is permanent. Destroy the excess permanganate with oxalic acid and wash thoroughly on a Buchner funnel.

Procedure
        Transfer an aliquot of the filtrate (5A1) to a 400-ml Pyrex beaker and evaporate to complete dryness. Cool, cover the beaker with a watchglass, and slowly add through the lip 10 ml concentrated HNO$_3$ and 2 ml concentrated HCl. Warm until the reaction has subsided and no more brown fumes are given off. Rinse the watchglass into the beaker. Evaporate to dryness at low heat to prevent spattering and continue to heat for about 10 minutes to dehydrate the salts. Then place the beaker in an electric muffle furnace at about 150°C, heat to 390° ± 10°, and hold at this temperature for about 20 minutes. Remove the beaker from the muffle furnace and cool. Treat the residue with 3 ml 6 *N* HCl, evaporate to dryness at low heat, and continue heating for about 30 minutes longer to dehydrate silica. Cool and dissolve the residue in 0.1 *N* HNO$_3$, using a rubber policeman to loosen the residue.
        Add 5 ml oxalic acid, heat the contents of the beaker almost to boiling, and add 1 ml brom cresol green. Adjust the pH of the hot solution to approximately 4.6 by slowly adding 1 *N* NH$_4$OH, stirring constantly. Let digest at about 80° C for 1 hour or until the supernatant liquid is clear. Collect the CaC$_2$O$_4$ precipitate on a compact asbestos pad in a Gooch crucible or in a Whatman No. 42 filter paper in filter funnel. Rinse the beaker four times with water or water saturated with CaC$_2$O$_4$ and pour the washings into the crucible. Wash the precipitate five more times with water saturated with CaC$_2$O$_4$.
        Remove the Gooch crucible from its holder, rinse the outside, and replace crucible in the beaker. If filter paper is used, pierce the paper and wash most of the precipitate into the beaker with 3.6 *N* H$_2$SO$_4$. Wash off excess H$_2$SO$_4$ with water and place filter paper on watchglass. Add 100 ml water and 7 ml concentrated H$_2$SO$_4$. Heat to 90°C and stir until CaC$_2$O$_4$ is dissolved. Titrate with standard KMnO$_4$ solution to a pink color. Add filter paper to solution and titrate to a permanent pink color.

Calculations

$$\text{Ca (meq/100 g)} = (A/B) \times N \times (C/D) \times 100$$

where
A = KMnO$_4$ (mL)
B = Sample weight (g)
N = Normality of KMnO$_4$
C = Volume extract (mL)
D = Volume aliquot (mL)

Report on ovendry basis.

References
Peech et al. (1947).

Oxalate Precipitation II, KMnO$_4$ Titration
(Fe, Al and Mn removed) (6N2c)

Proceed as in 6N2b but after muffle treatment and before oxalate precipitation, remove iron, aluminum, and manganese by the following procedure.

Reagents
Hydrochloric acid (HCl), 6 *N*.

Ammonium hydroxide (NH$_4$OH), 2 *N*.

Bromine water, saturated.

Ammonium chloride (NH$_4$Cl), 6 *N*.

Concentrated nitric acid (HNO$_3$).

Procedure
Dissolve salts and oxides by adding 5 ml 6 *N* HCl and heating on a hot plate until all salts and oxides are in solution. Add 75 to 100 ml water and heat the solution until it is nearly boiling. Immerse the pH electrodes into the hot solution and precipitate the hydroxides of iron, aluminum, and titanium by slowly adding 2 *N* NH$_4$OH until the meter indicates a pH of 6.2 to 6.4. Add 2 more drops of NH$_4$OH to neutralize the acidifying effect of the 15 ml saturated bromine water, which is slowly added next to precipitate manganese hydroxide. Since bromine water lowers the pH of the solution, readjust it to 6.2 to 6.4 with 2 *N* NH$_4$OH. Heat the solution with precipitate until it just begins to boil (l or 2 min on a Bunsen burner) and remove from the heat.

Place on a hot plate at a temperature of 80° to 90°C for 1 hour. Filter when the breaker has cooled enough to handle easily. Use an 11-cm Whatman No. 42 filter paper or its equivalent. Collect the filtrate in a beaker of the same size as those used for precipitating calcium. Wash and police the beaker containing the precipitate with hot 2-percent NH$_4$Cl. Wash the precipitate on the filter with the same solution. Five washings are usually enough. To the filtrate add 10 ml concentrated HNO$_3$ and evaporate to dryness; add 5.0 ml 6 *N* HCl, take to dryness, and use high heat to dehydrate silica. Proceed with the calcium precipitation (6N2b).

References
Washington (1930) and Fieldes et al. (1951).

Oxalate Precipitation, Cerate Titration (6N2d)

Proceed as in 6N2b except substitute the following for the permanganate titration.

Reagents
Ammonium hexanitrate cerate ((NH$_4$)$_2$Ce(NO$_3$)) in molar perchloric acid (HClO$_4$), 0.1 *N*. Add 85 ml 70- to 72-percent perchloric acid to 500 ml water. Dissolve 56 g ammonium hexanitrate cerate in the acid solution and dilute to 1 liter.

Ammonium hexanitrate cerate in molar perchloric acid, 0.05 *N*. Follow the directions for the preparation of the 0.1 *N* solution but use only 28 g cerate.

Perchloric acid ($HClO_4$), 2 N. Add 170 ml 70 to 72-percent perchloric acid to 500 ml water and dilute to 1 liter.

Nitro-ferroin indicator solution. Dilute a solution of nitro-orthophenanthroline ferrous sulfate with water to a convenient working strength. Two to four drops of the solution should give a sharp color change at the end point.

Standardize the cerate solutions against accurately weighed quantities of primary standardgrade sodium oxalate. Convenient weights of sodium oxalate are 0.10 to 0.11 g for the 0.05 N solution and 0.10 to 0.18 g for the 0.1 N cerate solution. Dissolve the sodium oxalate in 100 to 150 ml 2 N perchloric acid and titrate as directed in the following procedure.

Procedure

Dissolve the filtered and washed (use water) calcium oxalate in 100 to 200 ml 2 N perchloric acid. If a paper filter has been used, macerate it before titration. Add 2 to 4 drops of nitro-ferroin indicator solution and titrate with 0.05 N or 0.1 N cerate solution, depending upon the amount of oxalate present. The solution changes from red to colorless at the end point.

Calculations

$$Ca \ (meq/100g) = (A/B) \times N \times (C/D) \times 100$$

where
A = Volume Cerate (mL)
B = Sample weight (g)
N = Normality of Cerate
C = Volume extract (mL)
D = Volume aliquot (mL)

Report on ovendry basis.

NH_4Cl-Ethanol Extraction (calcareous soils) (6N3)

Apparatus
See figure 7.

Reagents
Ammonium chloride (NH_4Cl), 1 N, in 60-percent ethanol. To make 9 liters of extraction solution, dissolve 482 g NH_4Cl in 2,835 ml water and add 5,985 ml 95-percent ethanol. Adjust pH to 8.5 with 140 to 145 ml NH_4OH.

Celite.

Procedure
Fill extraction tube with water, set tube upright in holder, and let most of the water drain out. Close screw clamp and place filter paper on plate with a stirring rod. Let remainder of the water drain out of tube. The filter paper provides enough tension to keep the bottom part of the tube filled with water. Place tube on the rack and add about 1 1/2 teaspoons washed sand. Place an extra perforated plate (inverted) on top of the sand and cover the plate with more sand. Place heaping teaspoon of Celite on the sand and pour about 20 ml extraction solution into the tube. Pour remainder of 400 ml extraction solution into a 500-ml Erlenmeyer flask. Add soil sample slowly and then stir with a rod to mix soil and Celite. Allow sample to settle and then place filter paper on top of the soil column. Put upper tube in place, stopper, and let stand overnight.

In the morning, place a 500-ml volumetric flask under the delivery tip and open screw clamp on lower extraction tube slowly. When level of liquid is a few milliliters above the soil, invert the 500-ml Erlenmeyer flask containing remainder of extraction solution (delivery tube in place), place glass tip in the upper tube, and open the pinch clamp. Use the screw clamp on lower tube to adjust flow rate through soil column. When all the extraction solution has passed through the soil column, remove volumetric flask, make to volume with water, and mix.

EDTA Titration (6N3a)

Pipet a 50-ml aliquot for determination of Ca and Mg into a 100-ml beaker and evaporate to dryness. Add 10-ml concentrated HNO_3 and 1 or 2 ml concentrated HCl. Cover with watchglass, place on hot plate, and heat until no more brown fumes are evolved. Remove cover glass, rinse into beaker, and evaporate solution to dryness. Take up residue with 3 ml *N* HNO_3. Quantitatively transfer solution with ethanol to a 50-ml conical centrifuge tube and proceed with determination of Ca according to 6N2a.

References
Tucker (1954).

KCl-Triethanolamine Extraction (6N4)

Prepare extract as in procedure 5B2.

Oxalate-Permanganate Titration (6N4a)

Proceed as in 6N2b.

EDTA Titration (6N4b)

Reagents
Sodium hydroxide (NaOH), 4 *N*

EDTA 0.02 *N*. Dissolve 3.723 g disodium dihydrogen ethylenediamine tetraacetate in water and dilute to 1 liter. Standardize the solution against standard $CaCl_2$ prepared in the TEA buffer solution.

Ammonium purpurate (murexide) indicator. Thoroughly mix 0.5 g ammonium purpurate with 100 g powdered potassium sulfate.

Eriochrome Black T (Erio T) indicator. Dissolve 0.5 g Erio T in 100 ml of triethanolamine.

Procedure
Pipet a 5-ml aliquot of extract from procedure 5B3 into a 100-ml beaker. Add 20 ml water, 5 drops 4 *N* NaOH, and 50 mg murexide. Titrate with standard EDTA using a 10-ml microburet. Approach the end point slowly (orange-red to lavender or purple). Save the solution for the Mg^{++} determination.

Calculations

$$Ca \ (meq/100 \ g) = (A/B) \times N \times (C/D) \times 100$$

where
A = Volume EDTA (mL)
B = Sample weight (g)
N = Normality of EDTA
C = Volume extract (mL)
D = Volume aliquot (mL)

References
Bower and Wilcox (1965).

Atomic Absorption (6N4c)

Proceed as in 6N1b except use sample from KCl-TEA extraction.

HF Dissolution (6N5)

Obtain extract as in 7C3.

Atomic Absorption (6N5a)

Apparatus
Diluter.

Atomic absorption spectrophotometer.

Reagents
Standard Ca solutions, 0 to 30 meq/L.

Procedure
Dilute HF extracts from 7C3 and Ca standards fivefold to twentyfold with water. Compare absorbance of samples with that of standards at 442.7 nm.

Calculations

$$Ca \text{ (pct.)} = (A \times 10 \times \text{dilution} \times 20.04 \text{ mg/meq})/B$$

where
A = Ca (meq/L)
B = Sample weight (mg)

CaO (pct.) = Ca (pct.) x 1.40

Report on ovendry basis.

Saturation Extract (6O1)

EDTA Titration (6O1a)

Reagents

Buffer solution. Mix 33.75 g NH_4Cl with 285 ml concentrated (15 *N*) NH_4OH, add 5 g disodium Mg-versenate and dilute to 500 ml.

Eriochrome Black T indicator. Dissolve 0.5 g Eriochrome Black T (F241) and 4.5 g hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 100 ml 95-percent ethanol or dissolve 1.0 g

Eriochrome Black T in 100 ml triethanolamine.

