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January 2021 Edition

Microwave Plasma Atomic Emission Spectroscopy (MP-AES)

Application eHandbook

AGILENT TECHNOLOGIES

Atomic Spectroscopy Solutions

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How Microwave Plasma – Atomic Emission Spectroscopy works

Atomic spectroscopy describes a number of analytical techniques used to determine the elemental composition of a sample by examining its electromagnetic spectrum, or its mass spectrum. The techniques which identify an analyte element by its electromagnetic spectrum include flame atomic absorption spectroscopy (FAAS), inductively coupled plasma optical emission spectroscopy (ICP-OES) and microwave plasma atomic emission spectroscopy (MP-AES). Those which identify an element by its mass spectrum include inductively coupled plasma mass spectrometry (ICP-MS), and triple quadrupole inductively coupled plasma mass spectrometry (ICP-QQQ).

Atomic excitation

Microwave plasma atomic emission spectroscopy is an atomic emission technique. It uses the fact that once an atom of a specific element is excited, it emits light in a characteristic pattern of wavelengths – an emission spectrum, as it returns to the ground state. Sources for atomic emission include the microwave plasma (MP) and the inductively coupled argon plasma (ICP) both of which are high temperature sources, and therefore excellent excitation sources for atomic emission spectroscopy. The nitrogen-fuelled microwave plasma reaches temperatures nearing 5,000 K. At these temperatures, atomic emission is strong, producing excellent detection limits and linear dynamic range for most elements.

Inside a MP-AES instrument, microwave energy from an industrial magnetron is used to form a plasma from nitrogen that has been extracted from compressed air by Agilent's Nitrogen Generator (Figure 1). Effectively, the MP-AES runs on air.

Figure 1. The nitrogen generator extracts nitrogen from compressed air to fuel the plasma.

Using a magnetic field rather than an electric one for excitation generates a very robust plasma – capable of handling a wide range of sample types.

An optimized microwave waveguide creates concentrated electromagetic fields at the torch (Figure 2). Then an axial magnetic field and a radial electrical field focus and contain the microwave energy to create a plasma.

Figure 2. A microwave waveguide creates concentrated electromagnetic fields around the torch.

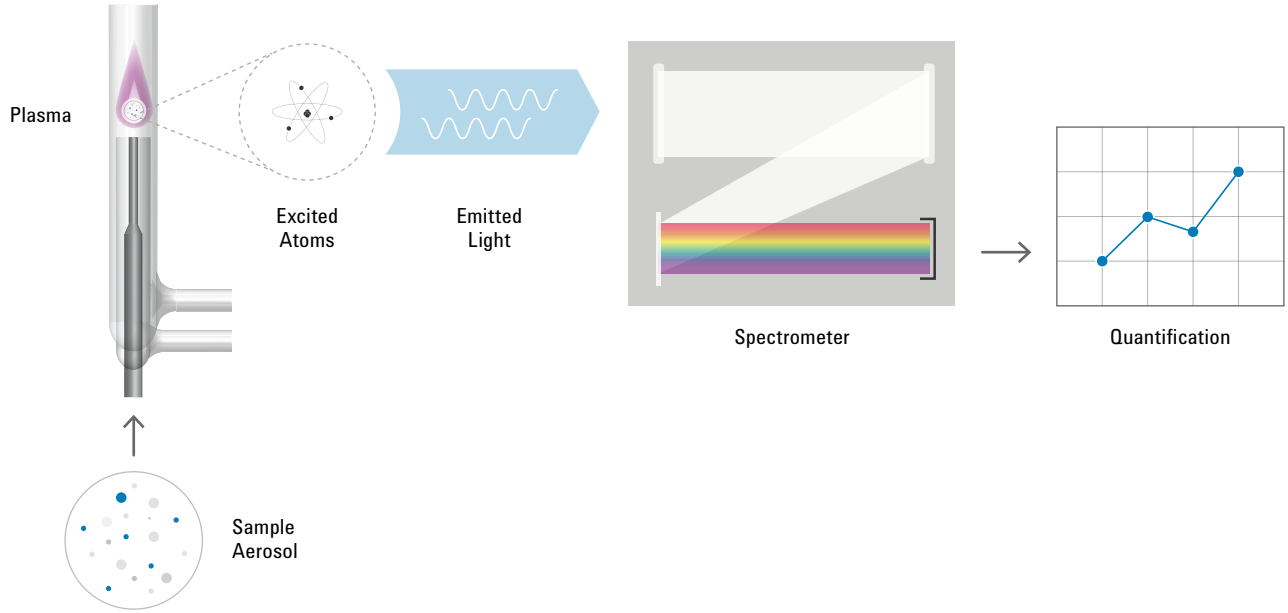

Figure 3. Schematic diagram of a microwave plasma atomic emission spectrometer

Sample introduction

Just like a flame AA instrument, an aerosol is created from a liquid sample using a nebulizer and a spraychamber. The aerosol is then introduced into the centre of the hot plasma.

The aerosol dries, decomposes and is then atomized. The atoms continue to be excited and emit light at wavelengths characteristic for each element as they return to lower energy states (Figure 3).

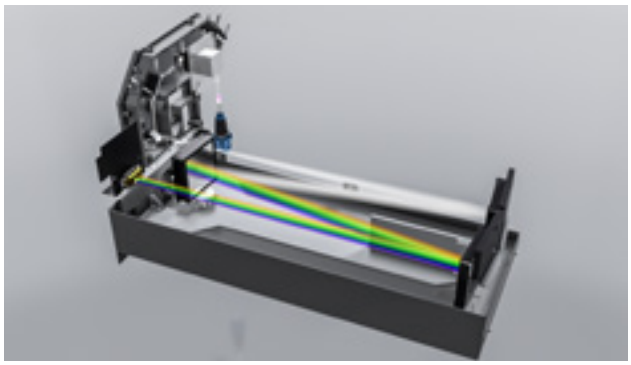

Figure 4. The emission from the plasm is directed into the optical system

Optical system

Emission from the plasma is directed into a fast scanning monochromator (Figure 4). The selected wavelength range is imaged onto the high efficiency CCD detector. This measures both spectra and background simultaneously for optimum precision.

Quantification

Just like flame AAS, MP-AES quantifies the concentration of an element in a sample by comparing its emission to that of known concentrations of the element, plotted on a calibration curve. The final result is the concentration of the element in the sample.

The benefits of MP-AES

Low cost of ownership

Gas supply is one of the highest costs associated with elemental analysis. Because the MP-AES runs on air, it vastly reduces the cost of ownership and eliminates the need for ongoing supply of flammable or expensive gases. There's no gas cylinders or lamps to buy and no standby operating costs. When a MP-AES is off, no gas or power is used. Simply switch it on again when needed for analysis

Safety

Removing the requirement for flammable gases means no gas leaks and ordering and transporting of cylinders. Removing all of these risks makes your laboratory a safer workplace.

Better performance than AA

An MP-AES has high sensitivity with detection limits down to sub ppb levels and is faster than conventional flame Atomic Absorption (AA) for a typical multi-element analysis.

Handling difficult matrices

The robust, magnetically excited microwave plasma source of a MP-AES handles difficult matrices with ease, including fuels and organic solvents, geochemical samples, fertilizers and foods. A vertically positioned torch gives the best performance with difficult samples, and features end-on axial viewing for excellent detection limits.

Remote operation

Requiring only electricity, an MP-AES can be located at a sampling point, instead of in a lab. This allows measurement turnaround to be much quicker, delivering timely data that could deliver huge benefits, such as preventing environmental spills or incorrectly manufactured products.

Fast & easy to use

Agilent's MP-AES instruments feature easy-to-use, application-specific software applets that automatically load a pre-set method so you can start analysis immediately without method development or alignment, and with minimal training.

The instrument´s torch loader automatically aligns the torch and connects gases for fast start up and reproducible performance.

Why switch from FAAS to MP-AES?

Why switch from FAAS to MP-AES?

Reducing ongoing operating costs, increasing safety, improving analytical performance and simplifying operation are some of the key challenges facing current users of Flame Atomic Absorption Spectroscopy (FAAS). With the introduction of the Agilent Microwave Plasma-Atomic Emission Spectrometer (MP-AES), these challenges have been overcome, making it the ideal instrument for laboratories looking to transition away from FAAS to a more powerful, less expensive and safer technique. Additionally, with the extra performance of the MP-AES, the sample preparation process can also be significantly simplified, saving time and money.

The Agilent 4210 MP-AES features a waveguide design and torch that is capable of running samples with high total dissolved solids without compromising detection limits.

Reduced running costs

The largest contributor to ongoing running costs for entry level spectroscopy is gases. FAAS uses a combination of air and acetylene, or nitrous oxide and acetylene for the flame. While air can be provided by an air compressor, the acetylene and nitrous oxide is supplied in cylinders and regularly needs to be replenished as it is consumed.

The 4210 MP-AES uses nitrogen extracted straight from air to sustain the plasma. The Agilent 4107 Nitrogen Generator coupled to an air compressor supplies all the free nitrogen required at greater than 99.5% purity. This leads to dramatic reductions in operating costs over the life of the instrument.

The potential cost saving of using the 4210 MP-AES for the determinaton of Ca, Mg, Na and K in fruit juice is illustrated by comparing a FAAS purchased with an air compressor and 1 year of consumables to an MP-AES purchased with air compressor, nitrogen generator, SPS 4 autosampler, and 1 year of consumables (Figure 1).

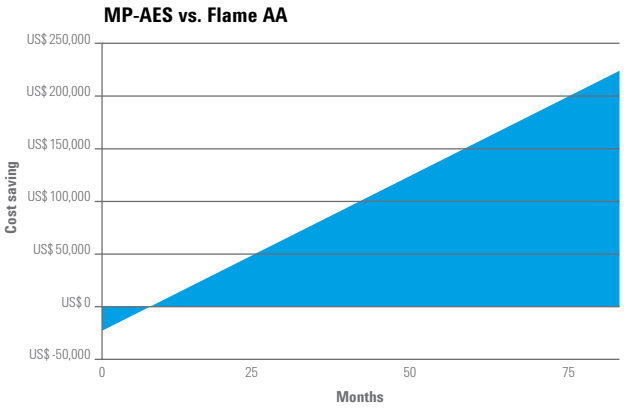

Figure 1. Online cost estimator showing the cost savings of using the MP-AES for the determination of Ca, Mg, Na and K in fruit juice.

The analysis requirements were assumed to be 500 samples per week and 4 elements per sample.

The calculation assumes that the FAAS is run without an autosampler and that 3 elements are determined with air/acetylene and 1 element with nitrous oxide/acetylene. In this example the results show an estimated cost saving of greater than US $220,000 over a 7 year evaluation period[1]. A global average gas cost was used in this calculation and results will vary from country to country.

Improved safety

Another major concern for FAAS users is the safety aspects related to the use of acetylene and nitrous oxide, from the storage and handling of cylinders, to the use of a flame in the instrument. Presence of a naked flame is of concern in all labs, particularly those that handle organic solvents, and for this reason it is not possible to run FAAS unattended.

It is also common to have to change burners to determine the full range of elements when running FAAS. While Agilent's FAAS instruments are fully interlocked to ensure the correct burners are used with the correct method, care must be taken when handling burners which can remain hot after use.

These issues are eliminated with the 4210 MP-AES. The requirements for acetylene and nitrous oxide can be avoided, along with the storage and handling concerns, and there is no need for burner change-over because of the increased performance of the higher temperature nitrogen plasma.

1 This example is intended to help you compare the running costs and savings of the MP-AES vs. flame AA. The applied formulas and parameters are correct to the best of our knowledge, but we cannot guarantee the results. Savings may vary depending on factors such as local gas and electricity costs, operator costs, number and types of elements. For this calculation operator labor costs were set to US$25/hour and electricity costs were set to US$0.18 per kW.

Improved analytical performance

The plasma of the 4210 MP-AES operates at around 5000 K which results in improved detection limits when compared to FAAS. The improvements in detection limit means that it's possible to analyse elements like phosphorus, which have very high detection limits on FAAS.

Table 1 shows the instrument detection limits (IDL) on MP-AES and FAAS for elements in a rice flour sample. The lower detection limits for P, Cu and Fe allow the major, minor and trace elements to be determined in one sample measurement.

Table 1. Comparison of typical instrument detection limits for the 4210 MP-AES and FAAS

Element	4210 Typical IDL 10 sec read µg/L	FAAS Typical IDL µg/L
Ca	0.04	0.4
Mg	0.1	0.27
Na	0.1	0.26
K	0.6	0.76
P	66	26000
Fe	1.7	7.3
Pb	2.5	14
Cu	0.5	1.2
Mn	0.2	1.0

The design of the waveguide and torch in the 4210 MP-AES, combined with the mass flow control and humidification of the nebulizer gas line, gives excellent long term stability in samples with a complex matrix common in mining and environmental samples. The introduction of elevated salt solutions into an air acetylene FAAS burner over an extended period, such as an 8 hr work day, will require maintenance to avoid blockage. If this routine maintenance is not performed, it can lead to signal drift.

Long term stability of the 4210 MP-AES was tested with a 2% TDS solution of digested rice flour. The results are shown in Figure 2.

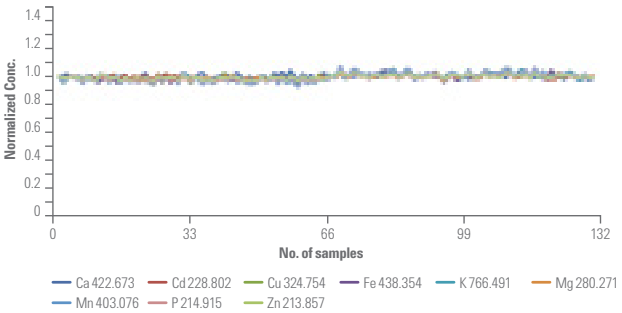

Figure 2. Digested rice flour with 2% TDS analyzed over 8 hrs. Recalibration was performed each 2 hrs and the resulting stability was <3% RSD for all elements. Default multi purpose sample introduction was used.

The 4210 MP-AES also features a greater linear dynamic range than FAAS. Table 2 gives the linear calibration range and correlation coefficient for major elements in a fruit juice sample for the 4210 MP-AES. Also shown is the optimum working range on FAAS for the same elements. The calibrations for FAAS used the default New Rational model. The greater linear range of the MP-AES compared to FAAS reduces the need to perform dilutions on over range samples which simplifies the analysis. Reducing the dilutions also means that if there are trace contaminants that need to be determined, it may still be possible to detect them. Furthermore, the improved linearity means that fewer calibration standards are required for an accurate calibration curve.

Simplifying sample preparation

A factor which greatly influences sample preparation procedures on FAAS is the presence of interferences. Presence of compounds that cannot be broken down in the low temperature flame lead to chemical interference and elements like Na and K can suffer from ionization interference.

Table 2. Linear concentration range of the 4210 MP-AES and optimum concentration range of FAAS for fruit juice samples

Element	4210 MP-AES linear concentration range (mg/L)	Linear correlation coefficient on MP-AES calibration	FAAS optimum working range (mg/L)
Ca 422.673	0 – 20	0.9999	0.01 - 10
Mg 518.360	0 – 100	0.99988	0.15 - 20 (for Mg 202.6)
Na 589.592	0 – 20	0.99996	0.01 – 2.0
K 769.897	0 – 100	0.99968	1 – 6.0

Table 3. Typical sample preparation requirements for FAAS and MP-AES

Element	Possible chemical interferences	FAAS specific sample preparation	MP-AES specific sample preparation
Ca	Refractory compounds Ionization effects	Lanthanum releasing agent Cesium ionization buffer	None
Mg	Ionization effects	Cesium ionization buffer	None
Na	Refractory compounds Ionization effects	Lanthanum releasing agent Cesium ionization buffer	None
K	Ionization effects	Cesium ionization buffer	None

Table 4. Certified Reference Material (CRM) recoveries of major elements in grapefruit juice, analyzed by MP-AES. No ionization suppressant was required and excellent accuracy for K was achieved. Additionally, no lanthanum nitrate was added and excellent recoveries for Ca was achieved

Grapefruit Juice T0842QC	Certified Value (mg/L)		Found (mg/L)	%Recovery
	Assigned Value	Range		
Calcium	145.6	123.6 – 167.6	158.3 ± 3.2	108.7
Magnesium	92.5	77.5 – 107.4	91.1 ± 0.6	98.5
Potassium	1102	979 – 1225	1100 ± 14.7	99.8

Various strategies for dealing with these interferences are well established. It is common to add releasing agents such as strontium or lanthanum to overcome chemical interferences, or alternatively the hotter nitrous oxide flame can be used. Ionization effects are usually overcome by adding an ionization buffer to the solution, such as sodium, potassium or cesium. Another strategy is to extract the elements of interest into an organic phase in order to remove the interfering elements. As a result the sample must be individually prepared for each element in the sample.

With the hotter plasma source of the 4210 MP-AES these chemical interferences are eliminated. This means that the element specific sample preparation required on FAAS is not needed which greatly simplifies the sample preparation process.

As an example the elements covered in a fruit juice analysis are shown above with a comparison of the sample preparation required for each element (Tables 3 and 4).

Conclusion

Agilent's 4210 MP-AES is the ideal instrument for customers looking to transition from Flame Atomic Absorption Spectroscopy (FAAS) to another technique. By using nitrogen as the source gas for the plasma, running costs are greatly reduced, and by removing the requirement for hazardous nitrous oxide and acetylene safety is greatly increased. Additionally the higher temperature nitrogen plasma atomization/ionization source improves detection limits, linear range, and long term stability, and allows the sample preparation process to be greatly simplified.

MP-AES accessories

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Expanding capabilities with accessories

Agilent offers a range of accessories for the MP-AES instruments. They add additional capabilities to the instrument, allowing you to optimise the setup for specific applications.

Advanced Valve System (AVS 4)

This four port switching valve enables high sample throughput and prolongs component lifetime due to the reduced exposure of sample introduction components to harsh samples.

Multimode Sample Introduction System (MSIS)

An innovative accessory for both ICP-OES and MP-AES that allows sample introduction via either vapor generation or nebulization modes, or both modes at the same time. Allows sub ppb detection of As, Se, and Hg.

SPS 4 Autosampler

Our fastest ever autosampler, the SPS 4 allows the unattended multi-element analysis of up to 360 samples.

4107 Nitrogen Generator

The nitrogen generator extracts nitrogen from compressed air, to fuel the plasma of an MP-AES instrument. It provides a continuous supply of nitrogen.

IsoMist

A temperature controlled spraychamber that offers improved stability for volatile organic solvents.

External Gas Control Module (EGCM)

The EGCM injects air into the plasma to minimize carbon build up, reduce background in organic applications and enable sulfur determinations.

Applications of MP-AES

The MP-AES technique can be used for elemental analysis for a wide range of sample types.