EDTA 0.02 *N*. Standardize with magnesium solution.

Procedure

To the sample just titrated for calcium (6N1a) add 3 or 4 drops concentrated HCl, stir until the murexide is destroyed, add 1 ml $NH_4Cl \cdot NH_4OH$ buffer solution, 1 or 2 drops Eriochrome Black T indicator, and complete the titration for magnesium, using EDTA. The end point should be a clear blue with no tinge of red.

Calculations

$$Mg \text{ (meq/100 g)} = (A/B) \times N \times (C/D) \times 100$$

where
A = Volume EDTA (mL)
B = Sample weight (g)
N = Normality of EDTA
C = Volume extract (mL)
D = Volume aliquot (mL)

Report on ovendry basis.

References
Cheng and Bray (1951).

NH_4OAc Extraction (6O2)

Prepare NH_4OAc extraction as described

EDTA Titration, Alcohol Separation (6O2a)

Reagents

Buffer solution. Dissolve 67.5 g NH_4Cl in about 400 ml water. Add 570 ml concentrated NH_4OH and dilute to 1 liter with water.

Hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), 5-percent aqueous solution. Prepare fresh solution every 10 days.

Potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$), 4-percent aqueous solution.

Triethanolamine, U.S.P.

Eriochrome Black T. Dissolve 1 g Eriochrome Black T

(Superchrome Black TS) in 100 ml triethanolamine.

Standard magnesium solution, 5.0 mg per milliliter. Transfer 2.500 g unoxidized reagent-grade magnesium metal to a 500-ml volumetric flask. Add 150 ml water and 20 ml concentrated HCl. When in solution, make to volume with water and mix. Dilute an aliquot of this solution to get a solution containing 0.5 mg magnesium per milliliter.

EDTA, 0.02 N. Standardize with magnesium standard solution.

Procedure

Place the Erlenmeyer flasks containing the alcohol solution retained from the $CaSO_4$ separation (6N2a) on a hot plate and evaporate the alcohol at moderate heat. Do not evaporate to complete dryness. Cool and dilute to 100 ml with water and add 5 ml buffer solution and 10 drops each of hydroxylamine hydrochloride, potassium ferrocyanide, and triethanolamine. Stir and let stand 5 to 10 minutes. Place the sample on the stirrer, add 2 drops Eriochrome Black T, and titrate with standard EDTA to the ice-blue end point. The color change is from red through wine to ice blue. A blank carried through this procedure usually requires 0.3 to 0.8 ml EDTA to get the proper ice-blue color. Correct for a blank carried through this procedure and use the corrected titration to calculate the magnesium in the sample.

Calculations

$$\text{Mg (meq/100 g)} = (A/B) \times N \times (C/D) \times 100$$

where
A = Volume EDTA (mL)
B = Sample weight (g)
N = Normality of EDTA
C = Volume extract (mL)
D = Volume aliquot (mL)

Report on ovendry basis.

References
Barrows and Simpson (1962).

Phosphate Titration (6O2b)

Reagents
Sodium hydroxide (NaOH), 0.1 N, standardized. Protect from CO_2 of the air with a sodalime trap.

Sulfuric acid (H_2SO_4), 0.1 N.

Ammonium hydroxide (NH_4OH), concentrated.

Diammonium hydrogen phosphate (($NH_4)_2 HPO_4$), 10-percent solution.

Brom cresol green, 0.1-percent aqueous solution.

Hydrochloric acid (HCl), 1:1.

Carbon-dioxide-free water. Boil water in a 5-liter round-bottom boiling flask for about 15 minutes. Cool and protect from CO_2 of the air with a sodalime trap.

Procedure

Transfer the filtrate from the calcium determination (6N2b, 6N2c, or 6N2d) to a 400-ml beaker, add 10 ml concentrated HN_3, cover with a 3.5-inch Speedyvap watchglass and evaporate to dryness. Dissolve the residue in 5 ml 1:1 HCl and transfer to a 250-ml Erlenmeyer flask, policing twice and rinsing the beaker twice after final policing. The volume of solution should be about 75 ml or more. Using 3 to 4 drops brom cresol green indicator, neutralize the solution with concentrated NH_4OH added by drops. Add 5 ml 10-percent $(NH_4)_2HPO_4$ and 10 ml concentrated NH_4OH. Heat the solution just to boiling, cool, stopper, and let stand overnight.

Filter through a 9-cm Whatman No. 40 filter paper, pouring the solution down a stirring rod. Rinse the flask five times with 1 N NH_4OH and pour the rinsings onto the filter. Wash the precipitate on the filter five more times with 1 N NH_4OH. Place the wet filter paper with precipitate on a watchglass and let dry at no more than 40°C until free of ammonia. Place the dry filter in the original flask, add 5 drops brom cresol green and 10 ml 0.1 N H_2SO_4 or more if necessary to dissolve the precipitate. The solution should be yellow. After most of the precipitate has dissolved, add 50 ml CO_2-free water, stopper the flask, and shake vigorously until the filter paper is macerated. Remove the stopper and rinse it and the flask walls with CO_2-free water. Back-titrate with standard 0.1 N NaOH to pH 4.5. To determine the correct end point, prepare a color standard by pipetting 5 ml potassium dihydrogen phosphate (2-percent solution) into a 250-ml Erlenmeyer flask, adding 65 ml water, 5 drops brom cresol green, and a macerated filter paper.

Calculations

$$Mg\ (meq/100\ g) = ((A - B)/C) \times N \times (D/E) \times 100$$

where
A = Volume NaOH blank (mL)
B = Volume NaOH sample (mL)
C = Sample weight (g)
N = Normalitiy of NaOH
D = Volume extract (mL)
E = Volume aliquot (mL)

Report on ovendry basis.

References
Peech et al. (1947).

Gravimetric, Magnesium Pyrophosphate (6O2c)

Reagents
Diammonium hydrogen phosphate $((NH_4)_2HPO_4)$, 10-percent solution.

Nitric acid (HNO_3), concentrated.

Ammonium hydroxide (NH_4OH), concentrated.

Ammonium hydroxide (NH₄OH), 1:1.

Hydrochloric acid (HCl), 6 N.

Procedure

Continue analysis on filtrate from oxalate precipitation (6N2b). This filtrate will probably fill a 150-ml beaker. Place cover glass on filtrate and heat at a low temperature. When volume has been reduced, add 20 ml concentrated HNO_3. Evaporate to complete dryness and wash cover glass and sides of beaker with water. Dissolve residue in 5 ml 6 N HCl and then dilute to about 75 ml. Add 2 or 3 drops brom cresol green and bring pH to 4.6 with 1:1 NH₄OH. Add 5 ml 10-percent diammonium hydrogen phosphate (make up fresh each time). Add 10 ml concentrated NH₄OH, stir solution vigorously until a precipitate forms, and let stand overnight.

On the next day filter on a 11.0-cm Whatman No. 42 filter paper, rinse beaker five times with 1 N NH₄OH, and pour washings into the filter. Wash the precipitate in the filter five more times with 1 N NH₄OH. Place filter in oven to dry (2 to 3 hours) and evolve NH₄OH to prevent any explosion in the muffle furnace. Place crucibles (Coors 000) with filters containing magnesium precipitate in muffle furnace. Raise temperature gradually to 1000°C and hold at 1000°C for 1 hour. Allow muffle furnace to cool down and remove crucibles. Place in desiccator and dry over phosphorus pentoxide (P_2O_5). Weigh $Mg_2P_2O_7$ and record.

Calculations

$$\text{Mg (meq/100 g)} = (A/B) \times (C/D) \times 1.797$$

where
A = $Mg_2P_2O_7$ (mg)
B = Sample weight (g)
C = Volume extract (mL)
D = Volume aliquot (mL)

NH₄Cl-Ethanol Extraction (calcareous soils) (6O3)

Proceed as in 6N3.

EDTA Titration (6O3a)

Proceed as in 6N3a except determine magnesium in alcohol extract by method 6O2a.

KCl-Triethanolamine Extraction (6O4)

Prepare extract as described in 5B2 or 5B3.

Phosphate Titration (6O4a)

Proceed as in 6O2b except use extract from 5B2 or 5B3.

EDTA Titration (6O4b)

Reagents
Concentrated hydrochloric acid (HCl).

Concentrated ammonium hydroxide (NH$_4$OH).

EDTA 0.02 *N*. Dissolve 3.723 g disodium dihydrogen ethylenediaminetetraacetate in water and dilute to a volume of 1000 ml. Standardize the solution against standard MgCl$_2$.

Eriochrome Black T (Erio T) indicator. Dissolve 0.5 g Erio T in 100 ml triethanolamine.

Procedure
         Add 4 or 5 drops concentrated HCl to the solution used for the calcium determination (6N4b). Set aside until the murexide turns colorless. Add 15 to 20 drops concentrated NH$_4$OH. This should bring the pH between 10.0 and 10.3. Add 1 drop Erio T and titrate with EDTA to a clear blue end point.

Calculations

$$Mg(meq/100g) = (A/B) \times N \times (C/D) \times 100$$

where
A = Volume EDTA (mL)
B = Sample weight (g)
N = Normality of EDTA
C = Volume extract (mL)
D = Volume aliquot (mL)

Report on ovendry basis.

Atomic Absorption (6O4c)

         Proceed as in 6O1b except use samples from the KCl-TEA extract.

HF Dissolution (6O5)

         Obtain extract as in 7C3.

Atomic Absorption (6O5a)

Apparatus
Diluter.
Atomic absorption spectrophotometer.

Reagents
Standard Mg solutions, 0 to 10 meq/L.

Procedure
         Dilute HF extracts from 7C3 and Mg standards fivefold to twentyfold with water. Compare absorbance of samples with that of standards at 285.2 nm.

Calculations

Mg (pct.) =

$$(A \times 10 \times \text{dilution} \times 12.16 \text{ mg/meq})/B$$

where
A   = Mg (meq/L)
B   = Sample weight (mg)

MgO (pct.) = Mg (pct.) x 1.66

Report on ovendry basis.

CHEMICAL ANALYSES (6)
SODIUM (6P)

Saturation Extract (6P1)
Flame Photometry (6P1a)

Apparatus
Beckman Model DU spectrophotometer with flame attachment.

Reagents
Standard sodium solutions, 0.0 to 2.0 meq per liter.

Concentrated hydrochloric acid (HCl).

Hydrochloric acid (HCl), 6 *N*.

Hydrochloric acid (HCl), 0.4 *N*.

Concentrated nitric acid (HNO_3).

Procedure
        Pipet an aliquot of appropriate size (5 to 25 ml) of the saturation extract into a 100-ml beaker and evaporate to dryness on a hot plate. Treat the residue with 1 ml concentrated HCl and 3 ml concentrated HNO_3 and again evaporate to dryness on the hot plate. Repeat the acid treatment on the residue. Add 5 ml 6 *N* HCl to the residue and bring to dryness. Then raise the temperature to high for 20 minutes to render the silica insoluble. Wash and filter the residue into 50-ml volumetric flasks, using 0.4 *N* HCl. Determine flame luminosity of samples appropriately diluted and compare with luminosity of standard solutions made up with 0.4 *N* HCl. The evaporation and dehydration steps are used only where there is enough silica to clog the burner. If they are not used, merely dilute the sample.

Calculations

$$\text{Na (meq/L)} = A \times \text{dilution}$$

where
A   = Na from curve (meq/L)

NH$_4$OAc Extraction (6P2)

Flame Photometry (6P2a)

Proceed as in 6P1a except make standard solutions in NH$_4$OAc. The evaporation and dehydration steps can be eliminated.

Calculations

$$\text{Na (meq/100 g)} = (A/B) \times \text{dilution} \times (C/10)$$

where
A = Na from curve (meq/L)
B = Sample weight (g)
C = Volume extract (mL)

Report on ovendry basis.

References
Fieldes et al. (1951).

HF Dissolution (6P3)

Obtain extract as in 7C3.

Atomic Absorption (6P3a)

Apparatus
Diluter.

Atomic absorption spectrophotometer.

Reagents
Standard Na solutions, 0 to 20 meq/L in HF and boric acid.

Procedure
Dilute HF extracts from 7C3 and Na standards fivefold to twentyfold with water. Compare absorbance of samples with that of standards at 589 nm.

Calculations

$$\text{Na (pct.)} = (A \times \text{dilution} \times 23.00 \text{ mg/meq})/B$$

where
A = Na (meq/L)
B = Sample weight (mg)

Na$_2$O (pct.) = Na (pct.) x 1.35

Report on ovendry basis.

CHEMICAL ANALYSES (6)
POTASSIUM (6Q)

Saturation Extract (6Q1)
Flame photometry (6Q1a)

Apparatus
Beckman Model DU spectrophotometer with flame attachment.

Reagents
Standard potassium chloride (KCl) solutions ranging from 0.0 to 1.0 meq per liter.

Procedure
Proceed as in 6P1a. Determine flame luminosity of potassium at 768 mµ and compare with that of the standard solutions.

Calculations

$$K\ (meq/L) = A \times dilution$$

where
A = K from curve (meq/L)

References
Fieldes et al. (1951).

NH$_4$OAc Extraction (6Q2)
Flame Photometry (6Q2a)

Proceed as in 6Q1a except make up standards in NH$_4$OAc solution.

Calculations

$$K\ (meq/100\ g) = (A/B) \times dilution \times (C/10)$$

where
A = K from curve (meq/L)
B = Sample weight (g)
C = Volume extract (mL)

Report on ovendry basis.

CHEMICAL ANALYSES (6)
SULFUR (6R)

NaHCO$_3$ Extract, pH 8.5 (6R1)
Methylene Blue Colorimetry (6R1a)

References
Kilmer and Nearpass (1960).

HCl Release (sulfide) (6R2)

Apparatus
Nitrogen tank (water pumped).

Scrubber. 250-ml Erlenmeyer flask equipped with three-hole rubber stopper to accommodate entry and exit for sweep gas, and a 4-foot glass tube to serve as a manometer.

Reaction flask. 250-ml Erlenmeyer equipped with three-hole rubber stopper to accommodate entry and exit for sweep gas, and a buret for adding acid. Reaction flask sits on a magnetic stirrer.

Collection bottles. Two 500-ml bottles (No. 8 rubber stopper), each fitted with a two-hole rubber stopper to accommodate entry and exit tubes for sweep gas. The entry tubes should be detachable below the rubber stopper (figure 8). Attach a pinch clamp to the exit tube to help control the flow rate of gases.

Procedure
Place 10 ml zinc acetate solution in collection flask. Add water to 150 ml volume and place flask in train. Add moist sample (collected as in 1A2b) in tared reaction flask (250-ml Erlenmeyer), introduce N_2 gas (unless sample is run immediately), stopper, and weigh. Determine moisture content on a separate sample. Place flask in collection train. Sweep with N_2 gas for about 5 minutes. Reduce flow until pressure drops enough so that 50 to 60 ml of 6 N HCl can be added to reaction flask. Adjust flow of N_2 to about 4 bubbles per second in collection flask and turn on stirrer. Collect sample for 45 to 60 minutes. Second collection bottle should be a blank. Cut flow, disconnect entry tube but leave in collection bottle, remove collection bottles, and stopper until ready to titrate.

Iodine Titration (6R2a)

Apparatus
Iodine applicator, approximately a 50-ml reservoir with stopcock delivery in a two-hole rubber stopper (No. 8). Fit a glass tube for air exit through the stopper.

Buret for thiosulfate.

Magnetic stirrer.

Reagents
Iodine 0.1 N, standardized.

Sodium thiosulfate 0.1 N, standardized.

Starch indicator.

Hydrochloric acid (HCl), 6 N.

Procedure
Mix an aliquot of standardized iodine solution and 5 ml of 6 N HCl in iodine applicator. Place applicator on bottle and add acidified iodine. Wash contents of applicator, quantitatively, into bottle. Remove applicator, stopper bottle, and swirl so that iodine enters the top of the entry tube from collection train. Any white precipitate of ZnS should dissolve off entry tube. Remove stopper and titrate with standardized thiosulfate until iodine color becomes faint. Add 1 or 2 ml starch indicator and titrate until blue color changes to clear. The end point is abrupt. Stopper bottle and again swirl so that solution passes through the entry tube. Blue color should reappear. Again titrate to the end point. Magnetic stirrer can be used to mix the sample.

Calculations

$$S \text{ (meq/100 g)} = ((A - B)/C) \times N \times 100$$

where
A = Volume thio for blank (mL)
B = Volume thio for sample (mL)
C = Sample weight (g)
N = Normality of thio

References
Pierce and Haenisch (1955), Johnson and Ulrich (1959), and Chapman and Pratt (1961).

SO2 Evolution (6R3)
KIO$_3$ titration (6R3a)

Apparatus
LECO induction furnace model 521.

LECO automatic sulfur titrator model 532.

LECO crucibles and lids.

Oxygen tank and regulator.

LECO starch dispenser and 0.2-ml scoop.

Reagents
Potassium iodate (KIO$_3$).

Potassium iodide (KI).

Arrowroot starch.

Hydrochloric acid (HCl) 7.7 *N*.

Hydrochloric acid (HCl) 0.18 *N*.

Magnesium oxide, (MgO).

Iron-chip accelerator.

Copper metal accelerator.

Procedure
Into a tared crucible, weigh approximately 1/2 g of 60-mesh soil, recording gross weight. Where high sulfur content might be present, either 1/4 or 1/10 g sample should be run. Add 2 scoops of MgO and a scoop of iron chips. Mix thoroughly. Add a half scoop of copper accelerator and a scoop of iron chips. Magnesium oxide scoops are heaping; all others are level. A cover is placed on the crucible, which is placed on the pedestal and raised into the combustion tube for ignition. The LECO instruction manual is followed in setting up the furnace and titrator. The timer is set to 8 min and grid tap switch to midposition. These settings should be adjusted as needed to get complete fusion of the mixture in the crucible; however, plate current should not exceed 350 mA. When the burette reading does not change

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for 2 min and plate current has achieved 300 to 350 mA, the titration is complete and the titer is recorded. A blank is run using all ingredients except soil. Sulfate removal before analysis may be desirable in some instances. Sample is leached with 50 ml of 7.7 N HCl followed by 500 ml of distilled water.

Calculations

The KIO$_3$ burette is direct reading in percent for a 1-g sample containing up to 0.2 percent sulfur, provided the KIO$_3$ concentration is 0.444 g/L. With 1.110 g KIO$_3$/L, multiply burette readings by 5 (1/2-g sample, 0.005 to 1.00-percent sulfur range).

References
Smith (1974).

CHEMICAL ANALYSES (6)
PHOSPHORUS (6S)

Perchloric Acid Digestion (6S1)

Perchloric acid is extremely hazardous and
subject to explosion if improperly handled. Do not attempt this procedure unless the hazards are well understood and the laboratory is specially equipped to handle perchloric acid digestion.

Reagents

Perchloric acid (HClO$_4$), 60-percent.

Concentrated nitric acid (HNO$_3$).

Concentrated hydrochloric acid (HCl).

Procedure

Weigh 2.000 g ovendry soil, ground to approximately 100 mesh, into a 300-ml Erlenmeyer flask, add 30 ml 60-percent HClO$_4$, and boil until the soil is white. Continue boiling 20 minutes longer to insure complete extraction. Soils high in organic matter should be pretreated with HNO$_3$ and HCl to destroy the readily oxidize organic matter.

Molybdovanadophosphoric Acid Colorimetry (6S1a)

Apparatus
Spectrophotometer.

Reagents
Solution I. Dissolve 20 g ammonium molybdate ((NH_4)$_6$Mo$_7$O$_{24} \cdot$4H$_2$O) in 250 ml water.

Solution II. Dissolve 1.25 g ammonium metavanadate (NH$_4$VO$_3$) in 300 ml boiling water, cool, and add 425 ml 60-percent HClO$_4$. Mix solution I and II and dilute to 1 liter in a volumetric flask. Store in a brown bottle.

Standard phosphorus solution. Weigh out 0.2194 g ovendry KH$_2$PO$_4$ and dilute to 1 liter. This solution contains 50 ppm phosphorus.

Concentrated nitric acid (HNO$_3$) for samples high in organic matter only.

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Concentrated hydrochloric acid (HCl) for samples high in organic matter only.

Procedure

Transfer the extract into 250-ml volumetric flasks, bring to volume, and let residue settle out. Pipet a 25-ml aliquot into a 50-ml volumetric flask, add 10 ml molybdovanadate reagent, bring to volume, and mix.

After 10 minutes, the color is fully developed on most samples and can be read at 460 mμ. Prepare a standard curve covering the range O to 5 ppm phosphorus in 50 ml solution. Plot on semilog paper.

Calculations

$$\text{Total P (pct.)} = (A/400) \times (250/B)$$

where
A   = P from curve (ppm)
B   = Volume aliquot (mL)

Comments

The color developed is molybdovanadophosphoric acid and is very stable, lasting 2 weeks or more.

To destroy organic matter in samples high in organic matter, add 15 ml HNO_3 and 5 ml HCl. When brown fumes stop coming off, add $HClO_4$, and follow the usual procedure.

Sediment disturbance during aliquot removal makes it impossible to take more than one aliquot a day. If more aliquots are necessary, remove the sediment by filtering the suspension into a 250-ml volumetric flack, using Whatman No. 50 filter paper.

Comparison of results by Na_2CO_3 fusion and by perchloric acid on lava samples indicate that extraction may not be complete for some silicate minerals. Extraction by $HClO_4$ should be complete on common phosphate minerals.

The volume of molybdo-vanadate reagent added is not critical but must be constant. The presence of chlorides slows down color development but does not interfere otherwise.

References
Sherman (1942), and Kitson and Mellons (1944), and Jackson (1956).

Adsorption Coefficient (6S2)

Apparatus
Automatic extractor, 24 place.

Syringes, 60 cc polypropylene; use one sample tube and one extraction syringe per sample.

Reagents
Extractant. Dissolve 4.5 g ammonium fluoride (NH_4F) and 85.6 g ammonium chloride (NH_4Cl) in about 4 L of distilled water, add 92 ml glacial acetic acid and 10 ml concentrated HCl, make to 8 L and mix.

Sulfuric-molybdate-tartrate solution. Dissolve 100 g ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ and 2.425 g antimony potassium tartrate $[K(SbO)C_4H_4O_6 \cdot 1/2H_2O]$ in 500 ml distilled water, heating if necessary but not to exceed 60°C. Slowly add 1,400 ml concentrated H_2SO_4 and mix well. Cool, dilute to 2 L with water and store in refrigerator in polyethelene or Pyrex bottle.