Food & Agriculture	Geochemical	Environmental	Chemical & Petrochemical
Major and toxic elements in foods, beverages and agricultural samples	Geochem samples in aqua regia digests	Hg, Pb, Cd and Cr in electronics and plastics (for WEEE/RoHs compliance)	Additives in lubricating oils
Cations in soils	Trace elements in geological samples	Automated remote river and waste water analysis	Wear metal contaminants in used oils
Nutrients in soils	Trace level gold in cyanide leach	Heavy metals in soils	Analysis of coolant
Metals in soil extracts	Analysis of high purity gold	As, Sb and Se in sediments and waste	Analysis of petroleum, diesel and biodiesel fuel
Metals in agricultural soil samples	Platinum group elements in ore grade material	Analysis of waste waters, sediments, plant waste products and soils	Major elements in polymers
Analysis of fertilizers	Various elements in plating solutions		Analysis of raw chemicals for contaminant levels

Agilent's Atomic Spectroscopy Portfolio

Agilent leads the way in atomic spectroscopy innovation. Our comprehensive and trusted portfolio offers you the most diverse application coverage for AA, ICP-OES and ICP-MS, while our unique MP-AES and ICP-QQQ technologies offer new possibilities for your lab.

Atomic absorption spectroscopy (AA)

- Low system cost
- Low to moderate productivity
- ppt for GFAAS. High ppb to % for FAAS
- Approximately 3% total dissolved solids for FAAS and up to 30% for Graphite Furnace

Agilent's Atomic absorption range includes both flame and graphite furnace models. The low-cost flame AA features unique fast sequential capability, simplicity of operation, and very good sensitivity, while the GFAAS models feature high sensitivity and accurate Zeeman background correction for your toughest samples.

Microwave plasma atomic emission spectroscopy (MP-AES)

- Moderate to high productivity
- Medium ppb to %
- Low running cost
- Approximately 3% total dissolved solids

The Agilent MP-AES saves you money because it runs on air. MP-AES delivers accurate and reliable performance.

Inductively coupled plasma optical emission spectroscopy (ICP-OES)

- Highest productivity (<30 s per sample) with AVS 6/7
- Low ppb to %
- Up to 30% total dissolved solids

Agilent's ICP-OES are the world's most productive ICP-OES. Utilizing a vertical plasma for axial and radial emissions, it delivers excellent sensitivity and high matrix capability.

Inductively coupled plasma mass spectrometry (ICP-MS and ICP-QQQ)

- High productivity (<60 s per sample) with ISIS 3
- Low ppq to %
- Up to 25% total dissolved solids with optional ultra high matrix introduction (UHMI)

Agilent's ICP-MS range includes both a instrument suitable for routine analysis as well as a high performance model with superior detection limits, wider dynamic range and high matrix tolerance.

Our Agilent ICP-QQQ with MS/MS mode provides ultimate accuracy for advanced applications.

Food & Agriculture

With high sample throughput and fast sequential measurement, Agilent MP-AES is ideal for food screening laboratories.

MP-AES is ideal for contract laboratories where fast turn around is key, including small to mid-sized screening laboratories needing to determine essential nutrients and elements at major levels, and toxic elements at trace levels.

- With the lowest cost of ownership, the MP-AES will give you the edge over your competition by reducing your cost per analysis and improving performance
- Eliminate downtime waiting for gas refills, and achieve fast sample turn around with safe, reliable unattended analysis
- Reduce sample preparation. The axially viewed vertical plasma handles a wide range of samples — from food and soil digests to high salt soil extractions
- Improved long term stability with integrated nebulizer gas humidification as standard on MP-AES
- Increase your sample throughput, compared to conventional flame AA systems, and never have to change burners/gases for different elements again
- Rapid method development and fast start-up means any user can achieve optimum performance
- A MultiCal feature allows the analysis of elements at high and low levels in the same run
- Complete wavelength coverage means you can avoid spectral interferences from majors by simply choosing another wavelength
- Achieve rapid sub-ppb detection of As, Hg and Se with the Multimode Sample Introduction System (MSIS)
- Include P and S in your elemental analysis suite with better detection limits using MP-AES plasma emission technology

Routine analysis of total arsenic in California wines using the Agilent 4200/4210 MP-AES

Application note

Food Safety

Authors

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Introduction

Arsenic (As) is a naturally occurring element found throughout the world. The environmental levels of As have been increasing due to natural sources, such as volcanic activity, and anthropogenic sources, such as smelting. The continuous release of As into the ecosystem has formed an accumulation of the element in the food chain.

Wine is a globally consumed beverage where total levels of As are regulated between 100-200 µg L^{-1}, depending on the country in question [1]. However, there are countries, such as the United States, that do not regulate levels

of all elements in wine. This necessitates investigating total As levels in wine produced in the United States to identify potential contamination, beyond the levels regulated by other countries.

Measuring total arsenic levels in wine with various spectrometric techniques typically deliver insufficient sensitivity due to the element's relatively high ionization potential. However, the use of vapor generation techniques to form volatile forms of As allow for a more sensitive detection of As.

This study investigates the use of the Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) coupled with the Multimode Sample Introduction System (MSIS) accessory to measure total As in wine samples from the California region. This application is also applicable for Agilent's 4210 MP-AES instrument.

The MP-AES offers high sensitivity, with superior performance in comparison to Flame Atomic Absorption Spectroscopy. The instrument uses nitrogen to sustain the plasma, either extracted from the ambient air (using a nitrogen generator) or supplied via a nitrogen Dewar. Compared with acetylene-based instruments, the MP-AES is much safer to run, as no flammable gases are required. Operating costs are also significantly less. The addition of the MSIS accessory assists with the production of hydride species which are separated from the liquid and introduced to the plasma, delivering better performance and lower detection limits, than with conventional nebulization.

Experimental

Instrumentation

All measurements were performed using the Agilent 4200 MP-AES fitted with the MSIS accessory, MicroMist glass nebulizer and Easy-fit torch.

The As 188.979 nm line was selected for analysis and the read time optimized in the easy to use MP Expert software that controls the instrument. The instrument operating and method settings are given in Table 1.

The Agilent MP Expert software allows for correction of background and spectral interferences. The Fast Linear Interference Correction (FLIC) background correction (refer to Figure 1) was used to correct for the complex structured background by modeling with the solution blank of 10% HCl and 5% ethanol as the interferent.

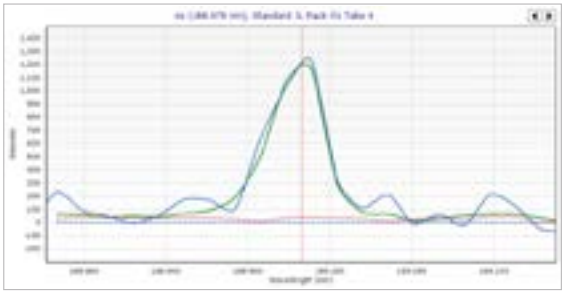

Figure 1. FLIC background correction applied to As (188.979 nm) calibration standard. Background and analyte peak (blue line), FLIC model applied to background and analyte peak (green line).

Table 1. Agilent 4200 MP-AES operating and method conditions.

Parameter	Setting
As wavelength (nm)	188.979
Pump speed (rpm)	20
Sample pump tubing	Black-black
Hydride reagent tubing	Black-black
MSIS waste tubing	Black-white
Read time (sec)	20
Number of Replicates	3
Sample uptake delay (s)	40
Nebulizer flow (L/min)	0.45
Fast pump during uptake	On
Stabilization time (s)	20
Background correction	FLIC
Calibration Fit	Linear
Nitrogen gas source	Agilent 4107 Nitrogen Generator

Samples

Forty commercially available wines, originating from various areas in California, were analysed in this study (Table 2). The wine varieties included: Pinot noir, Merlot, Cabernet Sauvignon, Rosé, Chardonnay, white Zinfandel, Sauvignon blanc, a white blend, sparkling wine and port-style wine.

Table 2. Wine samples used in the study, with corresponding sample number and regional origin.

Sample#	Wine type	Region
1	Cabernet Sauvignon	South Coast
2	Cabernet Sauvignon	Sonoma County
3	Cabernet Sauvignon	Lodi/Woodbridge Grape Commission
4	Cabernet Sauvignon	South Coast
5	Cabernet Sauvignon	Sierra Foothills
6	Cabernet Sauvignon	Napa County
7	Cabernet Sauvignon	Sierra Foothills
8	Cabernet Sauvignon	Napa County
9	Cabernet Sauvignon	Greater Bay Area
10	Cabernet Sauvignon	North Coast
11	Cabernet Sauvignon	North Coast
12	Cabernet Sauvignon	South Central Coast
13	Cabernet Sauvignon	Greater Bay Area
14	Cabernet Sauvignon	Sonoma County
15	Cabernet Sauvignon	Lodi/Woodbridge Grape Commission
16	Cabernet Sauvignon	North Central Coast
17	Cabernet Sauvignon	South Central Coast
18	Cabernet Sauvignon	South Coast
19	Cabernet Sauvignon	South Central Coast
20	Cabernet Sauvignon	Sonoma County
21	Cabernet Sauvignon	Sierra Foothills
22	Cabernet Sauvignon	South Central Coast
23	Cabernet Sauvignon	North Central Coast
24	Cabernet Sauvignon	North Coast
25	Cabernet Sauvignon	Greater Bay Area
26	Cabernet Sauvignon	Napa County
27	Cabernet Sauvignon	Sierra Foothills
28	Pinot Noir	Appellation Central Coast
29	White Blend	San Joaquin County
30	Rosé	Contra Costa County
31	Rosé	Lodi/San Joaquin County
32	Chardonnay	Santa Barbara County
33	White Zinfandel	Napa and Sonoma
34	Chardonnay	Central Coast
35	Chardonnnay	Napa County
36	Merlot	Napa County
37	White Zinfandel	Napa and Lodi
38	Sauvignon Blanc	Oakville/Napa County
39	California Brut sparkling wine	Sonoma County
40	Petite Sirah port-style wine	Clarksburg/Yolo County

Sample preparation

All wine samples were diluted by a factor of three with Millipore ultrapure water (Milli-Q™ Water System, Darmstadt, Germany) then further diluted with hydrochloric acid (34-37.5%, Environmental Grade, Alfa Aesar, Ward Hill, MA, USA) for a total acid concentration of 10%. This resulted in a final 3.3-fold wine dilution. Each wine was prepared in triplicate with the exception of sample 37, which was prepared with 5 replicates due to high residual sugar content.

Four wine samples were selected and prepared as spiked samples for additional analysis. Low and high concentration spikes were used at 10 μgL^{-1} and 50 μgL^{-1} and prepared in triplicate.

Calibration standards and reagents

A 1,000 μgL^{-1} single element calibration standard of As (VHG Labs, Manchester, NH, USA) was used to prepare working standards at 5, 10, 25, 50 and 100 μgL^{-1}. As (III) and As (V) calibration standards from SPEX CertiPrep (Metuchen, NJ, USA) were used as check standards to validate the method at 20 μgL^{-1} each. All calibration standards were matrix-matched with a 10% hydrochloric acid (34-37.5% Environmental Grade, Alfa Aesar, Ward Hill, MA, USA) and 5% ethanol (v/v) (200 proof, Gold Shield Distributors, Hayward, CA) solution.

Two separate solutions were created for hydride generation. The first consisted of 1.2% Sodium Borohydride ($NaBH_4$, 98%, J.T. Baker, Center Valley, PA, USA) and 1.0% Sodium Hydroxide (NaOH, ACS Grade, EMD Chemicals Inc., Gibbstown, NJ) in Millipore ultrapure water (Milli-Q™ Water System, Darmstadt, Germany). The second was a 1:1 solution of HCl (34-37.5%, Environmental Grade, Alfa Aesar, Ward Hill, MA, USA) and Millipore ultrapure water (Milli-Q™ Water System, Darmstadt, Germany).

A reduction solution of 25% (w/v) potassium iodide (ACS Grade, BDH Chemicals, West Chester, PA) was used to reduce As species prior to analysis. As (III) and As (V) are the most prevalent forms of As in wines. This reduction step aims to change the valence state of As from As (V) to As(III), because As (V) does not readily form a metal hydride. The potassium iodide solution was added to all samples and standards to create a final concentration of 1%. Best results were obtained when it was added at least 3 hours prior to analysis.

The setup of the MSIS (in Vapor Generation mode) for this analysis is displayed in Figure 2. The sample and 50% HCl solution were mixed using a 'tee' fitting after the peristaltic pump and the combined sample/HCl line was connected to the bottom of the MSIS. The reductant, NaOH/$NaBH_4$ solution, line was attached to the top of the MSIS. The unused sample line to the nebulizer was blocked during analysis as conventional nebulization was not required.

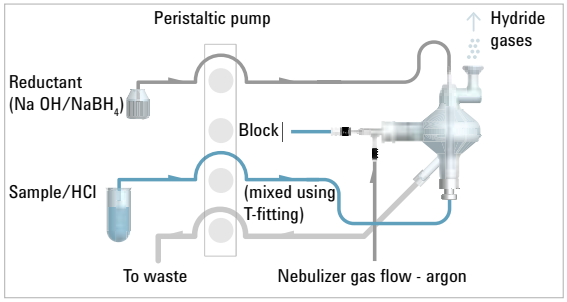

Figure 2. The MSIS setup for Vapor Generation mode.

Results and discussion

Calibration

The five-point calibration curve for As (188.979 nm) is shown in Figure 3. It shows excellent linearity with a calibration coefficient of greater than 0.999 and less than 6% error on each calibration point.

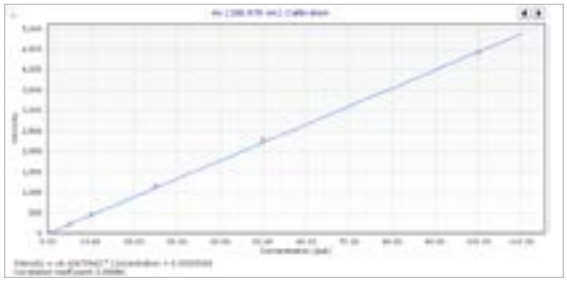

Figure 3. Calibration curve for As 188.979 nm showing excellent linearity across the 5-100 μgL^{-1} concentration range, illustrating the wide analytical range of the instrument.

Method Detection Limit

The Method Detection Limit (MDL) for As was determined from the analysis of ten replicate measurements of the blank solution. The results displayed in Table 3, show that the calculated MDL (confidence interval of 99.5%) for As was 0.34 μgL^{-1}.

Table 3. The calculated MDL and standard deviation results for As 188.979 nm.

Element	Concentration (μgL^{-1})
Mean (n=10)	0.01
SD	0.10
MDL (0.995)	0.34
MDL (0.99)	0.29
MDL (0.95)	0.19

Method validation

To check the validity of the method, Quality Control (QC) samples were run after the calibration and throughout the analytical run. The Continuing Calibration Verification (CCV) and Continuing Calibration Blanks (CCB) were measured every 10 samples. The initial calibration verification block included a 20 μgL^{-1} As (III) and As (V) sample. This was done to validate the calibration and confirm the efficiency of the KI reduction step of As (V) to As (III) prior to analysis. All CCV recoveries were within ± 10% of the assigned values (Table 4).

Table 4. QC recoveries of CCB, CCV and 20 μgL^{-1} As (V) and As (III) samples.

Solution	Concentration (μgL^{-1})	Recovery (%)
CCB, (mean, n=7)	0.46	-
25 µg L^{-1} CCV, (mean, n=7)	23.94	96
20 µg L^{-1} As (V)	20.59	103
20 µg L^{-1} As (III)	19.92	99.6

Analysis of wine samples

The method described above was applied to the analysis of 40 Californian wine samples. The results obtained for each sample are the average of 3 replicates and can be found in Table 5, along with the standard deviation and relative standard deviation (%RSD). As concentrations in the wine samples ranged from below the MDL to 48.81 μgL^{-1}, well below the range of 100-200 μgL^{-1} regulated in many countries.

Table 5. The quantitative results for total As (188.979 nm) concentration in 40 Californian wines using the 4200 MP-AES.

Sample	Mean Concentration (μgL^{-1}) (mean, n=3)	Standard Deviation	Relative Standard Deviation (%)
1	1.03	0.88	0.85
2	<MDL	0.71	N/A
3	1.48	2.12	1.43
4	1.43	0.84	0.59
5	<MDL	0.21	N/A
6	<MDL	0.40	N/A
7	<MDL	0.77	N/A
8	<MDL	0.74	N/A
9	<MDL	0.74	N/A
10	43.81	1.13	0.03
11	2.92	3.55	1.22
12	<MDL	1.17	3.95
13	<MDL	3.91	1.90
14	6.63	1.14	0.17
15	6.09	1.45	0.24
16	3.24	1.89	0.58
17	<MDL	0.22	N/A
18	2.33	1.33	0.57
19	<MDL	2.11	14.06
20	<MDL	1.52	6.70
21	0.75	0.92	1.23
22	<MDL	2.51	N/A
23	10.16	1.15	0.11
24	<MDL	1.63	N/A
25	<MDL	1.74	N/A
26	<MDL	1.66	N/A
27	<MDL	0.22	N/A
28	3.96	0.52	0.06
29	1.37	1.16	0.85
30	<MDL	0.71	N/A
31	<MDL	0.47	N/A
32	27.04	1.21	0.04
33	31.17	4.72	0.15
34	4.53	0.37	0.08
35	9.86	0.23	0.02
36	3.44	0.46	0.13
37	17.84 (mean, n=5)	0.63	0.04
38	11.23	0.28	0.02
39	9.76	0.24	0.02
40	2.64	0.90	0.34

<MDL = below Method Detection Limit

Analysis of spiked wine samples

Four wines, representing various total As concentrations, were selected for a spike recovery study. Two spikes were completed for each sample at 10 and 50 μgL^{-1}. This equates to spikes of 33 and 165 μgL^{-1} in the sample. The recoveries for each spike were within ± 10%, with the exception of one which had a recovery of 111%. Results seen in Table 6, show excellent recovery for As using the MP-AES at low and high μgL^{-1} levels.

Conclusions

The Agilent 4200 MP-AES coupled with the MSIS accessory provided an easy and accurate analysis of total As in wine. The MSIS technology increased sensitivity to levels lower than single digit μgL^{-1}. The resulting MDL would be approximately 100 times lower when compared to using direct nebulization. All 40 wine samples analyzed were found to have As concentrations less than the levels regulated by most countries worldwide.

The complex background on the calibration and samples was easily corrected with Agilent's Fast Linear Interference Correction (FLIC), improving analytical accuracy.

The nitrogen-based plasma significantly reduces operating costs when nitrogen is supplied with the use of a Agilent 4107 Nitrogen Generator. The generator extracts nitrogen from compressed air. Alternatively, nitrogen can be supplied by Dewar.

The Agilent 4200 MP-AES with MSIS accessory proved to be a reliable, cost-effective instrument for quantifying total As in wine.