Ascorbic acid solution. Dissolve 88.0 g ascorbic acid in distilled water, dilute to 1 L, mix, and store in glass bottle in refrigerator.

Phosphorus stock standard, 100 ppm. Weigh 0.4394 g dried monobasic potassium phosphate (KH_2PO_4) into a 1-L volumetric flask, dissolve, and make to volume with extractant solution.

Phosphorus working standards, 2 to 10 ppm. Pipette 2, 4, 6, 8, and 10-ml aliquots of phosphorus stock standard into a series of 100-ml volumetric flasks and make to volume with extractant solution. The standards contain 2, 4, 6, 8, and 10 ppm P.

Saturate stock solution. Dissolve 4.394 g dried monobasic potassium phosphate (KH_2PO_4) in distilled water and make to 1 L.

Saturate working solution. Pipette 20 and 80-ml aliquots of Saturate stock solution into two 1-L volumetric flasks. The resulting solutions contain 20 and 80 ppm P.

Color solution. Measure 40 ml ascorbic solution and 80 ml sulfuric-molybdate-tartrate solution into 2 L of distilled water. Bring to 4 L, mix, and store in refrigerator.

Apparatus
Colorimeter.

Automatic extractor.

Shaker.

Procedure

A. Saturation
Weigh three 2-g subsamples of ovendried soil into 50-ml Erlenmeyer flasks. To the first add 2 ml distilled water. To the second add 2 ml 20 ppm P solution. To the third add 2 ml 80 ppm P solution. Let stand for 1 hr then place in oven at 60° C and dry overnight.

B. Extraction
        To each of the dried samples in the 50-ml Erlenmeyer flasks, add 20 ml extractant reagent, and shake for 20 min (Burrell shaker). Extract samples using the automatic extractor.

C. Developing the color
        Standard curve. Using 50-ml Erlenmeyer flasks, pipette aliquots from the phosphorus working standards as follows:

Flask 1--2 ml extractant
Flask 2--2 ml 2 ppm P
Flask 3--2 ml 4 ppm P
Flask 4--2 ml 6 ppm P
Flask 5--2 ml 8 ppm P
Flask 6--2 ml 10 ppm P

        Samples. For each sample extracted in part B, pipette 2 ml of extract into clean 50-ml Erlenmeyer flasks corresponding with sample numbers. To all flasks, standards, and samples, add 25 ml of color solution, swirl to mix, and let stand for 15 min to allow color to develop. After color has developed fully, transfer to colorimeter tubes.

D. Reading the color
Using a wavelength setting of 880 μm, set colorimeter to 100 percent transmittance with No. 1 standard containing 2 ml extractant. Read percent transmittance of remaining standards and samples. Generally, the standard curve is around the following values:

```
ppm            %t

0              100
2               77
4               59
6               45
8               33
10              24

(t = transmittance)
```

E. Calculations

1. Develop standard curve by the least squares analysis using concentration of standards as a f(ln%t). This results in the equation:

concentration = m(ln%t) + b

2. Use this equation to determine solution concentrations of unknowns (leachate). Concentration of leachate x 10 is desorbed P in ppm of dry soil.

3. P retained of that added = P added (desorbed P at that conc. minus desorbed P at zero P addition).

4. Pa (adsorption coefficient) is the slope of the least square regression of P retained as a function of phosphorus added, f(P added).

Example

P (ppm)	T (%)	Added P (ppm)	T (%)
0	100		
2	77		
4	59		
6	45	0	84
8	33	20	73
10	24	80	45

```
1. Conc.= -7.023(ln%t) + 32.5158

2. Concentration
= -7.023 (ln84) + 32.5158 = 1.40
= -7.023 (ln73) + 32.5158 = 2.38
= -7.023 (In45) + 32.5158 = 5.78

Desorbed P (ppm) of dry soil
= 1.40 x 10 = 14.0
= 2.38 x 10 = 23.8
= 5.78 x 10 = 57.8

3. P (ppm) retained of that added
=  0 - (14.0 - 14.0) = 0
= 20 - (23.8 - 14.0) = 10.2
= 80 - (57.8 - 14.0) = 36.2

4. y = 0.4478(P added) + 0.5083
PÂ= 0.4478
```

References
Mehlich (1978).

CHEMICAL ANALYSES (6)
Boron (6T)

Saturation Extract (6T1)
Carmine Colorimetry (6T1a)

Refer to USDA Handbook 60, method 17 (p. 100) and method 73b (p. 142).

CHEMICAL ANALYSES (6)
SILICON (6V)

HF Dissolution (6V1)

Obtain extract as in 7C3.

Atomic Absorption (6V1a)

Apparatus
Diluter.

Atomic absorption spectrophotometer.

Reagents
Standard Si solutions, 400 and 800 mg/L in HF.

Procedure
Dilute HF extracts from 7C3 and Si standards fivefold to twentyfold with water. Compare absorbance of samples with that of standards at 252 nm.

Calculations

$$Si \; (pct.) = (A \times 10 \times dilution)/B$$

where
A   = Si (mg/L)
B   = Sample weight (g)

SiO_2 (pct) = (pct) x 2.14

Report on ovendry basis.

MINERALOGY (7)
INSTRUMENTAL ANALYSES (7A)

Preparation (7A1)

The treatment to be used in preparing samples depends on analysis objective and sample composition.

Carbonate Removal (7A1a)

Reagents
Sodium acetate (NaOAc), *N*, pH 5.0. Dissolve 82 g NaOAc, 27 mL glacial acetic acid L^{-1}, adjust to pH 5.0.

Procedure
Place 5 g soil in a 90-ml centrifuge tube, add 40 ml *N* NaOAc, pH 5.0, and heat at 95°C for 30 minutes, stirring occasionally. Centrifuge at 1,600 rpm for 5 minutes and decant supernatant liquid. Repeat if necessary until carbonates are removed. Wash twice with *N* NaOAc, pH 5.0. Save decantates for calcium and magnesium analysis. One washing is enough to prepare neutral or basic noncalcareous soils for optimum hydrogen peroxide treatment.

References
Jackson (1956).

Organic-Matter Removal (7A1b)

Reagents
Hydrogen peroxide (H_2O_2), 30- to 35-percent.

Procedure
Transfer sample to a 250-ml tall breaker, using a minimum of water, and add 5 ml H_2O_2. When frothing subsides, heat at 90° C. Continue to watch for frothing. Add 5- to 10-ml aliquots of H_2O_2 each hour until 25 to 30 ml H_2O_2 has been used. Wash five times, removing water by filter candles. Transfer to a 90-ml centrifuge tube.

References
Kilmer and Alexander (1949).

Iron Removal (7A1c)

Reagents
Sodium bicarbonate ($NaHCO_3$), *N*.

Sodium citrate ($Na_3C_6H_5O_7$), 0.3 *M*.

Sodium dithionite ($Na_2S_2O_4$) powder.

Procedure
     If iron reduction is intended, add 5 ml *N* $NaHCO_3$ and as much as 40 ml 0.3 *M* sodium citrate. Heat to 70°C (not above 80°C) in a water bath and add 1 to 2 g $Na_2S_2O_4$, stir for 1 minute, and then stir intermittently for 15 minutes. Decant supernatant liquid and save for iron analysis. Repeat treatment as needed if soil is high in iron. Wash twice with 0.3 *M* sodium citrate.

References
Aguilera and Jackson (1953) and Mehra and Jackson (1960).

Disaggregation and Particle-Size Fractionation (7A1d)

Reagents
Sodium bicarbonate ($NaHCO_3$), pH 9.5 to 10.0.

Sodium metaphosphate ($NaPO_3$). Prepare as in 3A1.

Procedure
     Use $NaHCO_3$ solution or sodium hexametaphosphate-sodium bicarbonate as a dispersing agent. Use hexametaphosphate carefully with amorphous materials since phosphates may be precipitated. A dilute HCl treatment may be useful for some highly allophanic soils. Do not use mechanical blenders for disaggregation if silt and sand are to be studied because they fracture large quartz grains. Separate sand from silt with a 300-mesh sieve and further separate the sands, using a nest of sieves (3A1). Separate clay ($<2\mu$) from silt by centrifuging at 750 rpm for 3 minutes (International No. 2 centrifuge with No. 240 head and solution depth of 10 cm). If silt and sand are to be studied, save these fractions in small vials after drying and weighing. If interested in separating fine clay ($<0.2\mu$) from the coarse clay (0.2μ to 2μ), centrifuge at 2,400 rpm for 30 minutes with a solution depth of 10 cm. Adjust time according to temperature. Add 50-ml aliquots of clay suspension after each centrifugation until the required amount of clay is obtained. Make each suspension of coarse and fine clay to known volume and determine its concentration and the concentration of the whole clay.

References
Kilmer and Alexander (1949) and Jackson (1956).

Particle-Size Distribution Analysis (PSDA) Pretreatment (7A1e)

     Mineralogical analysis can be performed on samples from the particle-size distribution analysis (3A1). These samples have undergone peroxide digestion and sodium metaphosphate dispersion.

X-ray Diffraction (7A2)

The minerals in soil clays of greatest interest are mostly flaky or platy, e.g., kaolinite, illite (mica), vermiculite, chlorite, and montmorillonite. They are most readily identified and distinguished from one another by observing the effect of different treatments on the interplanar spacings along the axis perpendicular to the platy surfaces. X-ray diffraction produces peaks on a chart corresponding to the various angles (2R) of goniometer from which the crystallographic spacing of the mineral or minerals can be calculated by Bragg's law. Tables of spacings corresponding to angles have been published in U.S. Geological Survey Circular 29 (Switzer et al. 1948).

The pretreatment used to distinguish montmorillonite from vermiculite and chlorite and to identify illite is saturation of the exchange complex of the clay with magnesium and treatment with ethylene glycol or glycerol. With this treatment, montmorillonite has a distinctive interplanar spacing of 17 Angstroms (17 A) to 19 A. Chlorite and vermiculite keep a 14 A spacing and mica a spacing of 10 A. To distinguish vermiculite from chlorite and to identify kaolinite, which has a 7 A spacing, the pretreatment consists of saturating the clay with potassium and heating on a glass slide at 500°C. Intermediate heat treatments 110 and 250°C, can be used to study interlayering in the collapsing minerals or other special problems. After the 500°C treatment, vermiculite and montmorillonite collapse completely to 10 A kaolinite becomes amorphous and chlorite still shows 14 A and sometimes 7 A peaks. Interstratified forms of these minerals are indicated by spacings intermediate between those of the individual components.

Clay suspensions are dried as thin films so that the plates are parallel to one another (preferred orientation). This results in greater X-ray diffraction peak intensities. For identification and semiquantitative estimation of nonplaty minerals such as quartz, feldspars, and crystalline iron and aluminum oxides, randomly oriented dry-powder samples can be used. This dry-powder method was used for nearly all analysis, including clay fractions, before 1951.

Various techniques are used to prepare the ion-saturated clays and to improve their parallel orientation. Details can be obtained from the soil survey laboratories.

References
Brindley (1951), Brown (1961), Brunton (1955), Grim (1953), Jackson (1956), and Switzer et al. (1948).

Thin film on Glass, Solution Pretreatment (7A2a)

Reagents
Potassium chloride (KCl), *N*.

Magnesium acetate (Mg(OAC)$_2$), *N*.

Magnesium chloride (MgCl$_2$), *1 N*.

Glycerol, 10-percent in ethanol by volume.

Procedure
Place an aliquot containing 50 mg clay in a 50-ml centrifuge tube. All a few ml 1 *N* KCl, centrifuge, and discard the clear supernatant. Combine sediments if necessary to get 50 mg in the tube. Wash four times by suspending and centrifuging in 20-ml portions *N* KCl. After the last washing with *N* KCl, wash with water until some of the clay remains suspended after centrifuging. Add a few drops of acetone or centrifuge at higher speed, or both, to flocculate the clay. Discard the supernatant. Clays are now free of chloride. Suspend the sediment in water and adjust the volume of the suspension to yield the desired weight of clay per slide. For most clays 50 mg per slide (27 by 46 mm) gives maximum intensity of reflection with minimum peeling of clay films. For amorphous clays, 25 mg per slide is adequate if glass slides are dried in a low-humidity atmosphere.

For magnesium saturation and glycerol solvation place an aliquot containing 100 mg clay in a 50-ml centrifuge tube. Wash twice with N Mg(OAC)$_2$ acetate and then three times with N MgCl$_2$. Wash the suspension free of chloride or until clay disperses. Place 2.5 ml clay suspension containing 50 mg clay on a glass slide (25 mg clay if the clay is amorphous). Solvate the remaining clay in the test tube with glycerol (about 1/2 ml of 10-percent glycerol in ethanol per 50 mg clay). Mix well and pipet 50 mg clay onto the glass slide. The slide should be moist but not wet. Or prepare the glycerol slide by adding 10-percent glycerol, a drop at a time, to the slides until the clay film is moist.

Thin Film on Glass, Resin Pretreatment (7A2b)

Reagents
Potassium-charged resin (Dowex 50W-X8).

Magnesium-charged resin (Dowex 50W-X8).

Glycerol, 10-percent in ethanol by volume.

Procedure
Add 1/4 teaspoon K-charged resin to 50 mg clay in a 1 ml volume in a 50-ml centrifuge tube. Mix and transfer a 1-ml aliquot to a glass slide (27 by 46 mm). Take the aliquot from the top of the suspension to avoid removing the resin.

Magnesium-clay and Mg-glycerol-clay slides can be prepared using a Mg-charged cation exchange resin. Add 1/2 teaspoon Mg-charged resin to the clay suspension (100 mg clay in a 4-ml volume) in a 50-ml centrifuge tube. Mix with the suspension, remove 1-ml aliquot, and place it on a glass slide. Add approximately 1/2 ml 10-percent glycerol in ethanol to the tube. Mix and transfer a 1-ml aliquot to a glass slide or use a Mg-clay slide for both Mg and Mg-glycerol solvated slides. Record a diffraction pattern for the Mg-saturated clay film. After solvating the clay film with 10-percent glycerol solution, record a second X-ray pattern.

References
Rex (1967).

Thin film on Glass, Sodium Metaphosphate Pretreatment (7A2c)

Shake soil overnight in sodium metaphosphate solution (3A2). Centrifuge to separate the clay or siphon off the clay. Pipet about 50 mg clay to a glass slide (47 by 26 mm). Concentrate the clay suspension if necessary. Scan the clay film at room temperature, again after heating to 500°C. The clay film is Na$^+$ saturated. The sodium metaphosphate peaks do not interfere with peaks of the more common clay minerals in this quick check method.

Thin Film on Tile, Solution Pretreatment (7A2d)

Apparatus
Ceramic tile (porous precipitate drying plate, sawed into 27- by 46- by 7-mm blocks).

Procedure
Prepare clay suspensions as in 7A2a except dry the suspensions on ceramic tile blocks. Clay suspensions dry in a few seconds on tile, preventing particle-size segregation. Partly immerse the Mg-saturated clay films in a 10-percent glycerol solution. The porous tile rapidly transfers the glycerol to the clay film. Blot off excess glycerol before recording the X-ray pattern.

Thin Film on Tile, Resin Pretreatment (7A2e)

Prepare clay suspensions as in 7A2b. Dry on ceramic tile blocks as in 7A2d. Solvate with glycerol as in 7A2d.

Thin Film on Tile, Sodium Metaphosphate Pretreatment (7A2f)

Prepare the sample as in 7A2c. Pipet the clay onto ceramic tile blocks as in 7A2d. Follow method 7A2c for the other treatments. Or solvate with glycerol as in 7A2d.

Powder Mount, Diffractometer Recording (7A2g)

Distinguishing dioctahedral and trioctahedral minerals requires random orientation of the sample. There is no completely satisfactory method for preparing a random mount, but several techniques are used.

Pack the sample in a box mount against a glass slide. When the box is full, tape the back of the box. Invert the box and remove the slide to expose the sample to X-rays. For more random packing, sprinkle the dry sample (ground to <100 mesh) on double stick tape fixed on a glass slide or on a thin film of Vaseline on a glass slide. Scan the sample by X-ray and measure the reflections with a geiger, proportional, or other counter.

Quick checks for whole samples, particularly for nonlayered minerals, can be made with a modified powder mount. Form the sample into a thick slurry, apply to a glass slide, and let dry. This for convenience rather than random orientation.

Powder Mount, Camera Recording (7A2h)

Photographic plates are still the best means of identifying minerals. Mount the sample in the center of a circular X-ray camera. Record the X-ray reflections on photographic film placed in a cylindrical film holder inside the camera. All diffraction peaks are recorded simultaneously.

Thin Film on Glass, NaPO$_3$ Pretreatment II (7A2j)

Apparatus
Hypodermic syringe (1.0 cc).

Glass slides 24 x 46 mm or 14 x 19 mm.
International No. 2 centrifuge with a No. 240 head.

100-ml centrifuge tubes (plastic).

Reagents
Glycerol-water mixture (1:8 glycerol-water).

Sodium hexametaphosphate solutions.

Procedure
Shake approximately 5 g ovendried soil (<2 mm) overnight with 5 ml sodium hexametaphosphate solution (3A1) and 35 ml of water in a 100-ml centrifuge tube, centrifuge at 750 rpm for 3 min for a 10-cm suspension depth, and decant clays. Draw about 0.5 cc of clay suspension into the syringe. Expel approximately 0.2 cc of the clay suspension onto an area approximately 20 x 27 mm in a

band across the middle of a 46- x 27-mm slide or expel approximately 0.1 cc of clay suspension, containing approximately 6 mg of clay, onto and covering the 14- x 19-mm slide. Prior to the deposition of the clay suspension, one small drop of glycerol-water mixture is placed on the slide which is to be solvated. Prepare four slides for X-ray diffraction: 1) Na^+--room temperature, 2) Na^+--solvated, 3) Na^+--heated 2 hr at 300°C, and 4) Na^+--heated for 2 hr at 500°C.

Powder Mounts (7A2k)

Two procedures are used for random orientation of mineral separates. In the first procedure, double-stick tape is affixed to a glass slide, a surplus of the sample is sprinkled onto the tape, the excess material is removed, and the slide is scanned by X-ray analysis. In the second procedure, a <2-mm soil sample is ground finer than 100 mesh prior to slide preparation. A thin film of Vaseline is applied to a glass slide, the 100-mesh sample is added, the excess removed, and the slide is scanned by X-ray analysis.

For quick check of a <2-mm sample, particularly for nonlayered minerals, a small portion is ground to less than 100 mesh and placed on a glass slide. Water is applied a little at a time until a thick slurry is formed. The slurry is allowed to dry and the slide is scanned by X-ray analysis. This method is also applicable for specific mineral separates, very fine sands or silts.

References
Brown (1961), Jackson (1956).

Differential Thermal Analysis (7A3)

Differential thermal analysis (DTA) is a measurement of the difference in heat absorbed by or evolved from a sample of soil material and a thermally inert material as the two are heated simultaneously at a constant rate. Thermocouples are in contact with two platinum pans; one pan contains an unknown and the other pan contains an inert material of similar composition. If a reaction occurs, a difference in temperature is registered on a stripchart recorder or photographically. The magnitude of the difference depends on the nature of the reaction and amount of reacting substance in the unknown. The temperature at which the reaction occurs identifies the substance if enough is known about the sample to predict the possibilities.

Apparatus
Columbia scientific instrument (CSI) system 200.

Mortar and pestle.

Analytical balance.

Desiccator.

Reagents
Reference sample, calcined kaolinite, 2 to 20 μ.

Ethyl alcohol, 95 percent.

Magnesium nitrate $(Mg(NO_3)_2 \cdot 6H_2O$

Procedure

The decanted clay from 7A2i or 7A2j is air-dried, ground in alcohol to approximately 100 mesh, and stored in a desiccator with $Mg(NO_3)_2 \cdot 6H_2O$. A 3- to 7-mg sample is placed on a small platinum pan in the sample holder. The temperature of the kaolinite reference sample and clay sample is increased at a rate of 20°C per minute to a maximum of 900°C. The sample can be heated in air or nitrogen.

The common endothermic reactions studied or recorded are loss of structural water in gibbsite, goethite, and kaolin and loss of carbon dioxide in carbonates. Change of state or rearrangement of crystal lattices can be either exothermic or endothermic. Oxidation reactions such as burning of carbon and oxidation of ferrous iron are exothermic.

Loss of structural hydroxyls can be measured quantitatively by calibrating areas of peaks of known mixtures of standard minerals, as is done commonly to determine the percentage of kaolin and gibbsite in soils. The standard curves are prepared by running the known mixtures under the same conditions as the unknowns. Kaolin has an endotherm at 500° to 600°C and gibbsite, at 310°C. Each worker should prepare a set of standard curves.

Endotherms at about 120°C indicate surface-adsorbed water. Montmorillonite produces a double peak at a low temperature if saturated with a divalent cation. The proportion of this mineral can be estimated if samples are kept in an atmosphere with a high (70 to 80 percent) relative humidity for 24 hr or more before analysis. Allophane has a broad endotherm at about 160°C.

Samples can be any well-powdered material, whole soil, or separated fractions. Organic matter is objectionable because it produces irregular exothermic reactions that obscure the important peaks. If a clay separate is used, it must be washed free of hygroscopic salts or salts containing water of crystallization.

References

Grim (1968), McKenzie (1957), and Tan and Hajek in Dixon and Weed (1977).

Thermal Gravimetric Analysis (7A4)
CSI Stone Model 10002B (7A4a)

Thermal gravimetric analysis is the detection and measurement of weight changes in a sample of soil material as the sample is being heated or cooled over a specific temperature range.

Apparatus

CSI Stone Model lOOOB used in conjunction with an RC-202 recorder-controller. Furnace is water cooled, with a rapid cooling Kanthal element. Furnace is capable of operation at temperatures of up to 1,200°C.

Procedure

Prepare sample as described in 7A3 and place in balance pan suspended above thermocouple assembly. Heat sample at rate of 20°C/min to desired temperature. If a weight loss occurs, it is registered on a stripchart recorder. The magnitude of the weight loss depends on the reaction and the amount of reacting substance in the unknown. The temperature at which the reaction occurs usually identifies the substance.

Infrared Analyses (7A5)

Soil or clay samples (7A2j) are incorporated into a potassium bromide (KBr) pellet for infrared analyses. Sample concentration in the pellet ranges from 0.1 to 1 percent.

Reagents

Potassium bromide, spectroscopic grade.

Apparatus

Infrared spectrometer. Perkin Elmer Model 283.

Pellet die.

Hydraulic press.

Analytical balance.