Table 6. The percent recovery results for the four As spiked wine samples at 10 and 50 μgL^{-1}, the results shown represent the concentration in the original sample, calculated accounting for the dilution factor.

Sample#	Spiked concentration (μgL^{-1})		Measured spiked concentration (μgL^{-1})	Measured unspiked concentration (μgL^{-1})	Recovery (%)
8	33	Ave	32.25	-1.53	102.36
		%RSD	0.03	-0.48	
8	165	Ave	153.26	-1.53	93.82
		%RSD	0.01	-0.48	
23	33	Ave	42.76	10.16	98.81
		%RSD	0.01	0.11	
23	165	Ave	164.79	10.16	93.72
		%RSD	0.01	0.11	
28	33	Ave	39.54	3.96	107.82
		%RSD	0.01	0.06	
28	165	Ave	161.48	3.96	95.46
		%RSD	0.04	0.06	
32	33	Ave	57.63	27.04	92.68
		%RSD	0.00	0.04	
32	165	Ave	211.12	27.04	111.56
		%RSD	0.01	0.04	

Reference

C. K. Tanabe, H. Hopfer, G. Gilleland, A. Liba, S. E. Ebeler and J. Nelson. Total arsenic analysis in Californian wines with hydride generation – microwave plasma – atomic emission spectroscopy (HG-MP-AES). *J. Anal. At. Spectrom*, 2016

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Determination of available micronutrients in DTPA extracted soils using the Agilent 4210 MP-AES

Application note

Food safety and agriculture

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Introduction

Micronutrient soil analysis is commonly conducted in agricultural laboratories to assess the quality of soil for plant development and crop yield. Micronutrients such as copper, iron, manganese and zinc can be extracted from soil using solutions containing chelating agents such as diethylenetriaminepentaacetic acid (DTPA).

Typically, the determination of micronutrients in soils is conducted using Flame Atomic Absorption Spectroscopy (FAAS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES); however, with agriculture

labs increasingly under pressure to reduce operating costs and improve safety, Microwave Plasma Atomic Emission Spectroscopy (MP-AES) is gaining recognition as a suitable alternative to these techniques.

Why use MP-AES over traditional techniques?

The advantages of MP-AES for the analysis of environmental samples, including soils include:

- Lower running costs and improved safety.
  MP-AES uses nitrogen gas from either a Dewar or extracted from air using the Agilent 4107 Nitrogen Generator. Eliminating the need for expensive and hazardous gases such as acetylene allows for unattended analysis. It is the ideal instrument for laboratories looking to reduce on-going operating costs or with safety concerns.

- Excellent analytical performance for difficult samples.
  The stable microwave plasma is capable of analyzing complex matrices such as DTPA soil extracts or soil digests containing high total dissolved solids (TDS), as well as aqueous solutions.

- Multi-elemental analysis.
  MP-AES offers improved analytical performance, lower detection limits and a wider calibration range compared to Flame Atomic Absorption Spectroscopy.

- Ease of use.
  MP-AES uses intuitive MP Expert software and plug-and-play hardware to simplify instrument setup, method development and analytical performance, with minimal training. Additionally, application specific software applets can be created in MP expert from pre-set templates, further simplifying analysis.

This application note describes the determination of micronutrients Cu, Fe, Mn and Zn in soils following DTPA extraction using the Agilent 4210 MP-AES.

Experimental

Instrumentation

All measurements were performed using the Agilent 4210 MP-AES with it's integrated humidifier accessory and SPS 4 autosampler. The instrument was set up with the standard sample introduction system comprising the Agilent OneNeb Series 2 nebulizer, double-pass glass cyclonic spray chamber and Easy-fit torch. Instrument method parameters and analyte settings are listed in Table 1.

Table 1. Agilent 4210 MP-AES instrument and method parameters.

Parameter	Value			
Element	Cu	Fe	Mn	Zn
Wavelength (nm)	324.754	259.940	257.610	213.857
Nebulizer	OneNeb Series 2			
Nebulizer flow rate (L/min)	0.75			
Pump rate (rpm)	15			
Sample pump tubing	Orange/Green Solvaflex			
Waste pump tubing	Blue/blue Solvaflex			
Read time (s)	3			
Number of replicates	3			
Sample uptake delay (s)	35			
Rinse time (s)	20			
Stabilization time (s)	10			
Background correction	Auto			
Gas source	Dewar nitrogen			

Standard and sample preparation

The soil samples were supplied dried and ground. The extraction solution comprised 0.005 M diethylenetriaminepentaacetic acid (DTPA), 0.01 M calcium chloride dihydrate ($CaCl_2.2H_2O$) and 0.1 M triethanolamine (TEA).

1.97 g of DTPA, 1.47 g $CaCl_2.2H_2O$ and 13.3 mL TEA were dissolved separately in distilled water and combined. The pH was adjusted to 7.3 using conc. HCl and the volume made up to 1 L with distilled water.

10 g of soil was weighed and 20 mL of the DTPA extraction solution was added. After shaking for 120 minutes, the sample was filtered using filter paper.

Multi-element calibration standards were prepared at the following concentrations: 0.5, 2.5 and 5.0 µg/mL of Cu and Zn, 5.0, 25.0 and 50.0 µg/mL of Mn and 25.0, 50.0 and 100.0 µg/mL of Fe. All calibration blanks and standards were prepared in the DTPA extraction solution.

Results and discussion

Working concentration range

Linear calibrations were obtained for all four elements with calibration coefficients greater than 0.999 (Table 2) and less than 10% calibration error for each point. As an example, Figure 1 shows the calibration curve for Cu 324.754 nm and the calibration error for each calibration point (Table 3).

Table 2. Wavelength and working calibration concentration range.

Element and line (nm)	Concentration range (µg/mL)	Concentration coefficient
Cu 324.754	0.5-5	1.000
Fe 259.940	10-100	0.999
Mn 257.610	5-50	0.999
Zn 213.857	0.5-5	0.999

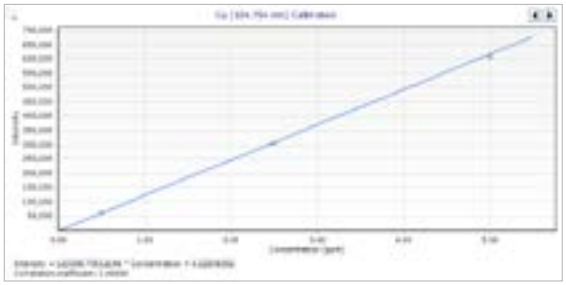

Figure 1. The calibration curve for Cu 324.754 nm shows excellent linearity across the calibrated range with a correlation coefficient of 1.00000.

Table 3. Calibration error (%) for each calibration point for Cu 324.754 nm.

Standards	Calibration error (%)
Blank	0.00
Standard 1	1.31
Standard 2	0.59
Standard 3	0.94

Method detection limits

Three sigma method detection limits (MDL) were determined from ten replicate measurements of the 0.5 µg/mL spiked blank DTPA extraction solution during the analytical run. The results shown in Table 4 are the average of 3 analytical runs.

Table 4. Agilent 4210 MP-AES element wavelengths used for analysis and MDLs at a sampling weight of 10 g for the DTPA extraction.

Element	Wavelength (nm)	MDL (mg/kg)
Cu	324.754	0.06
Fe	259.940	0.03
Mn	257.610	0.03
Zn	213.857	0.05

Spike recoveries

To verify the accuracy of the method, a DTPA-extracted soil sample was spiked with Cu, Fe, Mn and Zn at 5, 40, 20 and 5 mg/kg concentration levels respectively. The recoveries for the spiked sample are given in Table 5. The recovery results were within ± 10% of the expected value for all 4 analytes which highlights the suitability of the method for the application.

Table 5. Agilent 4210 MP-AES spike recoveries for all elements in the DTPA extracted soil sample.

Element and line (nm)	DTPA extracted soil sample (mg/kg)	Spiked concentration (mg/kg)	Measured concentration (mg/kg)	Recovery (%)
Cu 324.754	0.43	5	4.58	92
Fe 259.940	22.81	40	36.46	91
Mn 257.610	6.56	20	18.09	90
Zn 213.857	0.23	5	4.62	92

Long term stability

Long term stability of the Agilent 4210 MP-AES was measured by analyzing a DTPA extracted soil sample approximately every 2 minutes over 3 hours of continuous measurement. Figure 2 shows that excellent stability was achieved, with measurement precision <2% RSD for all elements (see Table 6), over the 3-hour period.

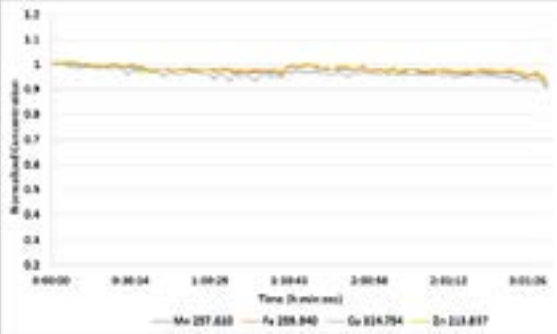

Figure 2. Normalized concentration of Cu, Fe, Mn and Zn in DTPA extracted soil sample, measured over 3 hours.

Table 6. Agilent 4210 MP-AES long term stability results (% RSD) for Cu, Fe, Mn and Zn in DTPA extracted soil sample.

Element	Wavelength (nm)	%RSD
Cu	324.754	1.77
Fe	259.940	1.45
Mn	257.610	1.38
Zn	213.857	1.21

Conclusions

The Agilent 4210 MP-AES proved suitable for the cost-effective analysis of micronutrients in DTPA extracted soil samples. As the microwave plasma is generated from nitrogen gas, it eliminates the need for expensive and flammable gases, which reduces operational costs and improves lab safety. Compared to FAAS, the high plasma temperature (5000 K) of
MP-AES provides a higher sample matrix tolerance, lower detection limits and an expanded working concentration range.

The method used in this study demonstrated:

- High analytical performance with excellent MDLs and spike recoveries for all elements within ± 10% of the target values.
- Excellent linearity across a wide concentration range.
- Excellent long term stability, with less than 2% RSD over a 3-hour period.

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Determination of major elements in milk using the Agilent 4200 MP-AES

Application note

Food testing & agriculture

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Introduction

Milk is one of the most important food commodities in the world and its consumption has grown, particularly in developing countries which have experienced strong economic growth and urbanization in recent decades.

As a substantial source of several nutrients such as proteins, enzymes, fats, vitamins and essential elements (also known as minerals), milk plays a key role during all phases of human life. Rapid growth during infancy and early childhood creates high demand for the nutrients that milk provides. This development phase requires a balanced amount of different elements, as mineral deficiencies may impair body development whilst excessive mineral intake may increase the osmotic load and cause complications in the developing kidneys of a child.

Essential elements such as Ca, K, Mg, Na and P have several physiological functions in the tissue structure of humans and other animals, such as maintaining osmotic/electrolyte balance, and acting as a cofactor for many enzymes. Deficiencies in these essential elements causes disturbances

in the physiological system in any stage of life and, for this reason, such elements must be monitored to ensure the nutritional value of foods. The accurate analysis of essential elements is particularly important in extensively consumed products, such as milk.

Several atomic spectroscopy techniques are routinely used for elemental quantification in milk and dairy products, in particular flame atomic absorption spectrometry (FAAS) and recently microwave plasma atomic emission spectrometry (MP-AES).

The recent introduction of microwave plasma atomic emission spectrometry was a breakthrough revolution in entry-level atomic spectroscopy techniques. The easy to use Agilent 4200 MP-AES has better performance and speed than a FAAS and requires no hazardous and expensive gases. This improves safety and reduces the cost of analysis.

This work shows the performance of the Agilent 4200 MP-AES for quantification of Ca, K, Mg, Na and P in fresh and powdered milk after acid digestion, with quality assurance performed by analysing a Certified Reference Material (CRM) and applying some of the concepts from the US EPA Contract Laboratory Program.

Experimental

Instrumentation
For this study a microwave plasma atomic emission spectrometer, the Agilent 4200 MP-AES (Agilent Technologies, Santa Clara, CA) was used for elemental determination of digested milk samples. Acid digestion was carried out using an UltraWAVE Single Reaction Chamber Microwave Digester (Milestone Inc., Shelton CT).

Standards and reagents
Analytical grade concentrated nitric acid (HNO_3 67-69%) and hydrochloric acid (HCl 32-35%) were used for sample digestion. The 18.2 MΩ deionized water used was obtained from a Milli-Q™ Water System (Millipore, Darmstadt, Germany). Calibration and accuracy verification standards were prepared using Agilent (Agilent Technologies, Santa Clara, CA) and Spex (SPEX CertiPrep, Metuchen, NJ) Calibration Standards. Method validation was achieved by analyzing the accuracy verification standards and a milk powder Certified Reference Material (CRM), NIST 1549a (NIST, Gaithersburg, MD).

Microwave sample digestion
Seven different powdered and liquid milk samples were purchased from a supermarket in California, USA and digested before analysis by MP-AES (refer to Table 4).

To prepare the milk samples for microwave digestion approximately 0.25 g of each powdered milk, 0.50 g of the powdered NIST 1549a CRM and 1 g of each fresh milk sample was accurately weighed and transferred to a 15 mL Teflon digestion vial. Before capping the vials, 6 mL of nitric acid and 1 mL of hydrochloric acid was added to each. A blank solution was also prepared, containing 6 mL of nitric acid and 1 mL of hydrochloric acid. Each milk sample and blank solution was prepared in triplicate in accordance with this procedure. Similarly, seven samples of the NIST 1549a CRM were prepared and digested in order to evaluate the accuracy of the analytical procedure.

At least two of the sample vials in each batch of 14 samples digested contained the NIST 1549a CRM. One blank solution was included in each batch.

Microwave digestion of the samples was carried out in accordance with the following procedure: The digestion chamber was initially pressurized to 40-45 mTorr with industrial grade nitrogen gas, before the temperature and pressure were gradually increased to 240 °C and 150 bar respectively over 20 minutes. These values were maintained for a further 15 minutes (the duration of the digestion) to ensure complete digestion.

Upon completion of the program each digested sample was diluted to a final volume of 10 mL with deionized water, before a further 10 times dilution with a solution of 2% nitric acid.

Elemental determination
The Agilent 4200 MP-AES has superior performance compared to FAAS in terms of detection limits, linear range, and sample throughput. The 4200 MP-AES uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. The use of nitrogen improves safety by eliminating expensive, hazardous gases and also results in low operational costs. The nitrogen plasma reaches around 5,000 K and eliminates the chemical interferences that are common in FAAS, such as the formation of refractory $CaPO_4$. This means that the element-specific sample preparation often required in FAAS can be simplified to a single sample preparation for all elements. The more powerful excitation source also enables phosphorus determinations, which is not possible on FAAS.

The instrument features mass flow control of the nebulizer gas, and a torch loader mechanism which automatically connects all gases. Method parameters can be automatically optimized in the MP Expert software, which also features automatic background correction.

Method conditions for digested milk sample analysis in the 4200 series MP-AES are listed in Table 1.

Table 1. MP-AES 4200 operational conditions for Ca, K, Mg, Na, P determination in digested milk

Common Conditions	
Background Correction	Auto
Nebulizer	Micromist
Spray Chamber	Double pass glass cyclonic
Pump Speed	10 rpm
Read Time	2 s
Replicates	3
Stabilization Time	20 s
Viewing Position	0

Elemental Conditions		
Element	Wavelength (nm)	Nebulizer Flow (L/min)
Ca	422.673	0.4
K	766.491	0.8
Mg	285.213	0.4
Na	588.995	0.4
P	214.915	0.35
Y (Internal Standard)	371.029	0.4

Results and Discussion

Concentrations working range and method detection limit

Calibrations for all elements were between 5 and 100 ppm, and the correlation coefficient was greater than 0.999 for all wavelengths. Method detection limits (MDL) were calculated as 3 times the standard deviation of 10 consecutive blank readings (3σ). From the MDL, the method quantification limit (MQL) was calculated as 3.33 x MDL. The MDL and MQL are summarized in Table 2.

Table 2. Method Detection Limits (MDL) and Method Quantification Limits (MQL) in mg/L.

Element/ Wavelength (nm)	MDL	MQL[1]
Ca 422.673	0.002	0.007
K 766.491	0.067	0.223
Mg 285.213	0.002	0.007
Na 588.995	0.117	0.351
P 214.915	0.318	1.059

(1) Quantification limits in sample must take into account the different dilution factors applied in powdered milk or fresh milk.

Quality Control

Two strategies were adopted to validate the method:

1. Analysis of the NIST 1549a milk CRM in seven independent digestions, analyzed among unknown samples.

2. Analysis of Initial Calibration Blank and Initial Calibration Verification solutions (ICB & ICV) immediately after the method calibration, followed by Continuing Calibration Blank and Continuing Calibration Verification (CCB & CCV) solutions every 10 samples. The ICB/CCB and ICV/CCV analyses totalled four runs each.

The results from this analysis, shown in Table 3, highlight the ability of the MP-AES to reliably analyze digested milk samples with excellent accuracy, precision and minimal carryover between solutions.

Table 3. Summarized results and recoveries of NIST 1549a CRM, ICB/CCB and ICV/CCV samples.

	Ca	K	Mg	Na	P
CRM Reference Value (mg/kg)	8810 ± 240	11920 ± 430	892 ± 62	3176 ± 58	7600 ± 500
CRM Measured Conc. (n=7) ± SD (mg/kg)	9031 ± 195	11683 ± 566	928 ± 15	3373 ± 108	7360 ± 96
CRM Recovery (%)	102.5	98.0	104.1	106.2	96.8
ICB/CCB (n=4) Average ± SD (mg/kg)	0.020 ± 0.001	0.780 ± 0.155	0.004 ± 0.001	0.411 ± 0.212	< MDL
ICV/CCV (n=4) Recovery %	99.9	102.6	96.7	101.9	99.7

Table 4. Analysis results of powdered and fresh milk digested samples by Agilent 4200 MP-AES.

Samples	Ca mg/kg (RSD)	K mg/kg (RSD)	Mg mg/kg (RSD)	Na mg/kg (RSD)	P mg/kg (RSD)
Powdered Instant Nonfat Milk	11953 (4.5%)	15296 (3.6%)	1242 (4.4%)	4141 (3.5%)	9611 (1.0%)
Powdered Nonfat Milk	11058 (3.8%)	16057 (6.6%)	1176 (1.9%)	4167 (5.4%)	9223 (1.1%)
Powdered Organic Buttermilk	9659 (1.5%)	27253 (1.37%)	1116 (3.8%)	4069 (3.7%)	8489 (2.3%)
Powdered Sweet Cream Buttermilk	8287 (6.6%)	14421 (8.8%)	1053 (5.9%)	4784 (7.5%)	7920 (5.9%)
Powdered Whole Milk	8592 (3.1%)	15157 (3.1%)	1218 (1.0%)	3010 (3.3%)	7750 (0.9%)
Fresh Whole Milk	1150 (2.9%)	1687 (1.9%)	109 (0.9%)	407 (1.9%)	898 (0.8%)
Fresh Nonfat Milk	1182 (1.6%)	1726 (0.6%)	112 (1.3%)	412 (0.4%)	904 (0.6%)

Sample Analysis

To evaluate the performance of the method with real samples, digested powdered and fresh milk samples were also analyzed (shown in Table 4). These results demonstrate the ability of this method to analyze a diverse collection of real samples with good precision, easily covering the vast range of major element concentrations determined (e.g. from 1150 to 11953 mg/kg for Ca).