Procedure

　　　　Mix 0.30 g KBr and 1 mg of sample in mortar and pestle. Transfer the mixture to the pellet die, and place die in hydraulic press. Apply 8 tons of pressure for 1 min. Place pellet in instrument holder and scan for 12 min. Peaks produced on chart recorder are used to identify the substance.

References

J. L. White in Dixon and Weed (1977).

MINERALOGY (7)
OPTICAL ANALYSES (7B)

Grain Studies (7B1)
Grain mounts, Canada balsam (7B1b)

　　　　For Canada balsam, heat slide plus balsam for 15 min at 125°C. Add mineral grains, stir, heat for an additional 5 min, place cover glass in position and press firmly, remove slide from hot plate, and cool.

　　　　The refractive index of Canadian balsam is close to that of quartz, which helps to distinguish quartz from other colorless minerals, particularly the feldspars. Other available commercial media cover the refractive index range of 1.53 to 1.55. Piperine with a refractive index of 1.68, which is close to that of many of the common heavy minerals, is best for mounting them.

Electron Microscopy (7B2)

　　　　Electron microscopy gives information on particle size and morphology of clay-size particles. Evidence of clay formation or weathering can also be seen. Positive identification of halloysite often depends on observation of rolled structures under the electron microscope.

Procedure

　　　　Place a drop of dilute clay suspension on a 200-mesh copper grid. After drying, insert this grid in the microscope.

MINERALOGY (7)
TOTAL ANALYSIS (7C)

Chemical (7C1)

　　　　The procedures follow the standard procedures for rock analysis set forth by Hillebrand and Lundell (1929) and modified by Robinson (1920) and by Shapiro and Brannock (1956).

X-ray Emission Spectrography (7C2)

X-ray emission spectrography is elemental analysis by measuring the X-ray fluorescence produced by bombarding a sample with high-energy X-rays. Each element yields fluorescent radiation of unique wave lengths, one of which is selected for measurement by using an analyzing crystal that diffracts according to Bragg's law. The intensity of the fluorescent radiation is generally proportional to the amount of the element present, but this is affected by sample homogeneity, particle size, and the absorption and enhancement of radiation by any other elements present in the sample (matrix effects). These effects can be overcome or compensated for by (1) comparing the intensities with those of standards of similar composition prepared in a similar manner, (2) fusing both samples and standards in borax or lithium borate to eliminate particle-size effects and to reduce matrix effects, and (3) making matrix corrections by calculation the absorption-enhancement coefficient of the sample for the particular radiation being measured.

References
Vanden Heuvel (1965).

MINERALOGY (7)
SURFACE AREA (7D)

Glycerol retention (7D1)

Apparatus
Weighing cans.

Reagents
Glycerol, 2-percent.

Procedure
Ovendry a clay sample (about 0.2 g) at 110°C for 2 hours. Cool and weigh. Add 5 ml 2-percent glycerol solution and mix. Heat in oven containing free glycerol at 110°C to constant weight. Record weight.

Calculations
To calculate the percent of glycerol retained subtract weight of ovendry sample from weight of glycerol and ovendry sample, divide by weight of ovendry sample, and multiply by 100. For the surface area of noncollapsible minerals (m_2/g), multiply glycerol retained by 19.1.

References
Kinter and Diamond (1958).

MISCELLANEOUS (8)
SATURATION EXTRACT, MIXED (8A)

Saturation Extract (8A1)

Apparatus
Richards or Buchner funnels.

Filter rack or flask.

Filter paper.

Vacuum pump.

Extract containers such as test tubes or 1-oz bottles.

Procedure
Transfer the saturated soil paste to a filter funnel with a filter paper in place and apply vacuum until air begins to pass through the filter. Collect the extract in a bottle or test tube. If carbonate and bicarbonate are to be determined on the extract, add 1 drop of 1000 ppm sodium hexametaphosphate solution for each 25 ml of extract to prevent precipitation of calcium carbonate on standing.

References
Richards (1954).

Conductivity of Saturation Extract (8A1a)

Apparatus
Conductivity bridge.

Conductivity cell.

Procedure
Determine temperature of the saturation extract obtained by methods 8A1 or 8B1. Draw the extract into the cell and read the meter. Correct for temperature and cell constant using Table 1 (Table 15, Richards 1954) and report as electrical conductivity, mmhos per centimeter at 25°C. If the instrument fails to balance, dilute the extract 1:9 with distilled water and redetermine. The conductivity of the diluted extract is approximately one-tenth the conductivity of the saturation extract.

References
Richards(1954).

Conductivity of Saturation Extract (quick test) (8A1b)

Apparatus
Extractor, miniature Richards-type (figure 9)

Conductivity cell, micropipet.

Filter paper, glass fiber, 3.0 cm.

Vacuum pump.

Procedure
Add 1 tablespoon soil to a 100-ml beaker or container. Make a saturated paste as in 8A. Place filter paper in recess of extractor and moisten with water. Insert the tip of the pipet conductivity cell through the other end of the extractor and into the paste. Apply suction to the cell until full. Proceed as in 8A1a.

Bureau of Soils Cup, Resistance (8A2)

Apparatus
Wheatstone bridge.

Bureau of Soils electrode cup.

Procedure
      Rinse the soil cup with water, dry, and fill with soil paste (8A). Jar cup to remove air bubbles strike off excess paste so the cup is level full, and connect cup to the bridge. Record resistance (ohms) and temperature of soil paste (°F).

Calculations
      Convert resistance of the soil paste in ohms to percentage of soluble salt by using the tables and formulas on pages 346-349, Soil Survey Manual.

References
Richards (1954) and Soil Survey Staff (1951).

MISCELLANEOUS (8)
SATURATED PASTE, CAPILLARY RISE (8B)

Apparatus
Sand table. Mariotte bottle.

Filter paper.

Polyethylene dish with lid.

Procedure
      Weigh 250 g airdry soil into cups made from Whatman No. 52 (15-cm) filter paper and place them on a sand table wetted at 5-cm tension with water. The sand table used consists of two nested plastic dishpans. The outer pan holds distilled water, which is kept at a constant level by a Mariotte bottle. The inner pan, containing medium to fine (35 to 80 mesh) pure quartz sand, rests on rubber stoppers and is suspended in the distilled water. Its perforated bottom is covered with a fine cloth-mesh screen that permits water to move upward by capillarity through the sand to the table surface. The sand on the table surface is then smoothed and covered with an absorbent paper towel. Lightweight porous firebricks can be used in place of the sand table.
      Keep the samples on the sand table 16 to 18 hours, remove them, and weigh. Water adsorption drops rapidly after an initial wetting of 2 hours and the rate becomes very slow after 6 to 9 hours. Moisture moves toward the top and center of the sample, which is wetted last, insuring retention of soluble salts in the soil. Calculate moisture at saturation from the wet- and dry-soil weights, correcting for the wet and dry filter paper weights. Add airdry moisture percentage to moisture at saturation and report on ovendry basis. After the wet weighing, transfer the sample to a pint polyethylene refrigerator dish, mix briefly with a spatula, and determine the pH. Keep a lid on the dish whenever possible to reduce evaporation.

References
Longenecker and Lyerly (1964).

Saturation Extract (8B1)

Proceed as in 8A1, using the saturated paste obtained by method 8B.

Conductivity of Saturation Extract (8B1a)

Proceed as in method 8A1a except use saturation extract obtained by method 8B1.

MISCELLANEOUS (8)
REACTION pH (8C)

Soil Suspensions (8C1)
Water dilution (8C1a)

Procedure

For 1:1 dilution add an equal weight of water to 20 or 30 g soil in a 50-ml beaker or paper cup. Stir at regular intervals for about an hour. Measure pH of the soil suspension with a glass electrode, stirring well just before immersing the electrodes in the suspension. For other dilutions vary the amount of soil, keeping the volume of water constant.

KCl (8C1c)

Procedure

Proceed as in method 8C1a except use N KCl instead of water.

CaCl$_2$ (8C1e)

Proceed as in 8C1a except use 0.01 M CaCl$_2$. This procedure can be combined with 8C1a by adding an equal volume of 0.02 M CaCl$_2$ to the soil suspension prepared for the water pH. Stir twice at 15-minute intervals before reading. The soil-solution ratio will be 1:2, but the pH difference between 1:1 and 1:2 suspensions is negligible.

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SOIL   Hayter silt loam   SOIL Nos.   S63Ky-74-6   LOCATION   McCreary County, Kentucky
SOIL SURVEY LABORATORY   Beltsville, Maryland   LAB Nos.   63776-63781

Figure 1. Laboratory data sheet for Hayter silt loam, McCreary County, KY.

Soil Type:	Hayter silt loam
Soil No.:	S63Ky-74-6
Location:	McCreary County, Kentucky, North off Hwy. 759 about 2 miles east of U.S. Hwy. 27.
Vegetation and land use:	Hickory, persimmon, yellow poplar.
Slope and land form:	50 percent.
Drainage:	Well drained.
Parent Material:	Colluvium from sandstone and shale.
Sampled by and date:	D.P. Franzmeier, E.J. Pedersen, C.R. Gass, L. Manhart, G. Chapman; October 15, 1963.
Described by:	J.H. Winsor, C.K. Losche.

Horizon and Beltsville Lab. No.	
01	1-1/2 to 0 inches. Hardwood leaf litter.
Ap1	0 to 1/2 inch. Very dark grayish brown (10YR 3/2) silt loam; moderate fine granular structure; very friable; 12 percent sandstone fragments (> 3 in. diameter); many roots; pH 7.0.
Ap2 63776	1/2 to 5 inches. Brown (10YR 4/3) silt loam; weak medium granular structure; very friable; 12 percent sandstone fragments; many roots; pH 5.0.
B1 63777	5 to 10 inches. Brown (7.5YR 4/4) silt loam; weak to moderate fine subangular blocky structure; friable; 25 percent sandstone fragments; many roots; pH 5.0.
B21 63778	10 to 19 inches. Brown (7.5YR 4/4) silt clay loam / silt loam; moderate medium blocky structure; friable; 25 percent sandstone fragments; common roots; pH 5.0.
B22t 63779	19 to 34 inches. Brown to dark brown (7.5YR 4/4 - 3/2) silty clay loam; moderate medium blocky structure; friable; common clay films; 20 percent sandstone fragments; few roots; pH 5.0.
B23t 63780	34 to 48 inches. Brown (7.5YR 4/4) silty clay loam; moderate medium subangular blocky structure; friable to firm; 30 percent sandstone fragments; common clay films; few roots; pH 5.0.
B3t 63781	48 to 60 inches. Brown (7.5YR 5/4) silty clay loam; weak to moderate medium subangular blocky structure; friable to firm; common clay films; 35 percent sandstone fragments; few roots; pH 5.0.

Notes: Colors are given for moist soil. The B21 and B23t layers were sampled for the Bureau of Public Roads. Reaction was determined by Soiltex.

Figure 2. Profile description of Hayter silt loam, McCreary County, KY.