Conclusion

An accurate and robust method has been developed for the determination of major elements in digested milk samples on the 4200 MP-AES. The detection limits achieved were found to be well below those required for milk analysis, and excellent recoveries were obtained for the CRM (between 110—90%) and ICV/CCV (between 105—95%).

The 4200 MP-AES is the ideal instrument for those looking to move away from FAAS and extend their laboratory's analytical capabilities. Recognized benefits of the MP-AES include reduced running costs, enhanced productivity through numerous ease-of-use features and simplified sample preparation, improved safety, and higher analytical performance such as better detection limits and greater linear dynamic range.

References

[1] Khan, N.; Jeong, I. S.; Hwang, I. M.; Kim, J. S.; Choi, S. H.; Nho, E. Y.; Choi, J. Y.; Park, K. S.; Kim, K. S; Analysis of minor and trace elements in milk and yogurts by inductively coupled plasma-mass spectrometry (ICP-MS), *Food Chemistry* 147 (2014) 220–224.

[2] US EPA Contract Laboratory Program, Statement of Works for Inorganics, Multi-Media, Multi-Concentration, Document Number ILMO 4.0.

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Agilent Technologies

Elemental profiling of Malbec Wines for geographical origin using an Agilent 4200 MP-AES

Application note

Food testing

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Introduction

Red wine produced from the Malbec grape is increasing in popularity in the United States. However, the US is a relatively small producer of the wine compared to Argentina, where it is the most extensively planted grape variety in the country. With rising imports into the US from Argentina there are growing concerns relating to the validation of the geographical origin of this wine.

Typically ICP-MS is used to distinguish between wines originating from different regions by comparing the relative concentrations of mineral elements, which are characteristic of the soil composition of the region of production. In this study, a cost-effective approach has been taken using Microwave Plasma-Atomic Emission Spectroscopy (MP-AES) to measure 6 elements (Sr, Rb, Ca, K, Na and Mg). Agilent's Mass Profiler Professional (MPP) integrated chemometrics software and another data analysis package were used to model the MP-AES results to distinguish the geographical origin of 41 Malbec wine samples produced in Argentina and the USA.

Experimental

Samples

Malbec grapes from the 2011 vintage were sourced from 41 different geographical sites; 26 from the Mendoza region of Argentina and 15 from California, USA. In order to reduce the impact of the wine making process on the elemental composition of each wine, and to preserve any elemental differences arising from the geographical origin, two central winemaking facilities only were used to produce the wine. Table 1 lists all the samples, with their detailed geographical origin. Details of the winemaking procedure can be found in the original study [1].

Calibration standards and reagents

Single-element calibration standards (Ca, K, Mg, Na at 10,000 mg/L, and Sr at 1,000 mg/L) were purchased from VHG Labs (Manchester, NH, USA), Rb 1,000 mg/L was from SPEX CertiPrep (Metuchen, NJ, USA), and concentrated nitric acid was obtained from JT Baker (Instra-Analyzed grade, Center Valley, PA, USA). The ionization buffer solution (100,000 mg/L Cs; Agilent, Santa Clara, CA, USA) was diluted to 2,000 mg/L in 1% HNO_3 prior to use. Ultrapure water (18 MΩcm, EMD Millipore Bellerica, MA, USA) and Uvasol spectroscopy grade ethanol from Merck (Whitehouse Station, NJ, USA) were used for the calibration solutions and dilutions.

Instrumentation

An Agilent 4200 MP-AES fitted with a MicroMist concentric nebulizer and baffled cyclonic spray chamber was used throughput the study. An External Gas Control Module (EGCM) was used to inject air into the nitrogen plasma to prevent carbon present in the wine samples from building up on the torch. This ensures stable results over the course of the analysis and reduces the background emissions generated by the organic species present in the sample. A 2,000 mg/L cesium (Cs) Ionization Buffer solution was constantly mixed with the sample stream immediately before entering the spray chamber, using a simple mixing tee.

Each element (Sr, Rb, Ca, K, Na and Mg) was monitored at a specific wavelength to ensure interference-free detection. EGCM and read time settings were optimized for each element. The instrument was calibrated and tuned daily using an Agilent wave calibration solution.

All wine samples were analyzed in triplicate after a 1:50 dilution in 5% HNO_3. A 6-point calibration between 0 and 500 mg/L was carried out for each element in matrix-matched calibration solutions (5% HNO_3 and 0.2% ethanol) to account for matrix interferences of the ethanolic wine solutions.

The sample introduction and calibration parameters used are given in Table 2 and 3 respectively.

Statistical data analysis

Data analysis of the concentrations of the 6 monitored elements monitored in each of the Malbec wines was carried out in RStudio (version 0.98.501, Boston, MA) and Agilent's Mass Profiler Professional (MPP; version 12.61). Multivariate analysis of variance (MANOVA) and individual univariate analysis of variance (ANOVA) for each element were run in RStudio. Elements that differed significantly among the wines were further used in an untargeted Principal Component Analysis (PCA) within the MPP software to visualize the sample differences. As a final analysis, Partial Least Squares – Discriminate Analysis (PLS-DA) was used for the geographical classification of the wines, according to country and to region within a country.

Table 1. Samples included in the study. For each wine sample, the district, department, and altitude is shown. *Denotes samples from the Yolo region - the only US region outside a recognized American Viticultural Area (AVA). *Source: Nelson et al [1].*

Sample code	District	Department / AVA or County	Altitude (meters above sea level)	Sample code	District	Department / AVA or County	Altitude (meters above sea level)
M1	La Consulta	San Carlos	999	M22	El Peral	Tupungato	1235
M2	Perdriel	Luján	964	M23	El Peral	Tupungato	1235
M3	La Consulta	San Carlos	999	M24	El Peral	Tupungato	1241
M4	La Consulta	San Carlos	999	M25	Gualtallary	Tupungato	1354
M5	La Consulta	San Carlos	999	M26	Gualtallary	Tupungato	1353
M6	Las Compuertas	Luján	1022	C1	Yountville	Napa	Not available
M7	Las Compuertas	Luján	1022	C2	Mount Veeder	Napa	315
M8	Las Compuertas	Luján	1022	C3	Mount Veeder	Napa	510
M9	Altamira	San Carlos	1024	C4	Mount Veeder	Napa	497
M10	Altamira	San Carlos	1043	C5	Oak Knoll District	Napa	25
M11	Altamira	San Carlos	1096	C6	Alexander Valley	Sonoma	58
M12	Altamira	San Carlos	1047	C7	Alexander Valley	Sonoma	68
M13	Altamira	San Carlos	1043	C8	Alexander Valley	Sonoma	53
M14	Altamira	San Carlos	1024	C9	Hames Valley	Monterey	214
M15	Gualtallary	Tupungato	1342	C10	Monterey County	Monterey	154
M16	Altamira	San Carlos	1052	C11	Lodi	San Joaquin	61
M17	El Peral	Tupungato	1235	C12	Winters*	Yolo	88
M18	Lunlunta	Maipú	931	C13	Winters*	Yolo	77
M19	Lunlunta	Maipu	930	C14	Winters*	Yolo	70
M20	El Peral	Tupungato	1235	C17	Red Hills	Lake	648
M21	El Peral	Tupungato	1235				

Table 2. 4200 MP-AES operating conditions. *Source: Nelson et al [1]*

Parameter	Value					
Element	Sr	Rb	Mg	Ca	Na	K
Monitored wavelength (nm)	407.771	780.027	279.553	396.847	589.592	769.897
EGCM setting	Low	Low	Med	High		
Pump rate (rpm)	10					
Sample tubing	Org-Grn					
Ionization buffer tubing	Org-Grn					
Waste tubing	Blue-Blue					
Read time (s)	5		2			
Number of replicates	3					
Sample uptake delay (s)	50					
Stabilization delay (s)	20					
Fast pump during uptake	Yes					
Background correction	Auto					

Table 3. Calibration parameters used for wine sample analysis. *Source: Nelson et al [1]*

Element	λ (nm)	Calibration Range (mg/L)	Background Correction	Calibration fit	Correlation Coefficient
Sr	407.771	0-5	auto	linear	0.9999
Rb	780.027	0-5	auto	linear	0.9997
Mg	279.553	0-5	auto	linear	0.9998
Ca	396.847	0-5	auto	linear	0.9999
Na	589.592	0-5	auto	linear	0.9999
K	769.897	0-20	auto	linear	0.99999

Results and discussion

Three sigma detection limits were determined by analyzing 10 sample blanks. All 6 of the elements monitored were detected in the 41 different wine samples at concentrations above their limits of detection (LODs), as shown in Table 4. All elements also differed significantly among the wine samples in a multi- and univariate analysis of variance at an α level of 5%. Thus, all 6 elements were included in the subsequent PCA and PLS-DA analyses.

Figure 1a shows a clear separation of the wines by country of origin, with only a slight overlap of two US wines. The component loadings plot (Figure 1a) shows that the elemental differences in Na and Sr primarily account for the separation by country of origin.

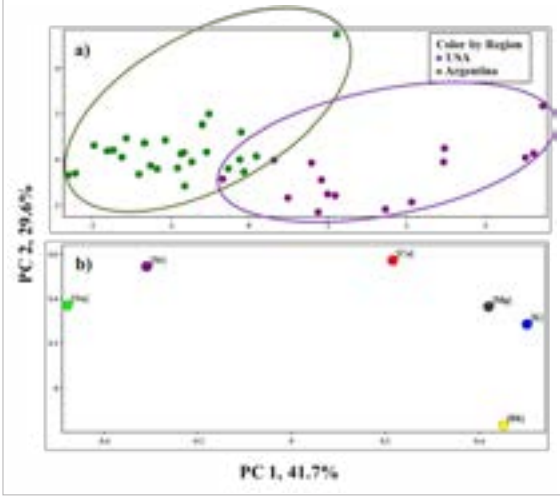

Figure 1. 2D PCA bi-plots using the 6 elements which differed significantly among the wine samples. (a) Product plot showing the wine samples color coded by geographical origin, (b) Loadings plot with 6 elements (Sr, Rb, Ca, K, Ca, Na and Mg). *Source: Nelson et al. [1].*

However, an almost 100% correct classification of the wines according to their country of origin was obtained using PLS-DA (Figure 2). Using cross-validation, the prediction accuracy for the USA wines was 93.3% and 96.2% for the Argentina wines, leading to an overall accuracy of 95.1% for the PLS-DA model (Table 5). The incorrectly classified wines (M1 for the Argentina wines and C12 for the USA wines), were most likely due to their higher/lower levels in Na, Mg, and K (M1 was low in Na, Mg, and K; C12 was high in Mg) compared to the other wines in the same class. Excellent classification was achieved. If a larger set of samples had been available, we would have tested to see how the model performs with complete unknown samples.

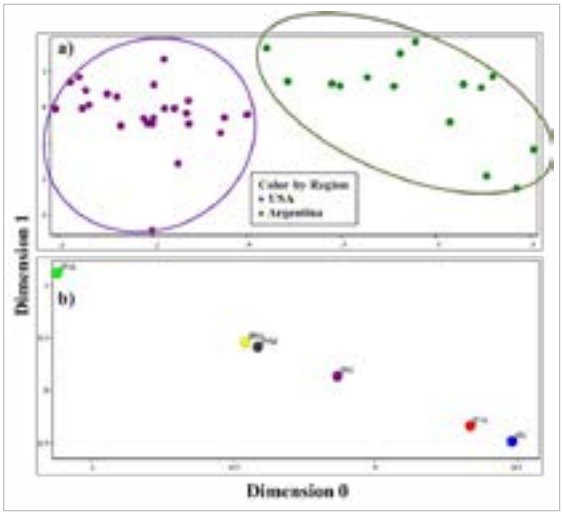

Figure 2. 2D PLS plots using the 6 elements which differed significantly among the wine samples. (a) Sample plot showing the separation of the wines according to geographical origin, with no overlap. (b) Element loadings plot. *Source: Nelson et al [1]*

Table 4. Detection limits (DL) and elemental concentrations for the wines from Argentina and the USA. Shown are mean $\bar{x}$, standard error of the mean $\sigma_{\bar{x}}$, and the minimal (min) and maximal (max) concentrations. Concentrations (mg/L) are given for the elements that differed significantly among the five wineries ($P \leq 0.05$). *Source: Nelson et al [1]*

		Wines from California, USA		Wines from Mendoza, Argentina	
	DL	$\bar{x} \pm \sigma_{\bar{x}}$	min – max	$\bar{x} \pm \sigma_{\bar{x}}$	min – max
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Sr	0.0018	0.45 ± 0.02	0.24 - 0.83	0.77 ± 0.04	0.23 - 1.59
Rb	0.0004	3.37 ± 0.03	0.57 - 7.83	0.99 ± 0.02	0.55 - 2.19
Mg	0.0012	80.87 ± 0.42	61.75 - 144.86	72.87 ± 0.54	53.55 - 116.29
Ca	0.0016	51.78 ± 0.19	43.26 - 74.01	50.46 ± 0.25	33.22 - 95.08
Na	0.0007	4.90 ± 0.09	3.38 - 8.46	37.48 ± 0.48	13.71 - 121.87
K	0.0020	1444.42 ± 10.53	1120.94-2219.84	1181.22 ± 15.45	976.85-1989.12

Table 5. Result of the cross validation (leave one out algorithm) for the PLS-DA run on the 2 countries. *Source: Nelson et al [1]*

	USA (predicted)	Argentina (predicted)	Accuracy
Argentina (true)	1 (= M1)	25	96.2%
USA (true)	14	1 (= C12)	93.3 %
Overall accuracy			95.1 %

Conclusions

The Agilent 4200 MP-AES is an easy-to-use, low cost instrument suitable for geographical origin analysis of wine samples when combined with a data analysis package such as Agilent's Mass Profiler Professional (MPP). Six elements, Sr, Rb, Mg, Ca, Na, and K, were useful for broad classification of geographic origin of Malbec wines from Argentina and the US, with 14 out of 15 US samples correctly classified and only 1 out of 26 of the Argentinian wines wrongly classified.

Reference

1. Jenny Nelson, Helene Hopfer, Greg Gilleland, Daniel Cuthbertson, Roger Boulton, Susan E Ebeler. Elemental Profiling of Malbec Wines Made Under Controlled Conditions by Microwave Plasma Atomic Emission Spectroscopy. Am. J. Enol. Vitic. Published ahead of print April 2015

www.agilent.com/chem/4210mp-aes

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Determination of major, minor and trace elements in rice flour using the 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES)

Application note

Food testing

Authors

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Introduction

The analysis of foodstuffs, such as rice, is of particular interest for nutrient elements present at high concentrations, and also for toxic elements such as cadmium that can be present at trace levels. The analysis is important to ensure product quality and safety, as well as determining product origin. Food scares related to contamination not only constitute a health risk but also undermine consumer confidence. This can lead to lost earnings through reduced sales and loss of credibility through adverse publicity.

Flame Atomic Absorption Spectroscopy (FAAS) is well established for the analysis of foods, but with lab budgets coming under increasing pressure and current market trends for lower cost of ownership, improved

performance, ease of use, and safety, many FAAS users are looking to transition to another technique to expand their analytical capabilities.

Agilent has expanded its atomic spectroscopy portfolio to include the Microwave Plasma-Atomic Emission Spectrometer. The Agilent 4200 MP-AES is the second generation microwave plasma instrument that features an improved waveguide design that is capable of running samples with high total dissolved solids without compromising detection limits. The 4200 MP-AES significantly reduces running costs through the use of nitrogen as its plasma gas. The use of nitrogen also increases safety, by removal of flammable gases, and allows unattended operation of the instrument. The 4200 MP-AES is easy to use, and is able to achieve lower detection limits than a standard FAAS, as well as being able to determine additional elements such as phosphorus.

This application describes the analysis of rice flour for cadmium and other major, minor and trace elements on the 4200 MP-AES.

Experimental

Instrumentation

The innovative 4200 MP-AES features a second generation waveguide and torch, with mass flow controlled nebulizer gas flow. The 4200 MP-AES has a robust toroidal plasma with a central channel temperature of ~5,000 K which eliminates many of the chemical interferences that are present in FAAS and also expands the concentration working range of the 4200 MP-AES when compared the FAAS. This means that the element specific sample preparation that is commonplace when using FAAS is not necessary when using the 4200 MP-AES, improving ease of use and reducing cost. The 4200 MP-AES also achieves lower detection limits than FAAS, particularly for phosphorus, which enables the analysis of extra elements. By running on nitrogen, the 4200 MP-AES offers reduced operating costs and increased lab safety compared to flame AA, through the avoidance of flammable and costly gases such as acetylene, and nitrous oxide.

The analysis was carried out using a 4200 MP-AES equipped with the standard sample introduction setup consisting of the OneNeb nebulizer and a double pass spray chamber. An SPS 3 autosampler was used to deliver samples to the instrument, allowing the system to be operated unattended.

The MP-AES features continuous wavelength coverage which allows the analyst to select wavelengths that are appropriate for the expected concentration range, and free from spectral interferences. Method conditions for the selected wavelengths are shown in Table 1 and common method conditions are shown in Table 2.

Table 1. Agilent 4200 MP-AES operating parameters

Element	Wavelength	Read time (s)	Nebulizer Flow (L/min)
P	214.915 nm	2	0.55
Cd	228.802 nm	10	0.55
Mg	280.271 nm	1	0.55
Zn	213.857 nm	5	0.55
Mn	403.076 nm	3	0.55
K	766.491 nm	1	0.55
Cu	324.754 nm	2	0.75
Fe	438.354 nm	5	0.75
Ca	422.673 nm	1	1.00

Sample preparation

NIES CRM No.10c Rice Flour (NIES, Japan) was analyzed to validate the analytical method. The rice flour samples were digested using a Milestone Ethos microwave digestion system[1]. Samples were prepared in duplicate with approximately 0.5 g of rice flour CRM accurately weighed into separate TFM vessels. This was followed by the addition of 7 mL of HNO_3 and 1 mL of H_2O_2 and placed in the microwave digestion unit. The samples were digested using the preloaded digestion methods, allowed to cool, and then made up to 25 mL with deionized water. The final solution contained 2% total dissolved solids. No ionization suppressants or matrix modifiers were required for the analysis.

Calibration range

The calibration concentration range of the standard solutions are summarized in Table 3. As the working range of 4200 MP-AES far exceeds that of FAAS (by up to 20x in some instances), only one dilution of the sample is required to measure the complete set of elements. The calibration fit for all wavelengths used was linear.

Results and Discussion

Method detection limits (MDLs)

MDLs were determined from the analysis of 10 digested blank samples. The MDLs (3σ) for the selected analytical wavelengths are listed in Table 4.

Table 2. Common method conditions

Parameter	Value
Replicates	3
Pump rate	15 rpm
Sample uptake delay	30 seconds
Rinse time	60 seconds
Stabilization time	10 seconds
Fast Pump during Uptake and Rinse	On (80 rpm)
Nebulizer	OneNeb
Spray chamber	Double pass cyclonic
Autosampler	Agilent SPS 3
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue

Table 3. Working concentration range of the 4200 MP-AES standard solutions

Element	Wavelength	Concentration range	
P	214.915 nm	0–100	ppm
Cd	228.802 nm	0–1.0	ppm
Mg	280.271 nm	0–40	ppm
Zn	213.857 nm	0–4.0	ppm
Mn	403.076 nm	0–1.0	ppm
K	766.491 nm	0–100	ppm
Cu	324.754 nm	0–1.0	ppm
Fe	438.354 nm	0–1.0	ppm
Ca	422.673 nm	0–4.0	ppm

Table 4. Agilent 4200 MP-AES element wavelength and MDL (mg/kg in sample)

Element/ Wavelength (nm)	Ca 422.673	Cd 228.802	Cu 324.754	Fe 438.354	K 766.491	Mg 280.271	Mn 403.076	P 214.915	Zn 213.857
MDL (mg/kg)	0.10	0.16	0.05	0.44	3.0	0.06	0.05	13	0.15

Results of the analysis of major, minor and trace elements in rice is listed in Table 5. The measured values (average result on two different 4200 MP-AES instruments carried out in duplicate) are in good agreement with the certified values for all CRM samples. The results demonstrate the capability of the 4200 MP-AES to achieve excellent results across a wide concentration range in a sample with 2% dissolved solids.

A digested rice flour sample was repeatedly analyzed under method conditions over 8 hours to test the long term stability of the method. The test was performed under controlled laboratory environmental conditions within the instrument operating specification, with a recalibration every 2 hours. The resulting stability plot is show in Figure 1. Excellent stability of < 3 % RSD for all elements was achieved, demonstrating the capability of the 4200 MP-AES, OneNeb nebulizer and mass flow controlled nebulizer gas flow to handle 2% total dissolved solids.

Table 5. Results of NIES No.10c Rice Flour. All results in mg/kg in the solid sample.

Element/ Wavelength (nm)	Ca 422.673	Cd 228.802	Cu 324.754	Fe 438.354	K 766.491	Mg 280.271	Mn 403.076	P 214.915	Zn 213.857
Mean	96.0	1.96	4.13	11.50	2700	1174	37.35	3139	22.02
SD	2.5	0.11	0.29	1.03	105	23	1.04	92	0.48
Certified value	95	1.82	4.1	11.4	2750	1250	40.1	3350	23.1
2SD certified	2	0.06	0.3	0.8	100	80	2.0	80	0.9
% difference	101.0	107.7	100.8	100.9	98.2	93.9	93.1	93.7	95.3

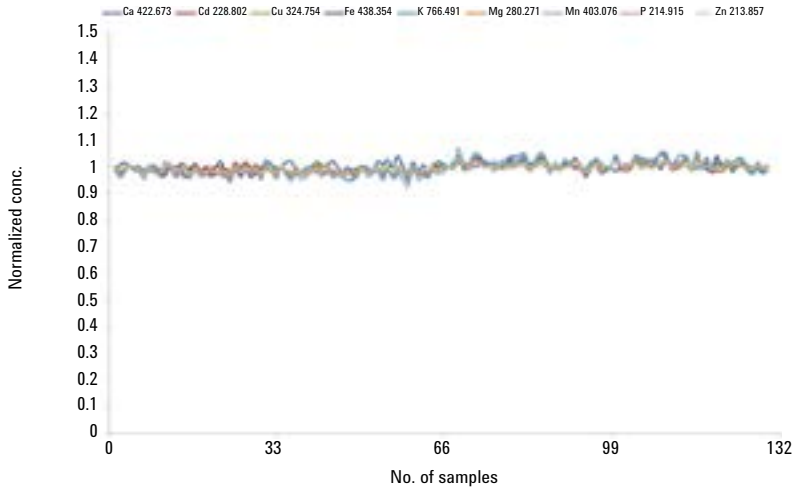

Figure 1. Normalized concentration of elements in a rice flour digest analyzed over an 8 hour time period, with recalibration every 2 hours.

Conclusion

A method for the determination of major, minor and trace elements in rice flour has been described. The next generation 4200 MP-AES achieved recoveries in a rice CRM of +/- 10 % of the assigned value, with MDLs sufficient for the analysis and excellent long term stability.

The excellent analytical performance, including phosphorus which is not practical by FAAS, multi-element unattended operation, improved safety and ease of use make the 4200 MP-AES the ideal alternative for FAAS users looking to transition to a new technique. Furthermore, the sample preparation process can be simplified, with no modifiers or ionization suppressants required due to the higher temperature excitation source of the MP-AES.

Reference

1. Milestone Application Note. Food/Feed. Rice Flour. ID HPR-FO-39. Milestone Ethos with internal temperature sensor, HPR1000/10S high pressure segmented rotor.

www.agilent.com/chem/4210mp-aes

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Determination of major elements in fruit juices using the Agilent 4200 MP-AES with the Agilent 4107 Nitrogen Generator

Application note

Food testing

Authors

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Introduction

Major elements such as calcium, magnesium, sodium and potassium are essential nutrients in food and the routine monitoring of the levels of these elements in fruit juices is a common quality control process. Flame Atomic Absorption Spectroscopy (FAAS) is well suited to this application as it delivers the performance required for the analysis at a reasonable price. However, with the introduction of the Agilent Microwave Plasma-Atomic Emission Spectrometer (MP-AES), several of the analytical challenges of using FAAS for this application have been overcome, making it the ideal instrument for laboratories looking to transition away from FAAS to a more powerful and safer technique.

The 4200 MP-AES main operating gas, nitrogen, is supplied from an Agilent 4107 Nitrogen Generator (with air supplied from an air compressor). This greatly reduces the running costs and eliminates the safety concerns associated with specialty gases required by FAAS such as acetylene and nitrous oxide. The nitrogen-based plasma source of the 4200 MP-AES operates at a higher temperature than the flame source of a FAAS, avoiding the chemical interferences present in FAAS (especially for elements such as Ca). This eliminates the time consuming, element specific sample preparation and burner head changeover that is required when analyzing Ca, Na, K and Mg in the same sample by FAAS. The analysis of this application by MP-AES also removes the need for costly and time consuming modifiers and ionization suppressants. The plasma source in the MP-AES also leads to improved performance with respect to detection limits and linear dynamic range when compared to FAAS, which is important in an analysis where the elements can be present over a wide range of concentrations. With no flammable gases required, the MP-AES is able to operate unattended which increases sample throughput.

This application note describes the analysis of fruit juice samples using an Agilent 4200 MP-AES running with an Agilent 4107 Nitrogen Generator.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES, with nitrogen supplied from an Agilent 4107 Nitrogen Generator. The sample introduction system consisted of a double pass spray chamber and OneNeb nebulizer.

The instrument was controlled by the powerful and easy-to-use MP Expert software. The MP-AES features continuous wavelength coverage and MP Expert features an extensive wavelength database that allows the selection of wavelengths that are appropriate for the concentration range required for the analysis. For instance, in this application, the less sensitive Mg 518.360 nm line was preferred over the more sensitive Mg 285.213 line.

Table 1. Agilent 4200 MP-AES operating conditions

Parameter	Value			
Element	Ca	Mg	Na	K
Wavelength	422.673	518.360	589.592	769.897
Nebulizer	OneNeb			
Nebulizer flow rate	Default (0.75 L/min)			
Spray chamber	Double pass glass cyclonic			
Pump rate	15 rpm			
Sample pump tubing	Orange/green			
Waste pump tubing	Blue/blue			
Autosampler	Agilent SPS 3			
Read time	1 second			
Number of replicates	3			
Fast pump during uptake	On			
Sample uptake delay	30 seconds			
Rinse time	40 seconds			
Stabilization time	20 seconds			
Background correction	Auto			
Gas source	Agilent 4107 Nitrogen Generator			

Standard and sample preparation

Two quality control (QC) test materials were analyzed to validate the method:

- Apple Juice T1650QC (certified by FAPAS*)
- Grapefruit Juice T0842QC (certified by FAPAS*)

*FAPAS – The Food and Environmental Research Agency, York, UK.

Materials were purchased from Graham B Jackson (Aust) P/L.

Additionally, a commercially available apple juice was analyzed in the long term stability studies.

All fruit juice samples were diluted 20x with 5% HNO_3 (ACS Grade, Merck). No other modifiers or ionization suppressants were required.

Standards were prepared from a 10,000 mg/L multi element standard (Inorganic Ventures). All calibration blanks and standards were prepared in 5% HNO_3.

Results

Working range

The working concentration range of the standard solutions are summarized in Table 2. As the working range of MP-AES far exceeds that of FAAS (by up to 20 times in some instances), only one dilution of the sample is required to measure the complete set of elements.

Table 2. Working concentration range of the 4200 MP-AES standard solutions

Element	4200 MP-AES concentration range (mg/L)	Correlation coefficient
Ca 422.673	0–20	0.99990
Mg 518.360	0–100	0.99988
Na 589.592	0–20	0.99996
K 769.897	0–100	0.99968

Recoveries

Table 3 shows the concentration and recovery results of the four elements in the two fruit juices. The recovery results for Ca, Mg, Na, K in the fruit juices using this method were within +/- 10% of the assigned value. All results measured in this study were within the certified ranges of the two quality control test materials.

Table 3. Recovery results of 4 elements in the fruit juices using the 4200 MP-AES with the nitrogen generator

Apple Juice T0840QC	Certified value (mg/L)		Found (mg/L)	% Recovery
	Assigned value	Range		
Magnesium	49.0	40.3–57.8	49.9 ± 0.6	102
Sodium	21.2	16.9–25.4	22.2 ± 0.5	105
Potassium	1044	926–1161	1039 ± 29.7	100

Grapefruit Juice T0842QC	Certified value (mg/L)		Found (mg/L)	% Recovery
	Assigned value	Range		
Calcium	145.6	123.6–167.6	158.3 ± 3.2	109
Magnesium	92.5	77.5–107.4	91.1 ± 0.6	99
Potassium	1102	979–1225	1100 ± 14.7	100

Long term stability

A commercial apple juice solution (diluted 20x with 5% HNO_3) was repeatedly analyzed over a period of 6 hours. The resulting stability plot is shown in Figure 1. All elements have an RSD of less than 4% over 6 hours. With the OneNeb nebulizer and mass flow controlled nebulizer gas flow, excellent stability results were obtained for a sample with a complex high sugar matrix.

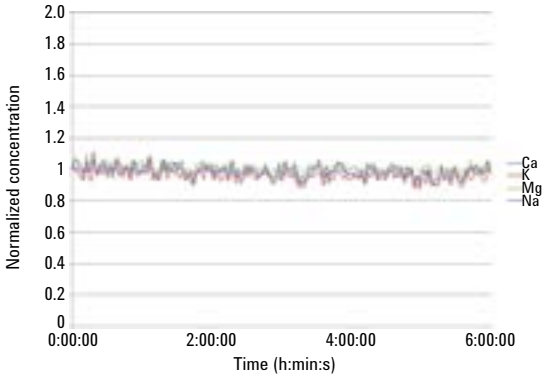
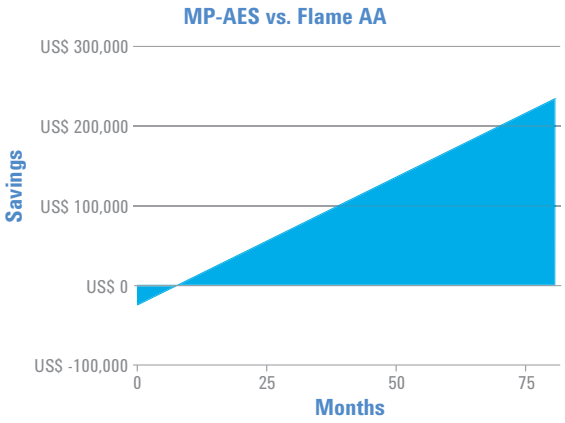


Figure 1. Normalized concentration of potassium in an apple juice sample over 6 hours

Cost savings with the 4200 MP-AES

The potential cost saving of using the 4200 MP-AES for this application was estimated by comparing an FAAS purchased with an air compressor and 1 year of consumables to an MP-AES purchased with air compressor, nitrogen generator, SPS 3, and 1 year of consumables. The analysis requirements were assumed to be 500 samples per week and 4 elements per sample. The calculation assumes that the FAAS is run without an autosampler and that 3 elements are analyzed with air/acetylene and 1 element with nitrous oxide/acetylene. In this example the results show an estimated cost saving of greater than US $220,000 over a 7 year evaluation period[1]. A global average gas cost was used in this calculation and results will vary from country to country.



[1]This example is intended to help you compare the running costs and savings of the MP-AES vs. flame AA. The applied formulas and parameters are correct to the best of our knowledge, but we cannot guarantee the results. Savings may vary depending on factors such as local gas and electricity costs, operator costs, number and types of elements. For this calculation operator labor costs were set to USD $25/hour and electricity costs were set to USD $0.18 per kW.

Conclusion

A simple and rapid method using MP-AES has been developed to analyze Ca, Mg, Na and K in fruit juice. The recoveries obtained from the analysis of the two QC test materials were within +/- 10% of the assigned values and within the certified concentration range. Using the standard sample introduction system supplied with the 4200 MP-AES, excellent long term stability was obtained over a 6 hour period.

The 4200 MP-AES is the ideal instrument for those customers who are looking to transition away from FAAS and extend their laboratory's analytical capabilities. Recognized benefits of MP-AES include reduced running costs, enhanced productivity through numerous ease-of-use features and simplified sample preparation, improved safety, and higher analytical performance such as better detection limits and greater linear dynamic range.

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Agilent Technologies

Direct analysis of milk using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES)

Application note

Food Testing

Authors

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Abstract

Milk samples, which had been diluted in aqueous solutions containing 10% v/v of a mixture of tertiary amines at pH 8.0, were analyzed using an Agilent 4100 MP-AES. Al, Cr, Cu, Fe, Mg, Mn and Zn were determined in a non-fat liquid milk sample and in a standard reference material of non-fat milk powder. Sample introduction via a OneNeb nebulizer, which incorporates the Flow Blurring technology, and automatic background correction with the MP Expert software, contributed to minimizing matrix effects and background emission and to improving sensitivity and accuracy. Limits of detection are between 0.8–76 µg/L and adequate accuracies were obtained using either external calibration or the method of standard additions (MSA). In addition to the lower operational and maintenance costs of MP-AES, the detection limits achieved by the new method are comparable to ICP-OES and significantly superior to FAAS.

Agilent Technologies

Introduction

The direct analysis of milk is an intuitively attractive sample preparation choice considering its relatively high solubility in water. However, milk is a complex colloidal system with distinct components such as fat emulsion, casein micelle suspension and aqueous phase [1]. It has been demonstrated that some analytes can be distributed differently in each of these phases [2] and problems related to sample nebulization and atomization interferences may compromise accuracy and precision in the direct analysis of milk solutions [3,4].

An interesting strategy to overcome some of these problems is to dilute samples in a mixture of tertiary amines [5,6]. This reagent can dissociate casein micelles and stabilize cations present in the aqueous phase [5]. Another approach to improve precision and accuracy is to employ efficient nebulization systems. Recent studies have demonstrated that nebulizers based on the Flow Blurring nebulization technology, such as the OneNeb nebulizer, can produce smaller, narrowly-distributed aerosol particles, resulting in better sensitivity, precision and accuracy [7,8].

In this application note we describe the determination of Al, Cr, Cu, Fe, Mg, Mn and Zn in milk using an Agilent 4100 MP-AES. The nitrogen used to generate the plasma can be supplied via a simple air compressor and nitrogen gas generator. A clear advantage of in-house gas generation is the reduced costs of operation and maintenance compared to conventional gas resupply. In addition, the superior stability of the microwave-induced plasma, combined with the OneNeb nebulizer, allow sensitive and accurate determinations in milk samples following a simple dilution in a mixture of tertiary amines.

Experimental

Instrumentation

All measurements were performed using an Agilent 4100 MP-AES. The sample introduction system consisted of a double-pass cyclonic spray chamber and the OneNeb nebulizer. The Agilent MP Expert software was used to automatically subtract the background signal from the analytical signal. In this case, a background spectrum from a blank solution is recorded and subtracted from each reference and sample solution that is analyzed. This software was also used to optimize the nebulization pressure and the viewing position for each analyte. Because of this optimization, and considering that all determinations are carried out sequentially, each analyte is determined under optimized conditions rather than under compromised acquisition conditions.

Tables 1 and 2 list the instrumental operating conditions used in the direct analysis of milk.

Table 1. Agilent 4100 MP-AES operating conditions

Instrument parameter	Operating condition
Nebulizer	OneNeb
Spray chamber	Cyclonic double-pass
Read time (s)	5
Number of replicates	3
Stabilization time (s)	15
Background correction	Auto

Table 2. Wavelengths, viewing positions, nebulizer pressures for Al, Cr, Cu, Fe, Mg, Mn and Zn determinations by MP-AES

Element	Wavelength (nm)	Viewing position (nm)	Nebulizer pressure (kPa)
Al	396.152	0	240
Cr	425.433	-10	220
Cu	324.754	-20	240
Fe	385.991	10	80
Mg	285.213	-10	200
Mn	403.076	0	220
Zn	213.857	10	100

Reagents and standard solutions
Nitric acid (Merck, Darmstadt, Germany) previously purified by a sub-boiling distillation system (Milestone, Sorisole, Italy) was used in the preparation of all solutions. Stock monoelement solutions containing 1000 mg/L of Al, Cr, Cu, Fe, Mg, Mn and Zn (Tec-Lab, Hexis, São Paulo, SP, Brazil) were used to prepare standard reference solutions and to carry out spike experiments. The analytical blank was a solution containing 10% v/v of a water-soluble mixture of tertiary amines, which was prepared by diluting the stock solution (CFA-C, Spectrasol, Warwick, NY, USA) with distilled-deionized water (18.2 MΩ cm, Milli-Q, Millipore, Bedford, MA, USA) and adjusting the pH to 8.0 with ultrapure HNO_3. The analytical blank was used to prepare all of the reference standard solutions that were analyzed to generate an analytical calibration curve for each element.