A   Indicarb
B   Soda lime
C   Flow rate
D   Allihn con
E   100 ml Kj
F   KI
G Ag_2SO_4
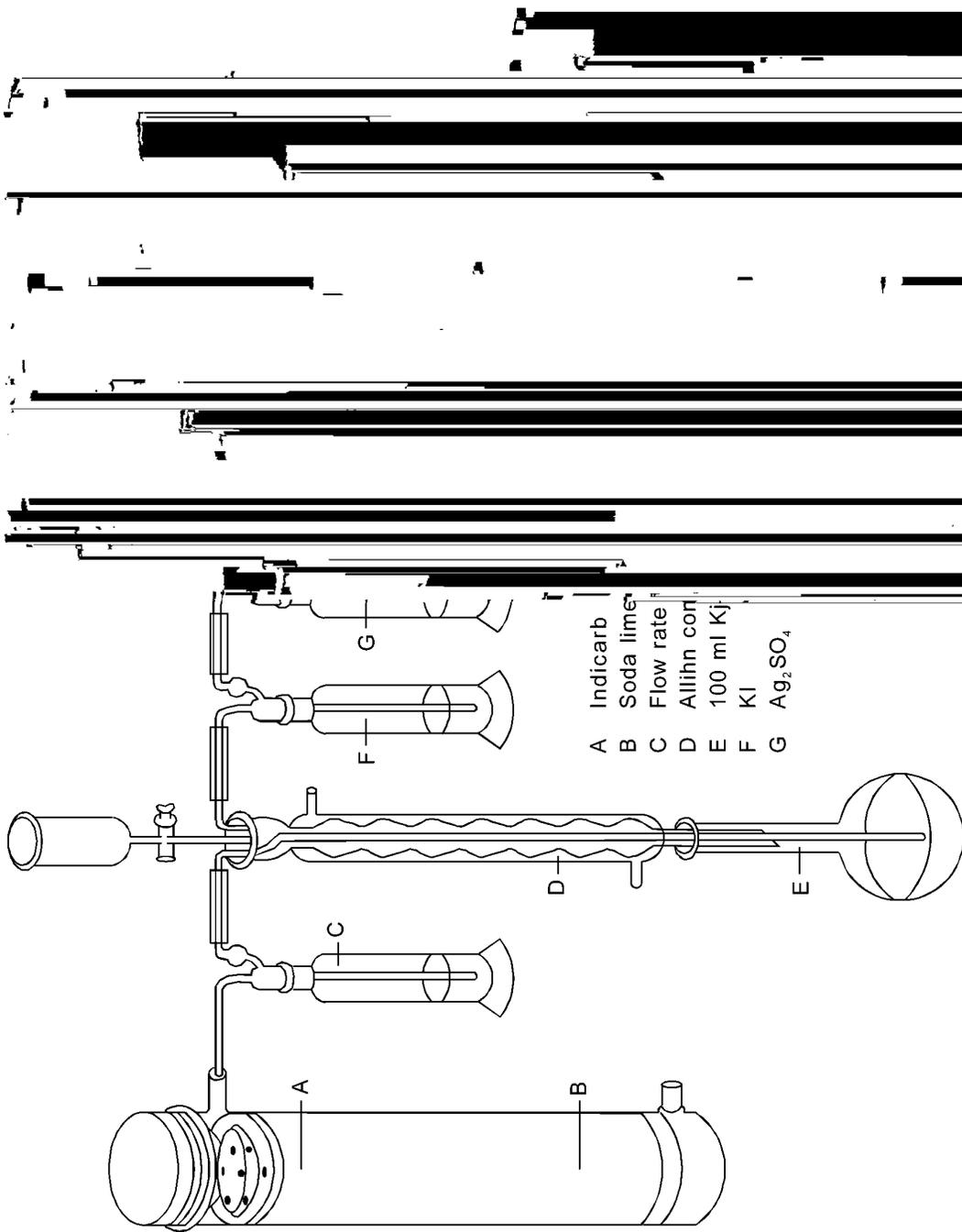
Figure 3. Apparatus for organic carbon determinat
dichromate (6AIb).
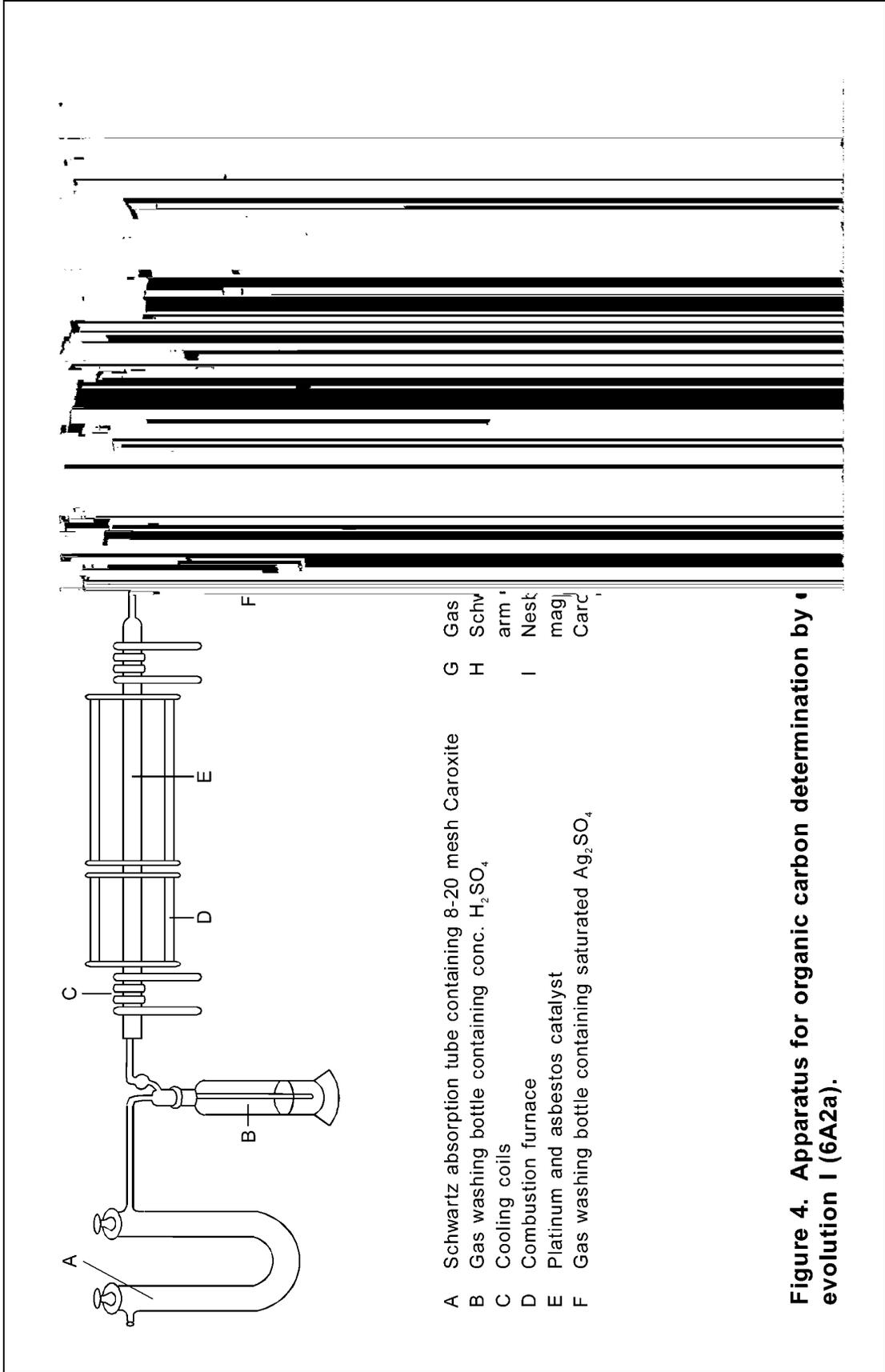
A Schwartz absorption tube containing 8-20 mesh Caroxite
B Gas washing bottle containing conc. H_2SO_4
C Cooling coils
D Combustion furnace
E Platinum and asbestos catalyst
F Gas washing bottle containing saturated Ag_2SO_4

G Gas
H Schw
   arm
I Nesk
  mag
  Carc

Figure 4. Apparatus for organic carbon determination by evolution I (6A2a).
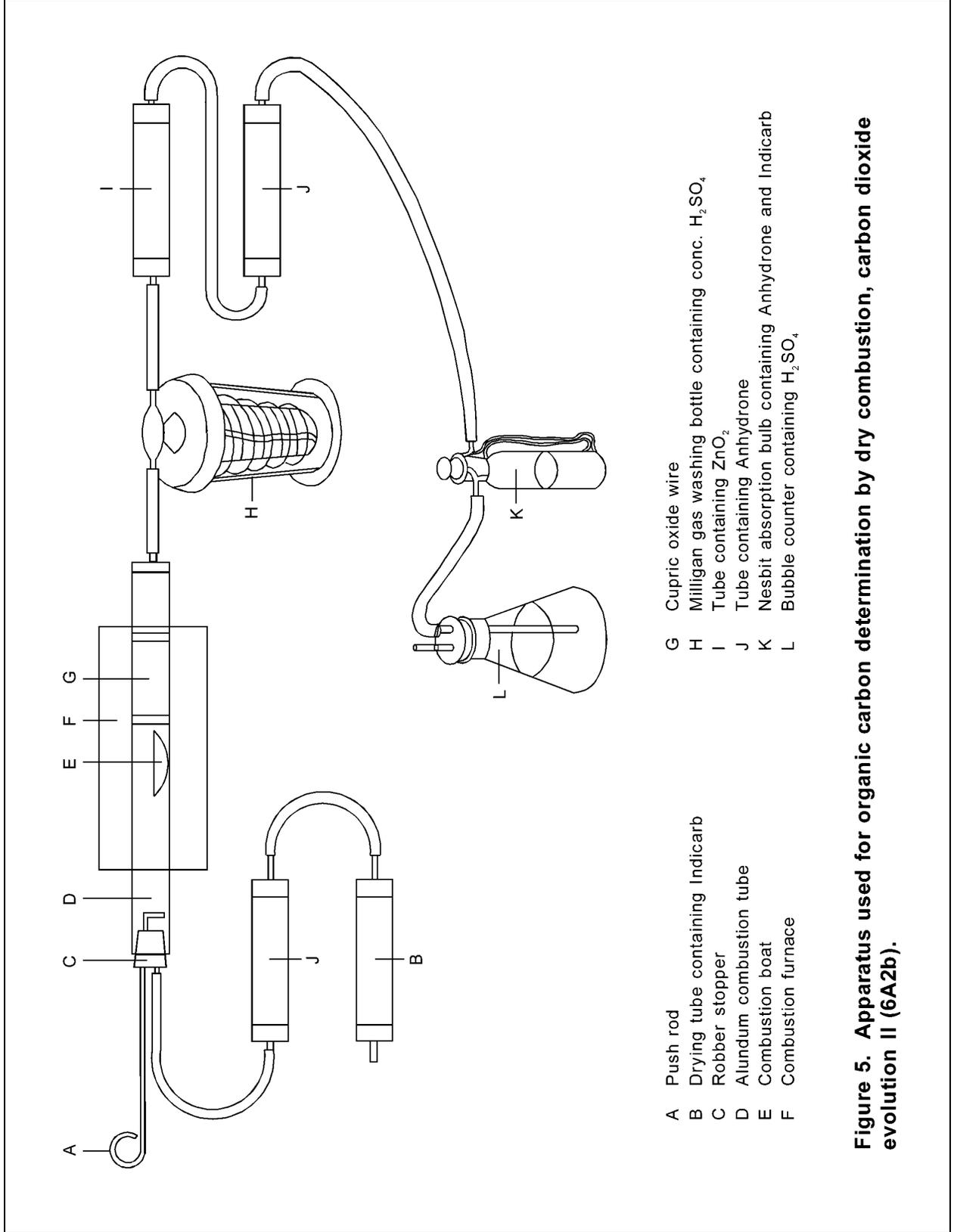
A   Push rod
B   Drying tube containing Indicarb
C   Robber stopper
D   Alundum combustion tube
E   Combustion boat
F   Combustion furnace
G   Cupric oxide wire
H   Milligan gas washing bottle containing conc. H_2SO_4
I   Tube containing ZnO_2
J   Tube containing Anhydrone
K   Nesbit absorption bulb containing Anhydrone and Indicarb
L   Bubble counter containing H_2SO_4

Figure 5. Apparatus used for organic carbon determination by dry combustion, carbon dioxide evolution II (6A2b).