Samples and sample preparation
A standard reference material of non-fat milk powder (SRM 1549) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) was used to check the accuracy of the procedure. Aliquots of approximately 0.1 g of milk powder were dissolved in 10% v/v CFA-C at pH 8.0 to a final volume of 10 mL. A relatively translucent solution was obtained after vortex mixing for 2 minutes.

A non-fat liquid milk sample obtained in a local market was also analyzed. Sample aliquots of 0.5 mL were diluted with 10 % v/v CFA-C at pH 8.0 to a final volume of 10 mL. Spike experiments were also carried out to check the accuracy of the procedure. Standard reference solutions of Al, Cr, Cu, Fe, Mg, Mn and Zn were added to the sample to a final concentration of 20 µg/L (Al, Cr and Cu), 500 µg/L (Mg), or 2500 and 5000 µg/L (Fe, Mn and Zn).

Results

Limits of detection (LOD) and quantification (LOQ) were calculated from three and ten times the standard deviations for 16 consecutive blank measurements divided by the calibration curve slope, respectively. Table 3 presents the values obtained for all analytes. The results highlight the high detection power of the 4100 MP-AES. The microwave plasma is especially advantageous when compared to methods such as flame atomic absorption spectrometry (FAAS) in which an oxidizing gas such as nitrous oxide would be required to determine Cr and Al. In addition, the LODs obtained using the 4100 MP-AES are almost one order of magnitude lower than those typically obtained by FAAS.

Table 3. Limits of detection and limits of quantification for Al, Cr, Cu, Fe, Mg, Mn and Zn determined by MP-AES

Element	LOD[a] (µg/L)	LOQ[a] (µg/L)	LOD in liquid milk sample[b] (µg/L)
Al	1.4	4.5	28
Cr	0.8	2.8	16
Cu	2.4	7.9	48
Fe	0.4	1.5	8.0
Mg	76	250	1500
Mn	3.8	13	76
Zn	28	95	560

[a] Instrumental limits of detection and quantification
[b] Limits of detection considering sample dilution (1:20 v/v milk in CFA-C 10% v/v, pH 8.0)

To evaluate the accuracy of the method, a non-fat milk powder (NIST SRM 1549) standard reference material was analyzed. Recoveries of 100% and 108% were obtained for Al and Mg, respectively (Table 4). Concentrations for Cr, Cu, Fe, Mn and Zn in this SRM were below the LODs, therefore spike experiments were also carried out using a non-fat liquid milk sample. Adequate accuracies were observed for Cu, Fe and Mg. However, recoveries for Al, Cr, Mn and Zn were poor using external calibration, indicating the occurrence of matrix interferences on these elements. It must be pointed out that external calibration was performed without any matrix matching. Adequate recoveries were also obtained for these elements by applying the method of standard additions (MSA). (Table 4).

Table 4. Determination of Al, Cr, Cu, Fe, Mg, Mn and Zn in CFA-C-diluted milk by MP-AES

Sample	Analyte	Reference/ added (µg/L)	Measured (µg/L)	Recovery (%)
NIST SRM 1549[a]	Al	2.0	2.0 ± 0.2	100
	Mg	1200 ± 30	1300 ± 60	108
Non-fat liquid milk	Al[b]	0	< 1.4	-
		20	21 ± 6	105
	Cr[b]	0	< 0.8	-
		20	18 ± 1	90
	Cu	0	216 ± 8	-
		20	20 ± 1	100
	Fe	0	< 0.4	-
		2500	2688 ± 0.2	107.5
		5000	4807 ± 0.2	96.1
	Mg	0	138000 ± 2000	-
		500	480 ± 60	96
	Mn[b]	0	< 3.8	-
		2500	2506 ± 0.06	100.3
		5000	5141 ± 0.02	102.8
	Zn[b]	0	0.131 ± 0.002	-
		2500	2809 ± 0.008	112.4
		5000	5339 ± 0.117	106.8

[a] Values in mg/kg
[b] Values determined using the method of standard additions (MSA)

Conclusion

The direct analysis of milk combining sample dilution in CFA-C, the OneNeb nebulizer with the Flow Blurring nebulization technology and determination with the Agilent 4100 MP-AES is a simple and effective procedure that can be easily implemented in routine analysis. In addition to the relatively low costs of operation and maintenance, the powers of detection achieved using the 4100 MP-AES are comparable to ICP-OES, and significantly better than FAAS methods.

Considering the complexity of the milk colloidal system and that no internal standardization or matrix matching was applied, adequate accuracies were obtained using either external calibration or the standard additions method depending on the analyte.

References

1. R. G. Jensen, Ed., *Handbook of Milk Composition*, Academic Press, London, 1995, 919p.
2. P. Pohl and B. Prusisz, Determination of Ca, Mg, Fe and Zn partitioning in UHT cow milks by two-column ion exchange and flame atomic absorption spectrometry detection, *Talanta* 71 (2007) 715-721.
3. S. E. Emmett, Analysis of liquid milk by inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 3 (1988) 1145-1146.
4. E. Coni, A. Stacchini, S. Caroli and P. Falconieri, Analytical approach to obtaining reference values for minor and trace elements in human milk, *J. Anal. At. Spectrom.* 5 (1990) 581-586.
5. J. A. Nóbrega, Y. Gélinas, A. Krushevska and R. M. Barnes, Direct determination of major and trace elements in milk by inductively coupled plasma atomic emission and mass spectrometry, *J. Anal. At. Spectrom.* 12 (1997) 1243-1246.
6. C. C. Nascentes, M. A. Z. Arruda, A. R. A. Nogueira and J. A. Nóbrega, Direct determination of Cu and Zn in fruit juices and bovine milk by thermospray flame furnace atomic absorption spectrometry, *Talanta* 64 (2004) 912-917.
7. [7] A. M. Gañán-Calvo, Enhanced liquid atomization: from flow-focusing to flow-blurring, *Appl. Phys. Lett.* 86 (2005) 214101.
8. [8] M. A. Aguirre, N. Kovachev, B. Almagro, M. Hidalgo and A. Canals, Compensation for matrix effects on ICP-OES by on-line calibration methods using a new multi-nebulizer based on Flow Blurring® technology, *J. Anal. At. Spectrom.* 25 (2010) 1724-1732.

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Agilent Technologies

Analysis of aluminum in beverages using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES)

Application note

Food Testing

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Abstract

Aluminum present in a beverages can affect the taste. This application note describes the determination of aluminum in beverages using an Agilent 4100 MP-AES. Beverages contain a variety of matrix constituents, including salt, sugar, and alcohol. A study was performed to determine how these matrix constituents affect aluminum measurements, and what could be done to reduce such effects. It was determined that sufficient analysis is possible so long as the matrix concentration and alcohol concentration are known to some extent.

Introduction

At present, absorption spectrophotometry, atomic absorption spectrophotometry and inductively coupled plasma-atomic emission spectroscopy have been adopted for performing elemental analyses of food. Aluminum content in food and beverages is restricted by municipal water supply quality standards to a maximum of 0.2 mg/L on the basis of the Japanese Waterworks Law. When flame atomic absorption spectroscopy (FAAS) is utilized, low sensitivity for aluminum and high matrix constituents in the beverage can cause problems with burners getting clogged. This study was conducted to see if an MP-AES, instead of an FAAS, could be used for beverage analysis.

Experimental

Instrumentation

The measurements were performed on an Agilent 4100 MP-AES. The 4100 MP-AES is a compact bench-top spectrometer that generates a robust, magnetically-excited nitrogen plasma.

A 2.45-GHz air-cooled magnetron is used to generate a magnetic field around a torch. The skin effect of that magnetic field causes plasma to form in the shape of a donut, just as with inductively coupled plasma, and it becomes possible to introduce liquid samples at a steady rate (see Figure 1). The nitrogen used to generate the plasma can be supplied via a simple air compressor and the Agilent 4107 Nitrogen Generator.

A clear advantage of in-house gas generation is the reduced costs of operation and maintenance compared to conventional gas resupply.

The sample introduction system used for this application consisted of a standard torch, a single pass cyclonic spray chamber and a glass concentric nebulizer.

Table 1 lists the instrument operating conditions.

Table 1. Agilent 4100 MP-AES operating conditions

Parameter	Value
Microwave power	1.0 kW
Pump speed	15 rpm
Integration time	3 seconds

Standard and Sample Preparation

Samples included:

- Barley tea
- Green tea
- Black tea
- Coffee
- Cola
- Sports drink
- Beer
- Shochu highball

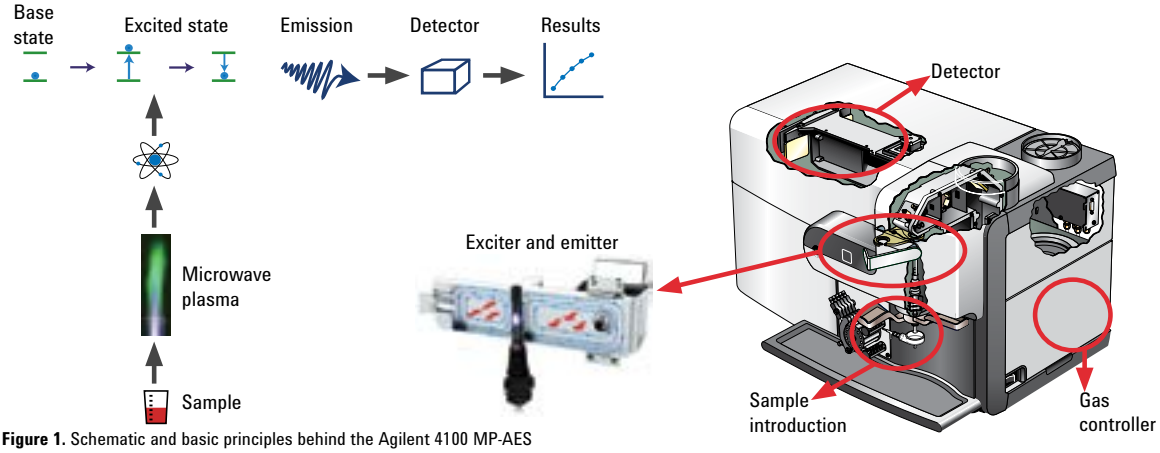

Figure 1. Schematic and basic principles behind the Agilent 4100 MP-AES

Results

Quantitative lower limits and stability

The quantitative lower limits and stability in aqueous solutions and in ethanol were measured. A 0.1% nitric acid solution and ethanol diluted at 0.2 mg/L was prepared using standard solutions.The quantitative lower limit was assumed to be a concentration ten times the standard deviation (σ) obtained from repeatedly measuring the blank ten times. The stability was calculated by repeatedly measuring each of the 0.2 mg/L solution ten times (see Table 2).

Table 2. Method detection limits (MDL) by MP-AES

Aluminum	Limit of quantification (µg/L)	Stability at 0.2 mg/L (%RSD)
Aqueous solution	1.9	1.4
Ethanol (100%)	7.9	0.7

The results for limit of quantification and stability confirm that microwave plasma atomic emission spectroscopy is sufficiently applicable for the analysis of aluminum in beverages.

The effects of sugar

With the emission intensity of aluminum at 0.2 mg/L with a sugar concentration of 0 g/100 mL given a value of 1, the effects of varying the sugar concentration between 0 and 50 g/100 mL were measured. The sugar concentrations of the samples were: approx. 2–5 g/100 mL for black tea (with sugar), and 11 g/100 mL for cola (see Figure 2).

The measurements show that sugar concentrations up to approximately 10 g/100 mL do not have a significant effect. Additional standards and matrix matching are needed for concentrations above 10 g/100 mL. The samples examined had a sugar concentration of about 11 g/100 mL, so the analysis was performed using the absolute calibration method.

The effects of ethanol

An additional study was conducted to see if the 4100 MP-AES could be used to determine aluminum content in alcoholic beverages sold in aluminum cans. Subjecting alcohol to plasma produced a relatively large amount of carbon in relation to the concentration of alcohol. Carbon can cause the torch injector to become blocked. To prevent this, air was mixed with the support gas before subjecting it to the plasma.

With the emission intensity of aluminum in a 0.2 mg/L solution set to 1, the effects of varying the ethanol content from 0 to 10% in the solution were examined (see Figure 3).

There were no significant variations either with or without air at ethanol concentrations of about 5%, but emission intensity declined at concentrations above 5% with no air added. Beer is approximately 5% alcohol, while some shochu highballs are higher, at about 8%. For that reason, the sample analysis was performed with air added.

Aluminum was added to each sample, and the results of the recovery tests are given in Table 3.

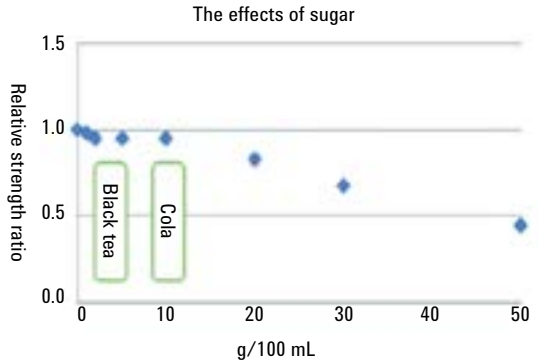

Figure 2. Variation in emission intensity due to differences in sugar concentration

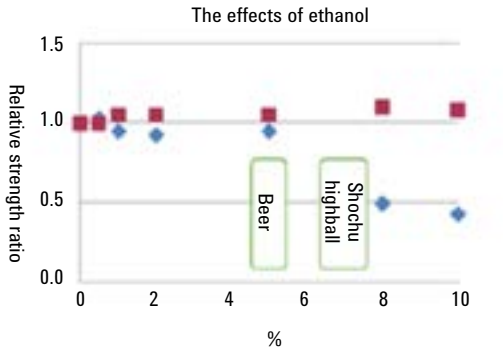

Figure 3. Variation in emission intensity due to differences in ethanol concentration, with and without adding air.
Red squares = with air, blue diamonds = without air

Table 3. Aluminum addition recovery tests

Al	Unspiked (mg/L)	0.2 mg/L added (mg/L)	Recovery rate (%)
Barley tea	0.00	0.22	110
Coffee	0.01	0.23	109
Sports drink	0.01	0.22	105
Cola	0.05	0.24	96
Beer	0.04	0.23	96
Shochu highball	0.01	0.22	105

Al	Unspiked (mg/L)	1.0 mg/L added (mg/L)	Recovery rate (%)
Green tea	1.14	2.12	99
Black tea	2.45	3.38	98

Conclusion

This study has shown that the limit of quantification for aluminum is 1.9 µg/L in aqueous solutions and 7.9 µg/L in ethanol, which adequately meets municipal water supply quality standards as stated in the Japanese Waterworks Law. Favorable results with regard to stability were also obtained. The results of the examination for the effects of beverage matrices (sugar and alcohol) showed that direct measurements without matrix matching can be done for concentrations of about 10 g/100 mL of sugar in beverages, and that the Agilent 4100 MP-AES can also easily and rapidly analyze samples with differing alcohol concentrations if air is mixed in. Thus, it has been demonstrated that the MP-AES has low running costs, is easy to operate, and can perform analyses of aluminum in beverages.

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Agilent Technologies

Determination of metals in soils using the 4100 MP-AES

Application note

Agriculture

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Introduction

It is well known that the presence of elevated levels of metals (for example, As, Cr, Cu, Pb, Ni and Zn) is a considerable concern to human health, and agricultural, livestock and aquatic industries. Certain metals (for example, Cu and Zn) are also essential for biotic and human health and, therefore there is an effective threshold for both deficiency and toxicity. The presence of these contaminants in the environment is likely due to discharge of effluents from small to medium industries, emissions from vehicles, disposal of rural domestic sewage, indiscriminate use of fertilizers and metal-containing pesticides, and disposal of solid waste in unprotected sites. These various contaminant sources have the potential to pollute not only agricultural and urban land, but also surface and ground waters used for agriculture and drinking. Therefore, it is clear that monitoring of metal contamination in soils is critically important for environmental monitoring and to determine the effects of metals on human health.

This application note describes an analytical method for the determination of metals in soils using a new, simple, and relatively inexpensive Microwave Plasma-Atomic Emission Spectrometer (MP-AES). The Agilent 4100 MP-AES generates a self-sustained atmospheric pressure microwave plasma (MP) using nitrogen gas and a torch specifically designed for the MP-AES. Sample introduction to the MP is pneumatic using a concentric nebulizer and cyclonic spray chamber. Emission line isolation and detection is sequential using a Czerny-Turner monochromator and charge-coupled device detector. This MP-AES allows easy entrainment of sample aerosols, both aqueous and organic. The tolerance level of aqueous and organic solvent loads as well as ambient air is significantly higher compared to other analytical plasmas. Refer to Reference [1] for more details about the operational characteristics of the MP-AES.

Experimental

Sample preparation

Soil samples used for analysis were:

- NIST Standard Reference Material 2710 — Montana Soil (Highly Elevated Trace Element Concentrations)
- NIST Standard Reference Material 2711 — Montana Soil (Moderately Elevated Trace Element Concentrations)

For the comparison of MP-AES and NIST results, US EPA Method 3050B sample preparation procedure relating to the acid digestion of sediments, sludges, and soils was used. A short description of this digestion procedure is given below.

Initially, 10 mL of 1:1 HNO_3 was added to 1.00 g of soil sample in a 25 x 150 mm glass digestion tube. The samples were then heated to 95 ± 10 °C for about 15 minutes. When cool, 5 mL of HNO_3 was added and heat was applied for another 30 minutes. The digests were again allowed to cool, before 2 mL of Milli-Q water and 3 mL of 30% H_2O_2 was added and heated to 95 ± 5 °C. After the digests were cooled again, another 1 mL of 30% H_2O_2 was added. Heating continued until the sample volumes reduced to approximately 5 mL. The digests were then allowed to cool again before being diluted to 50 mL with Milli-Q water. Prior to analysis, the soil digests were further diluted tenfold. The 2% moisture content given in the certificate of analysis for NIST 2710a and NIST 2711a was incorporated into the calculation [2].

Instrumentation

Instrument operating conditions are listed in Table 1.

Table 1. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	Concentric
Spray chamber	Single-pass glass cyclonic
Sample tubing	Black/black
Waste tubing	Blue/blue
Read time	3 s
Number of replicates	3
Stabilization time	10 s
Fast pump during sample uptake	On
Pump speed	15 rpm

Table 2 provides the instrumental parameters used for the sample analysis. The criterion for wavelength selection was to provide a wide working range and to avoid line overlaps.

Table 2. Agilent 4100 MP-AES parameters used for soil digest analysis

Analyte	Wavelength (nm)	Read time (s)	Nebulizer pressure (kPa)	Background correction
Al	396.152	3	240	Auto
As	234.984	3	120	FLIC
Cr	425.433	3	240	Auto
Cu	510.554	3	220	Auto
Fe	259.940	3	120	Auto
Mn	259.372	3	120	Auto
Ni	341.476	3	200	Auto
Pb	405.781	3	120	Auto
Zn	472.215	3	120	Auto

Background and interference corrections

The auto-background correction feature in the MP Expert software was used for background correction. Fast Linear Interference Correction (FLIC), an Agilent proprietary spectral interference correction method, was used to correct and remove the iron interference on determination of As using the 234.984 nm line. As illustrated in Figure 1, this type of interference can easily be corrected by running a blank, and analyte and interferent standards. MP Expert then automatically corrects the relevant interference.

Calibration

Analytical calibration was carried out using multi-element standard solutions, except for As. Separate calibration solutions were used for As because of the Fe spectral interference on the As 234.984 nm emission line. Table 3 provides calibration fit types and maximum applicable analyte concentration. Rational fit is a non-linear curve fit and allows an extended working range so that sample analysis can be carried out using a single wavelength without further dilutions being required. Figure 2 depicts a typical non-linear calibration using rational fit. The acceptance criterion for the calibration curve correlation coefficient is 0.999.

Figure 1. Illustration of spectral interference correction using FLIC. Figure 1 represents the FLIC page showing blank, analyte and interferent spectra

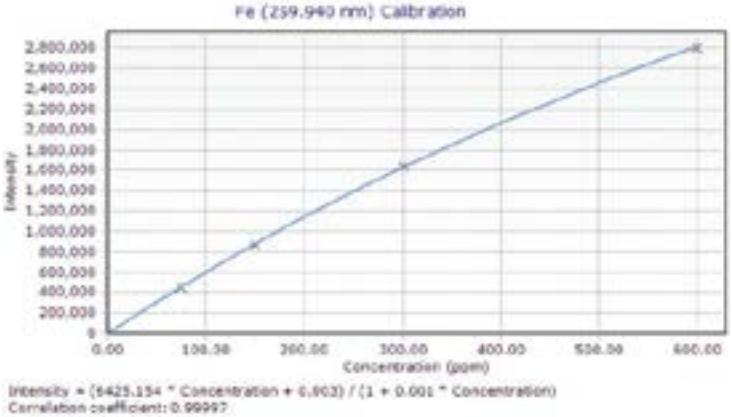

Figure 2. A typical non-linear calibration curve in MP-AES

Table 3. Calibration parameters used for soil digest analysis

Analyte	Wavelength (nm)	Calibration fit	Weighted fit	Through blank
Al	396.152	Rational	On	On
As	234.984	Linear	On	On
Cr	425.433	Rational	On	On
Cu	510.554	Linear	On	On
Fe	259.940	Rational	On	On
Mn	259.372	Rational	On	On
Ni	341.476	Linear	On	On
Pb	405.781	Rational	On	On
Zn	472.215	Rational	On	On

Results and discussion

There are several digestion methods available for the analysis of soils. For example, US EPA Method 3050B: Acid digestion of sediments, sludges, and soils is a strong acid digest, but it is not a total digest. US EPA Method 200.2: is a sample preparation procedure for spectrochemical determination of total recoverable elements. It is common practice for routine analytical laboratories to use US EPA Method 200.2 because of its simplicity for large-scale routine use. However, analytical results can be different to those obtained using US EPA Method 3050B, because leachable metal content depends on several factors such as leach medium, leach time and temperature, and the pH of the sample-leach medium.

The results for the analysis of NIST 2710 and 2711, along with the target values [3], for the selected metals using US EPA Method 3050B, can be seen in Tables 4 and 5. The digestions were performed in triplicate before analysis by MP-AES. It should be noted here that the range values quoted in Tables 4 and 5 for the NIST results were provided by several laboratories as a part of contract work for US EPA. Some of the laboratories used different or modified digestion procedures and therefore, as can be seen, the NIST results cover a wide concentration range. Therefore, these NIST soil results are not certified values. The results obtained using MP-AES are well within the acceptable range provided by NIST, and therefore clearly indicate that MP-AES is a suitable analytical atomic spectrometric technique for soil analysis.

Table 4. Results for the analysis of NIST Standard Reference Material 2710 — Montana Soil (Reference values only)

Analyte	MP-AES results Average ± SD (mg/kg)	NIST results Range (mg/kg)
Al	24300 ± 400	12000–26000
As	550 ± 20	490–600
Cr	21 ± 1	15–23
Cu	2800 ± 20	2400–3400
Fe	28000 ± 300	22000–32000
Mn	8500 ± 200	6200–9000
Ni	9.5 ± 0.6	8.8–15
Pb	5600 ± 300	4300–7000
Zn	6100 ± 200	5200–6900

Table 5. Results for the analysis of NIST Standard Reference Material 2711 — Montana Soil (Reference values only)

Analyte	MP-AES results Average ± SD (mg/kg)	NIST results Range (mg/kg)
Al	20000 ± 200	12000–23000
As	90 ± 15	88–110
Cr	21 ± 3	15–25
Cu	90 ± 1	91–110
Fe	23000 ± 2000	17000–26000
Mn	600 ± 10	400–620
Ni	17 ± 3	14–20
Pb	1400 ± 30	930–1500
Zn	300 ± 10	290–340

Table 6 provides the results for the analysis of the highest calibration standard, used as a continuing calibration verification standard (CCV). It was analyzed at the end of the sequence, about four and a half hours after the beginning of the run. CCV recoveries for all analytes are within 100 ± 15% after four and a half hours of continuous operation of the instrument, with most elements within 100 ± 5%. Note that As was not present in the CCV solution, as explained previously. These CCV recoveries indicate that MP-AES is stable for long hours of continuous operation, which removes the need for time-consuming recalibration over longer instrument runs.

Table 6. Recoveries for CCV solution analysis after four and a half hours of operation

Analyte	Al	As	Cr	Cu	Fe	Mn	Ni	Pb	Zn
CCV recovery (%)	101.8	N/A	99.9	104.1	98.0	97.8	112.1	97.9	100.4

Conclusions

The results obtained using the Agilent 4100 MP-AES indicate that MP-AES is a suitable atomic emission spectrometric technique for metal analysis of soils. Method development, instrument optimization and sample analysis can be easily carried out using the intuitive MP Expert software. The analytical working range can easily be extended using non-linear rational curve fitting for a single wavelength, therefore eliminating most sample dilutions. Spectral interferences can be easily corrected using the proprietary Agilent algorithm (FLIC). A highly stable, self-sustained atmospheric pressure plasma is generated using nitrogen, and therefore the running costs for busy commercial laboratories are very low. The simplicity of the instrument and easy-to-use MP Expert software is even suitable for novice analysts, with minimal training required for routine sample analysis.

References

1. M. R. Hammer, A magnetically excited microwave plasma source for atomic emission spectroscopy with performance approaching that of the inductively coupled plasma, Spectrochimica Acta, 456-464, 63B, 2008.

2. NIST Special Publication 260-172, Certification of Three NIST Renewal Soil Standard Reference Materials for Element Content: SRM 2709a San Joaquin Soil, SRM 2710a Montana Soil I, and SRM 2711a Montana Soil II, http://www.nist.gov/srm/upload/SP260-172.pdf.

3. NIST published leachable concentrations, Addendum to SRM Certificates SRMs 2709 San Joaquin Soil, 2710 Montana Soil, and 2711 Montana Soil, August 23, 1993.

www.agilent.com/chem/4210mp-aes

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Cost-effective analysis of major, minor and trace elements in foodstuffs using the 4100 MP-AES

Application note

Foods and beverages

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Introduction

Whether the goal is food safety, ensuring quality or establishing provenance, measuring the trace element content of foods and beverages that we all consume is of paramount importance. While some elements are essential for our well being at low concentrations, others like lead and chromium are highly toxic and more still are being linked to viral, neurological and other diseases. Food scares related to contamination or poor quality not only constitute a health risk, they also undermine consumer confidence. This can lead to lost earnings through reduced sales and loss of credibility through adverse publicity.

Atomic spectroscopy is well established for the analysis of metals in foods and the technique employed often depends on the requirements of the application in terms of elements of interest, expected concentrations, and number and type of samples. Other important procurement factors that influence instrument selection include purchase and operational budget for consumables, gases, power and labor, as well as service and maintenance costs.

Food & Agriculture Applications

With lab budgets coming under increasing pressure, Agilent has expanded its atomic spectroscopy portfolio to include the 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). MP-AES is a new analytical technique that uses a microwave-induced nitrogen plasma to provide elemental analysis, with significantly reduced running costs through the use of nitrogen as its plasma gas.

Experimental

This work describes the analysis of various certified and standard reference materials per the sample descriptions below:

- NIES CRM No.7 Tea Leaves: from National Institute of Environmental Studies (NIES), Japan.
- NIES CRM No.10c Rice Flour: from National Institute of Environmental Studies (NIES), Japan.
- NIST SRM 1577 Bovine Liver: from National Institute of Standards and Testing, USA.
- CRM-Wheat Flour: from High Purity Standards, USA
- CRM-Milk Powder: from High Purity Standards, USA
- CRM-Oyster Tissue: from High Purity Standards, USA

Sample preparation
A simple acid digestion method was used to prepare three of the samples. Initially, 0.25 g of the tea leaves CRM, 0.5 g of bovine liver SRM and 1 g of rice flour CRM were weighed into separate 250 mL beakers. This was then followed by the addition of 10 mL of HNO_3 and each beaker was covered with a watch glass. The samples were heated on a hot plate until completely dissolved. After cooling to room temperature, each digest was transferred to a 100 mL volumetric flask and made up to the required volume by adding Milli-Q water.

Pre-prepared sample solutions of CRM-Wheat Flour, CRM-Milk Powder and CRM-Oyster Tissue in 4% HNO_3 were purchased from High Purity Standards, USA.

Working standards and a blank were matrix-matched with the samples.

Instrumentation
The innovative 4100 MP-AES with its proprietary Microwave Excitation Assembly is a sequential atomic emission spectroscopic technique capable of fast, unattended multi-element analysis at varying concentration levels using a nitrogen plasma. The unique Microwave Excitation Assembly focuses and contains the microwave energy that is created via a concentrated axial magnetic field around the torch. This creates a robust toroidal plasma that allows the stable introduction of liquid samples. With a central channel temperature of ~5,000 K, MP-AES is highly suited to spectroscopic analysis, as it creates high intensity atomization emission lines. In addition to simplified spectra, nitrogen-MP-AES offers reduced operating costs and increased lab safety compared to flame AA, through the avoidance of costly and highly flammable gases such as acetylene.

The analysis was carried out using an Agilent 4100 MP-AES equipped with a standard MP-AES torch, concentric nebulizer, and glass cyclonic spray chamber.

Operating parameters are shown in Table 1.

Table 1. Agilent 4100 MP-AES operating parameters

Instrument parameter	Setting
Nebulizer pressure	160–180 kPa
Read time	3 s (10 s for MDL)
Number of replicates	3 (10 for MDL)
Stabilization time	15 s
Background correction	Auto

Results

Method detection limits

The Method Detection Limits were determined from the analysis of digested blank samples. The selected analytical wavelengths and method detection limits (3σ) are listed in Table 2.

Table 2. Agilent 4100 MP-AES element wavelength and method detection limits (ppb)

Element	Wavelength (nm)	MDL (ppb)
Al	396.152	0.5
Ba	455.403	0.02
Ca	445.478	14
Cd	228.802	1.2
Co	340.511	4
Cr	425.433	0.5
Cu	327.396	0.4
Fe	371.993	3
K	769.897	3
K	404.414	280
P	213.618	100
Pb	405.781	5
Pb	368.343	12
Mg	518.361	4
Mn	403.076	0.5
Mo	379.825	1.5
Na	589.592	3
Na	568.821	140
Ni	341.476	2
Ni	352.453	2
Sr	407.771	0.01
Zn	213.857	4

Analysis of foodstuffs

Results of the analysis of major, minor and trace extractable elements in six different foodstuffs are listed in Tables 3 to 8. The measured values (carried out in triplicate) are in good agreement with the certified values for all CRM and SRM samples.

Table 3. Results of NIES No.7 Tea Leaves

Element	Measured values	Certified values
	wt%	**wt%**
Ca	0.314 ± 0.013	0.320 ± 0.012
Mg	0.150 ± 0.004	0.153 ± 0.006
K	1.861 ± 0.074	1.86 ± 0.07
	mg/kg	**mg/kg**
Ba	5.76 ± 0.57	5.7*
Cd	nd	0.03 ± 0.03
Co	nd	0.12*
Cr	nd	0.15*
Cu	7.13 ± 0.81	7 ± 0.3
Pb	nd	0.8 ± 0.03
Ni	6.03 ± 0.63	6.5 ± 0.3
Sr	3.63 ± 0.43	3.7*
Zn	34 ± 3	33 ± 3

* Reference values only

Table 4. Results of NIES No.10c Rice Flour

Element	Measured values	Certified values
	wt%	**wt%**
Mg	0.127 ± 0.006	0.125 ± 0.008
K	0.279 ± 0.012	0.275 ± 0.010
P	0.300 ± 0.010	0.335 ± 0.008
	mg/kg	**mg/kg**
Al	1.49 ± 0.13	1.5*
Ca	95.4 ± 7.0	95 ± 2
Cd	1.83 ± 0.14	1.82 ± 0.06
Co	nd	0.007*
Cr	nd	0.08*
Cu	4.03 ± 0.32	4.1 ± 0.3
Fe	10..6 ± 0.15	11.4 ± 0.8
Mo	nd	1.6 ± 0.1
Ni	nd	0.30 ± 0.03
Sr	0.2	0.2*
Zn	21.8 ± 1.0	23.1 ± 0.8

* Reference values only

Table 5. Results of NIST 1577 Bovine Liver

Element	Measured values	Certified values
	wt%	**wt%**
Na	0.247 ± 0.006	0.243 ± 0.013
K	1.00 ± 0.08	0.97 ± 0.06
	mg/kg	**mg/kg**
Ca	131	123*
Cd	nd	0.27 ± 0.04
Co	nd	0.18*
Cu	185 ± 6	193 ± 10
Fe	266 ± 5	270 ± 20
Pb	nd	0.34 ± 0.08
Mg	625 ± 45	605*
Mn	10.4 ± 1.41	10.3 ± 1
Mo	nd	3.2*
Sr	0.15 ± 0.07	0.14*
Zn	125 ± 4	130 ± 10

* Reference values only

Table 6. Results of CRM-Wheat Flour

Element	Measured values (mg/kg)	Certified values (mg/kg)
Al	0.83 ± 0.02	0.85 ± 0.01
Ca	9.64 ± 0.97	9.5 ± 0.1
Cd	nd	0.0015*
Co	nd	0.001*
Cr	0.013 ± 0.001	0.014*
Cu	0.09 ± 0.008	0.1 ± 0.002
Fe	0.81 ± 0.04	0.90 ± 0.01
K	62.5 ± 0.5	65 ± 0.7
P	61.1 ± 1.7	65 ± 0.7
Pb	0.05 ± 0.001	0.050 ± 0.003
Mg	20.8 ± 0.1	20.0 ± 0.2
Mn	0.36 ± 0.02	0.4 ± 0.008
Ni	nd	0.009 ± 0.001
Zn	0.47 ± 0.05	0.50 ± 0.01

* Reference values only

Table 7. Results of CRM-Milk Powder

Element	Measured values (mg/kg)	Certified values (mg/kg)
Al	nd	0.020 ± 0.002
Ca	131 ± 9	130 ± 1
Co	nd	0.0004*
Cr	nd	0.0003*
Cu	0.006 ± 0.001	0.007 ± 0.001
Fe	0.018 ± 0.002	0.020 ± 0.001
K	178 ± 6	170 ± 2
P	98.7 ± 1.3	100 ± 1
Pb	nd	0.002*
Mg	11.9 ± 0.2	12 ± 0.1
Mn	0.003 ± 0.002	0.003*
Na	48.7 ± 2.6	50 ± 1
Zn	0.48 ± 0.05	0.50 ± 0.01

* Reference values only

Table 8. Results of CRM-Oyster Tissue

Element	Measured values (mg/kg)	Certified values (mg/kg)
Al	2.92 ± 0.07	3*
Ca	15.0 ± 0.49	15*
Cd	nd	0.03*
Co	nd	0.004*
Cr	nd	0.007*
Cu	0.56 ± 0.05	0.6*
K	100 ± 0.96	100*
P	79.1 ± 0.9	80*
Pb	nd	0.005*
Mg	12.1 ± 0.2	12*
Mn	0.18 ± 0.01	0.2*
Na	48.9 ± 0.8	50*
Ni	nd	0.01*
Zn	8.3 ± 0.4	9*

* Reference values only

Conclusions

MP-AES offers any food testing facilities dependant on acetylene-based instrumentation a real alternative in terms of sensitivity, multi-element capability and speed of analysis, while cutting operating costs and improving the safety of the lab environment through the use of non-flammable nitrogen.

This study shows that following a quick and simple acid digestion sample preparation procedure (required for three of the six diverse food samples), all six certified and standard reference materials can be analyzed for trace and major element concentrations with good accuracy by MP-AES. The addition of the Agilent 4107 Nitrogen Generator is also possible in order to perform this analysis with significantly lower gas costs or for analysis in remote locations where sourcing of gases is costly or difficult.

www.agilent.com/chem/4210mp-aes

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Determination of metals in wine using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer

Application note

Food Testing and Agriculture

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Introduction

The concentrations of certain metals in wine are of great interest because of their influence on the wine-making process. Strict analytical control of the trace element content is required during the entire wine making process. For example, metals such as potassium, calcium, and iron can produce precipitates, cause cloudiness, or affect the taste.

The wine maker needs to properly control the production process so that the quality of the product can be assured. During vintage, when monitoring trace elements is most critical, sample turnaround time (and to a lesser extent sample throughput) becomes important. Most wine labs are small to medium in size, and hence value ease of use and reduced infrastructure requirements.

Metals in wine can be determined by a number of analytical techniques[1-10]. The most common technique used is Flame Atomic Absorption (FAA), while ICP-OES is sometimes used in larger central laboratories where extra sample throughput is required, although having elemental analysis capabilities close to the winery during vintage is generally preferred.

This work describes an alternative, safer and cheaper analytical method for the determination of metals in wine using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES).

Which measurement technique is right for you?

There are many factors to be taken into account when selecting the right analytical technique. In many cases several techniques will provide adequate detection range, so the technique of choice will depend on factors such as sample throughput requirements, ease-of-use, infrastructure required, and on-going operating costs.

The MP-AES offers significantly reduced on-going operating costs over both FAA and ICP-OES by running on nitrogen that can be supplied via a nitrogen generator. This eliminates the need for on-going gas resupply and avoids flammable gases (required for FAA), enhancing safety and allowing unattended, overnight operation. The reduced infrastructure required for MP-AES also makes it well suited to remote sites where supply of expensive specialty gases can be difficult.

The 4100 MP-AES fits between FAA and ICP-OES in many aspects such as detection power, dynamic range, and speed of analysis. For these key performance metrics, the MP-AES offers a unique alternative to both FAA and ICP-OES.