685
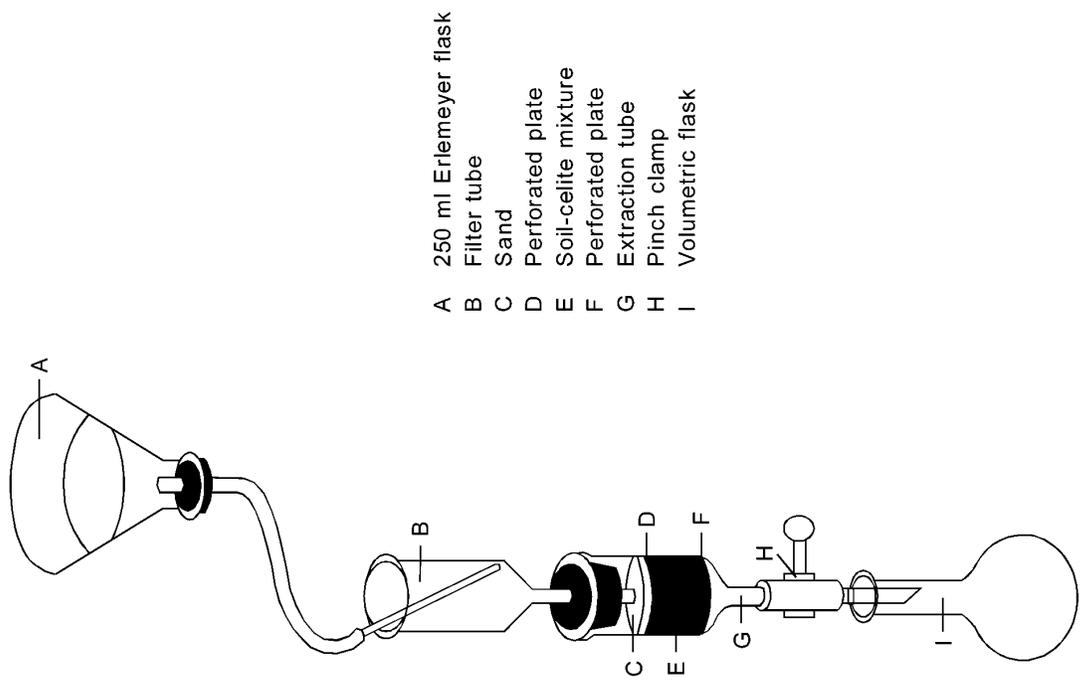
A   250 ml Erlemeyer flask
B   Filter tube
C   Sand
D   Perforated plate
E   Soil-celite mixture
F   Perforated plate
G   Extraction tube
H   Pinch clamp
I   Volumetric flask

Figure 7. Apparatus for ammonium chloride-ethanol extraction for calcium (6N3).
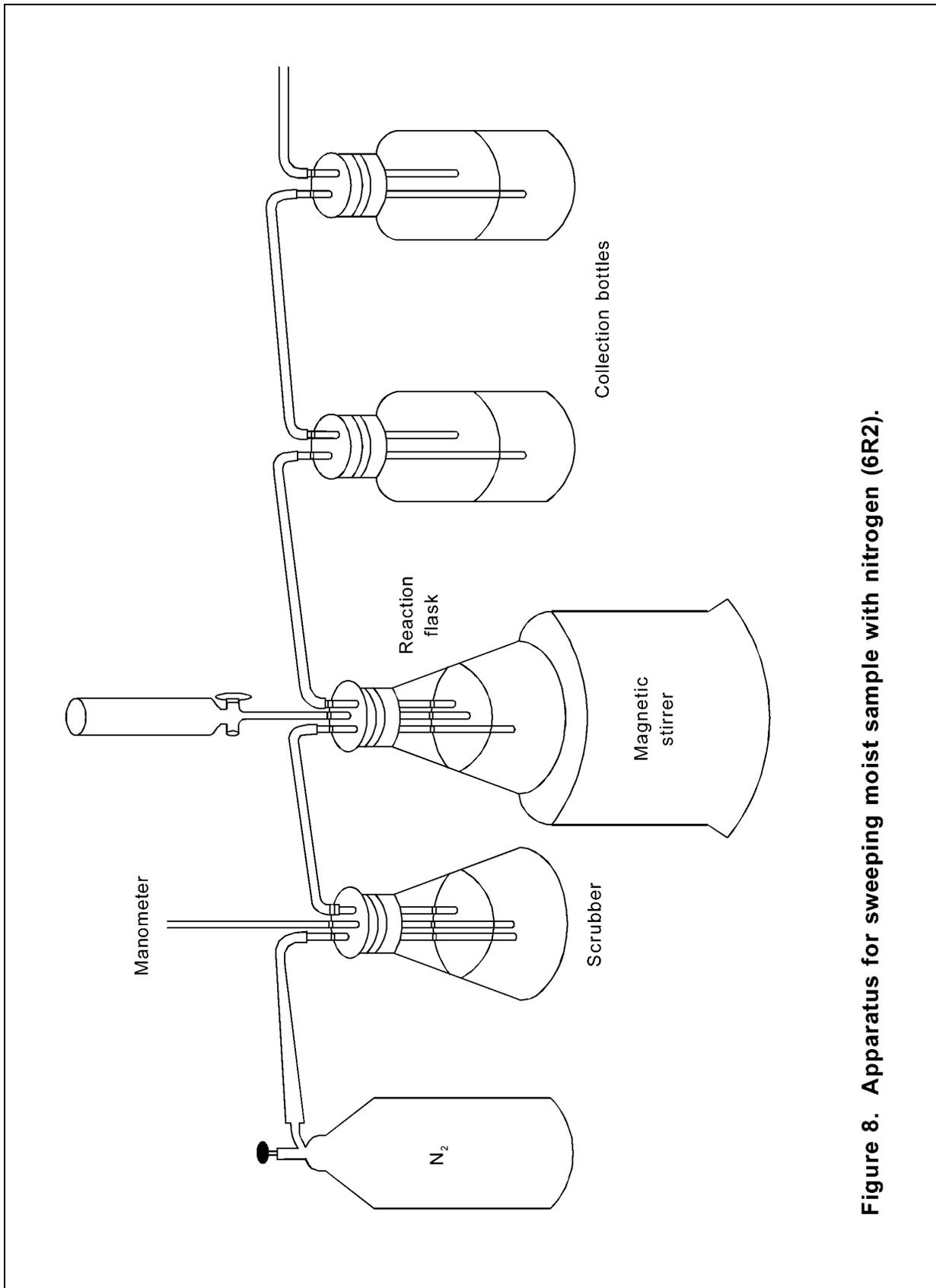
Figure 8. Apparatus for sweeping moist sample with nitrogen (6R2).

SIDE VIEW

Insert pipet conductivity
cell here

.5 cm

.25 cm

3.0 cm

3.2 cm

1.8 cm

BOTTOM VIEW

Insert filter paper

3.2 cm

3.0 cm
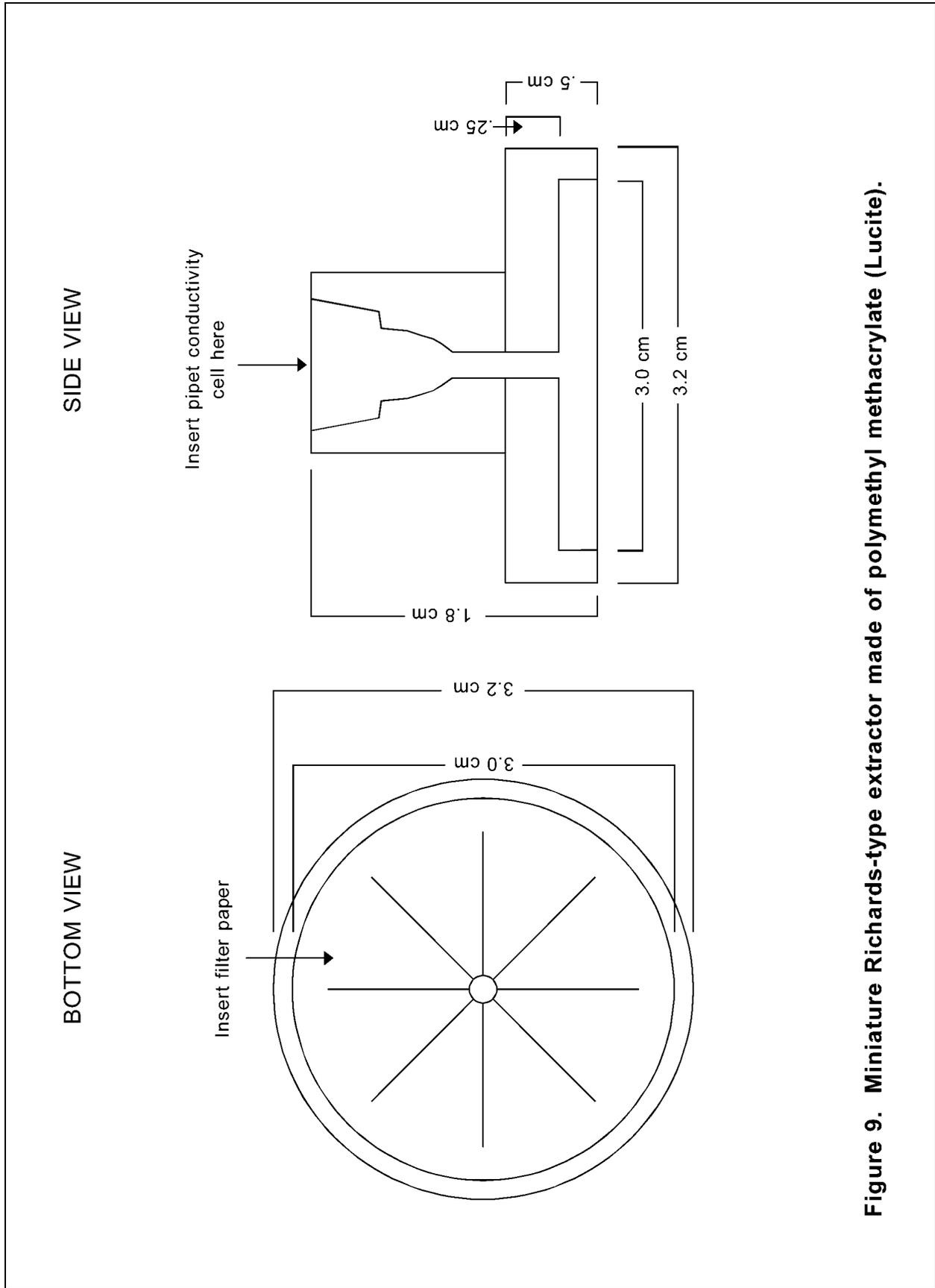
Figure 9. Miniature Richards-type extractor made of polymethyl methacrylate (Lucite).