These features make the MP-AES an attractive technique for many small to medium size laboratories, particularly those at remote locations, and for an increasing number of laboratories requiring the lowest possible on-going operating costs.

Experimental

Instrumentation

The measurements were performed on an Agilent 4100 MP-AES using a dewar nitrogen supply. The 4100 MP-AES is a compact bench-top microwave plasma atomic emission spectrometer that generates a robust, magnetically-excited nitrogen plasma. Operating the instrument with the optional Agilent 4100 Nitrogen Generator further reduces the operating costs.

The sample introduction system used for this application consisted of a standard torch, a double pass glass cyclonic spraychamber and an inert OneNeb nebulizer.

The determination of Ca, K, Na and Mg benefits from the use of an ionization suppressant. The ionization suppressant was mixed with the sample via a T piece placed before the nebulizer. The on-board three channel peristaltic pump was used to deliver the sample through the sample introduction system. A 0.1% w/v Cs (CsCl Analar, Merck) solution was used as an ionization suppressant.

The External Gas Control Module (EGCM) was used to inject air into the plasma when running the diluted wine matrix that contained a small amount of alcohol. The air injection prevents any carbon build up in the torch, ensuring stable results when running these samples over a long time period.

The air injection also reduces the background emissions generated by the organics present in the sample. The EGCM is automatically controlled by the instrument software, and as such requires minimal user interaction.

Because the amount of alcohol in diluted wine samples is low, the air injection rate is selected at a lower rate than the default setting for each wavelength.

The instrument operating conditions are listed in Table 1.

Table 1. Agilent 4100 MP-AES operating conditions

Parameter	Value				
Element	Ca	K	Na	Mg	Fe
Wavelength (nm)	396.847	769.897	589.592	285.213	371.993
EGCM setting	Low	Low	Low	Low	Medium
Nebulizer	OneNeb				
Spraychamber	Double pass glass cyclonic				
Pump rate	15 rpm				
Sample tubing	Orange/green				
Waste tubing	Blue/blue				
Read time	1-10 seconds*				
Number of replicates	3				
Sample uptake delay	15 seconds				
Stabilization delay	20 seconds				
Fast pump during uptake	On				
Background correction	Auto				

*Can be varied based on sample concentrations

For comparison purposes, the samples were also measured on an Agilent 725 radially-viewed ICP-OES instrument and an Agilent 240FS FAA spectrometer.

Standard and Sample Preparation

A variety of wine samples were selected for this study, covering both red and white varieties.

- Wine 1 : Shiraz
- Wine 2 : Cabernet Sauvignon
- Wine 3 : Chardonnay
- Wine 4 : Sauvignon Blanc
- Wine 5 : Viognier

Additionally, two certified reference materials were analyzed to validate the method:

- Red wine: TM-Wine-R1A (Spex CertiPrep)
- White wine: TM-Wine-W1A (Spex CertiPrep)

For MP-AES and ICP-OES analysis, the samples were degassed in an ultrasonic bath, then diluted 1 in 10 (v/v) with 5% HNO_3 (Suprapur, Merck). Standards and blank were prepared in 5% v/v HNO_3 and 2% v/v ethanol (Merck) to matrix match the alcohol content of the wine samples. Care must be taken when adding ethanol into 5% HNO_3. Ethanol should be added gradually drop-wise with a Pasteur pipette.

For AA analysis, the samples were also degassed and further sample preparation for AA depends on the element of interest.

- For Ca samples were diluted 1 in 10 with 5% HNO_3 and 2000 mg/L Sr (Strontium chloride, Laboratory reagent, BDH).
- For K and Na samples were diluted 1 in 10 with 5% HNO_3 and 1000 mg/L Cs.
- For Mg and Fe samples were diluted 1 in 10 with 5% HNO_3.

The standards and blanks were matrix matched with the samples, as described above.

Results

Method detection limit

Method detection limit (MDL) is expressed as 3 times the standard deviation of 10 replicate measurements of the blank. Analytical wavelengths used and the MDL by MP-AES are listed in Table 2.

Table 2. Method detection limits (MDL) by MP-AES

Element	Wavelength (nm)	MDL (µg/L)
Ca	396.847	8
K	769.897	110
Na	589.592	15
Mg	285.213	11
Fe	371.993	15

Certified Reference Material and Wine Samples

The accuracy of the measurement of metals in wine samples by MP-AES was verified by the analysis of the certified red and white wine reference material. Good agreement was obtained with certified values, with recoveries between 94% and 110% (see Table 3). Results for the analysis of wine samples by all three techniques can be seen in Table 4. For the five wines analyzed, the MP-AES results are in good agreement with the AA and ICP-OES results.

Table 3. Analysis of CRM samples by MP-AES

Element	Measured	Certified-TM-Wine-W1A	% Recovery
	mg/L	mg/L	
Ca	79 ± 1	82.2 ±2	96
K	980 ± 23	939 ± 142	104
Na	27.6 ± 0.4	25.1 ± 3	110
Mg	119 ± 1	123 ± 3	97
Fe	2.03 ± 0.01	1.97 ± 0.2	103
Element	**Measured**	**Certified-TM-Wine-R1A**	**% Recovery**
	mg/L	mg/L	
Ca	47 ± 0.31	50 ±2	94
K	1160 ± 32	1120 ± 142	104
Na	21.0 ± 0.4	22.4 ± 3	96
Mg	127 ± 1	123 ± 3	103
Fe	2.43 ± 0.03	2.49 ± 0.2	98

Table 4. Comparison of the analysis of wine sample by three techniques

Element	Concentration (mg/L)		
	4100 MP-AES	240FS AA	725 ICP-OES
Wine 1			
Ca	52	52	54
K	1205	1116	1112
Na	37	37	35
Mg	148	149	150
Fe	1.2	1.1	1.0
Wine 2			
Ca	6.6	6.9	6.9
K	1206	1197	1154
Na	30	34	32
Mg	103	100	102
Fe	2.2	2.2	2.0
Wine 3			
Ca	56	59	59
K	900	848	839
Na	34	33	31
Mg	87	86	90
Fe	0.9	0.9	0.7
Wine 4			
Ca	70	70	77
K	756	718	741
Na	10	11	9.0
Mg	78	77	83
Fe	0.4	0.4	0.3
Wine 5			
Ca	32	31	34
K	689	627	661
Na	48	48	45
Mg	121	125	134
Fe	1.8	1.7	1.7

Conclusion

The MP-AES is an accurate and reliable technique for this application and is an ideal alternative to FAA and ICP-OES. Results for certified samples were in good agreement with the CRM reference values and results for various wine samples were in good agreement across all three techniques.

The MP-AES also offers significant benefits over the commonly used FAA, including enhanced productivity through greatly simplified sample preparation and unattended multi-element analysis, higher performance through improved detection limits and greater linear dynamic range, and lower cost of ownership and operating costs by running on nitrogen and eliminating flammable gases such as acetylene and nitrous oxide.

www.agilent.com/chem/4210mp-aes

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References

1. "Use and limitations of ICP-OES in wine analysis", H. Eschnauer, L. Jakob, H. Meierer, R. Neeb, Mikrochimica Acta, 111, **1989**, 291.

2. "Trace metal studies of selected white wines : an alternative approach", L. Sauvage, D. Frank, J. Stearne, M. B. Milikan, Anal. Chim. Acta, 458, **2002**, 223.

3. "Comparative spectrophotometric determination of the total iron content in various white and red Greek wines", K. A. Riganakos, P. G. Veltsistas, Food Chemistry, 82, **2003**, 637.

4. "Differentiation of sparkling wines (cava and champagne) according to their mineral content", Talanta, 377, **2004**, 377.

5. "Atomic Absorption Spectrometry in Wine Analysis – A Review", T. Stafilov, I. Karadjova, Maced. J. Chem. Chem. Eng, 28, **2009**, 17-31.

6. "Metal contents in "oloroso" sherry wines and their classification according to provence", P. Paneque, M. T. Alvarez-Sotomayor, I. A. Gomez, Food Chem., 117, **2009**, 302.

7. "Metal content in southern Spain wines and their classification according to origin and ageing", P. Paneque, M. T. Alvarez-Sotomayor, A. Clavijo, I. A. Gomez, Microchemical Journal, 94, **2010**, 175.

8. "Elemental analysis of wines from South America and their classification according to country", F. R. S. Bentlin, F. H. Pulgati, V. L. Dressler, D. Pozebon, J. Braz. Chem. Soc., 22, **2011**, 327.

9. "Content in metallic ions of wines from the Madeira and Azores archipelagos", Food Chem., 124, **2011**, 533.

10. "Arsenic and other trace elements in wines of eastern Croatia", Z. Fiket, N. Mikac, G. Kniewald, Food Chem., 126, **2011**, 941.

Total metals analysis of digested plant tissue using an Agilent 4200 Microwave Plasma-AES

Application note

Agriculture

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Introduction

Plant growth and development largely depends on the composition and concentration of mineral nutrients available in the plant leaves and other tissues. These essential nutrients are divided into macronutrients (required in larger quantities because of their structural roles in the plant) and micronutrients (required in smaller quantities because they tend to be involved in regulatory roles in the plant). A deficiency or enrichment of nutrients may result in decreased plant productivity, crop yield or plant quality.

Analysis of the total metal content in plants is often carried out by Flame Atomic Absorption Spectrometry (FAAS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). More recently, agricultural testing labs looking to upgrade or replace their FAAS with a more powerful technique are looking to Microwave Plasma–Atomic Emission Spectrometry (MP-AES) with its many advantages. MP-AES is a multi-element technique that offers better detection limits over a wider working analytical range than FAAS and more elements are available for analysis by MP-AES, including

phosphorus, an expensive and widely used major nutrient in soil fertilization.

For laboratories that have difficulty in sourcing gases, are looking to reduce operating costs or are under pressure to improve safety by removing flammable gases, the MP-AES is ideal as it uses nitrogen gas, that can be generated from air.

This application note describes the sample preparation procedure and analytical method used to determine Cu, Fe, Mn, Zn, Na, K, Ca, Mg, B and P in a plant reference material using the Agilent 4200 MP-AES.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES with nitrogen plasma gas supplied via an Agilent 4107 Nitrogen Generator. The generator alleviates the need and expense of sourcing analytical grade gases. The sample introduction system comprised a double-pass cyclonic spray chamber and the OneNeb nebulizer.

An Agilent SPS 3 autosampler was used to deliver samples to the instrument, allowing the system to be operated unattended. The instrument operated in a fast sequential mode and featured a Peltier-cooled CCD detector. Background and spectral interferences could be simutaneously corrected easily and accurately using Agilent's MP Expert software. Method parameters are given in Table 1.

Table 1. MP-AES method parameters

Parameter	Value
Replicates	3
Pump rate	15 rpm
Sample uptake delay	35 seconds
Rinse time	30 seconds
Stabilization time	15 seconds
Fast Pump during uptake and rinse	On (80 rpm)
Autosampler	Agilent SPS 3
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue

Samples

Botanical reference material (RM) ASPAC 80 Pasture was obtained from the Australasian Soil and Plant Analysis Council (ASPAC, Carapook, VIC, Australia).

Sample preparation

Microwave digestion was used to prepare the ASPAC 80 RM for total metals analysis of Cu, Fe, Mn, Zn, Na, K, Ca, Mg, B and P by MP-AES. 7 mL of HNO_3 and 1 mL H_2O_2 was added to 0.18 g of the sample. A preloaded method for the MARS (CEM, Corporation, USA) microwave was used to digest the sample. Once cooled, the solution was diluted to 50 mL using ultrapure water. No further sample preparation was required and no modifiers or ionization buffers were added.

Wavelength selection and calibration range

Details of wavelength selection and calibration range are given in Table 2. Continuous wavelength coverage allows lines to be chosen that have appropriate sensitivity for the concentration range, and avoid spectral interferences.

Table 2. Wavelength and working calibration concentration range

Element and wavelength (nm)	Calibration range (ppm)
Cu 324.754	1–5
Fe 259.940	5–25
Mn 257.610	5–25
Zn 213.857	1–5
Na 568.820	2–100
K 766.491	1–100
Ca 445.478	20–100
Mg 383.829	1–100
B 249.772	0.25–1.0
P 213.618	10–80

Results and discussion

Calibration

A typical calibration curve for phosphorus is displayed in Figure 1. The curve shows excellent linearity across the concentration range. The large linear dynamic range means that less sample dilutions are needed which improves productivity and reduces the risk of sample contamination.

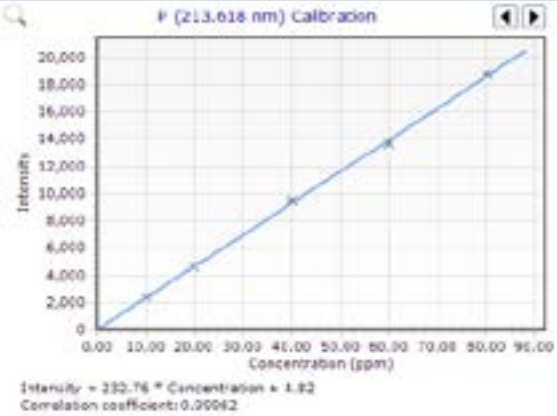

Figure 1. Calibration curve for phosphorus

Sample analysis

The plant RM sample was analyzed for all elements in a single measurement. The quality of the MP-AES results was evaluated by comparing them with the reference values for ASPAC 80. Table 3 shows good accuracy was achieved for all elements over a wide concentration range. The ability of the MP-AES to determine all elements in a single sample measurement greatly simplifies the workflow when compared to an FAAS, and eliminates the need for lamp changes, measurements in absorption and emission, and in the case of B and P, analysis of the samples by other techniques.

Table 3. MP-AES results for total metals content of plant reference material ASPAC 80.

Element	Wavelength nm	Measured value µg/g	Reference value µg/g	Accuracy %
Cu	324.754	13.6	14.7 ± 1.2	93
Fe	259.940	316.13	324 ± 32	98
Mn	257.610	125.8	138 ± 10	91
Zn	213.857	54.6	58.1 ± 5.3	94
Na	568.263	2512	2460 ± 210	102
K	766.491	27302	26700 ± 1850	102
Ca	445.478	10563	11100 ± 600	95
Mg	383.829	3239	3350 ± 220	97
B	249.772	21.65	23.7 ± 3.4	91
P	213.618	3223.35	2970 ± 250	109

Conclusions

The study shows the effectiveness of the Agilent 4200 MP-AES for the analysis of total metal content of a plant-based reference material following microwave digestion. Elements that are difficult to analyze by FAAS such as B and P were included, with all data acquired in a single run. Accurate determinations over a wide concentration range were obtained showing the suitability of MP-AES for the application. When compared to an FAAS, the workflow on the MP-AES is also simplified by eliminating the need for multiple sample preparations, lamp changes and measurements in absorption and emission modes.

Current trends in the market for lower detection limits, lower cost of analysis, improved ease of use and improved safety, are all met by the Agilent 4200 MP-AES. The instrument uses nitrogen, eliminating expensive and hazardous gases such as acetylene, increasing safety, and allowing for unattended operation of the instrument, even in remote locations. When the N_2 is supplied using the Agilent 4107 Nitrogen Generator that extracts N_2 from air, running costs are greatly reduced compared to an FAAS or ICP-OES that rely on a constant supply of analytical grade gases.

With greater sensitivity, linear dynamic range, and sample throughput compared to FAAS, the Agilent 4200 MP-AES is the ideal replacement for labs looking to extend their analytical capabilities.

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Determination of chromium in pharmaceutical gelatin capsules using the Agilent 4100 MP-AES

Application note

Pharmaceutical

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Introduction

Excessive levels of chromium were discovered in edible gelatin capsules used in pharmaceutical products in China. To ensure consumer safety, the State Food and Drug Administration (SFDA) in China issued an alert in April 2012.

Chromium consumed at excessive levels is known to cause acute and long-term health effects, including kidney, liver and blood cell damage. Chromium is also a known carcinogen. As defined by the 2010 edition of Chinese Pharmacopoeia, the maximum limit for consumption of chromium in gelatin is 2 mg/kg.

This application note describes the determination of chromium in a selection of gelatin capsules acquired in China, using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). Samples were prepared by digestion in a mixture of HNO_3 and H_2O_2 and heated to 200 °C by microwave digestion.

Method detection limits of 0.12 mg/kg were achieved, well below the maximum limit of 2 mg/kg.

The 4100 MP-AES is an innovative fast sequential atomic emission spectrometer that uses magnetically-coupled microwave energy to generate a robust and stable nitrogen plasma. By using nitrogen, the 4100 MP-AES eliminates the need for expensive or flammable gases, such as acetylene, resulting in lower running costs, unattended operation and improved productivity when compared to traditional elemental analysis techniques like flame atomic absorption spectrometry.

Experimental

Instrumentation

The instrument was operated using the conditions defined in Table 1.

Table 1. Operating conditions of the Agilent 4100 MP-AES

Instrument parameter	Setting
Spray chamber type	Single pass glass cyclonic
Nebulizer type	Concentric glass
Nebulizer pressure	200 kPa
Read time	3 s
Stabilization time	15 s
Chromium wavelength	427.480 nm
Background correction	Auto

The instrument was controlled using Agilent's intuitive worksheet-based MP Expert software, and features an automated optimization tool to accelerate method development by novice operators.

A microwave digestion system was used to digest the samples under the conditions shown in Table 2.

Table 2. Microwave digestion procedure

Step	Temperature	Time
1	150 °C	5 min
2	180 °C	10 min
3	190 °C	10 min
4	200 °C	5 min
5	100 °C	1 min

Reagents

- High-purity water: >18.2 MΩ.cm
- 1000 mg/L single element Cr standard from the National Standard Research Center
- High-purity 30% H_2O_2 from Merck
- High-purity 10 M HNO_3 from Sigma Chemicals.

Sample preparation

Five different varieties of emptied gelatin capsules were acquired for analysis. Approximately 0.5 g of each sample was accurately weighed into microwave digestion vessels and 8 mL nitric acid and 4 mL hydrogen peroxide was added.

The digestion vessels were sealed and the samples microwave digested using the program conditions defined in Table 2. Upon completion, the contents of the digestion vessels were allowed to cool, then transferred to 25.00 mL volumetric flasks and made up to volume with high-purity water. A reagent blank was also prepared following the same procedure.

Three additional samples were prepared and spiked with 50 µg/L of Cr.

Calibration standard preparation

Six calibration standards ranging from 5 µg/L to 500 µg/L were prepared in 5% HNO_3.

Results and discussion

Linearity

Figure 1 demonstrates the linearity of the Cr calibration graph over the concentration range.

Table 3. Concentration of Cr standard solutions (unit: mg/L)

Element	Std 1	Std 2	Std 3	Std 4	Std 5	Std 6
Cr	0.005	0.01	0.02	0.05	0.1	0.5

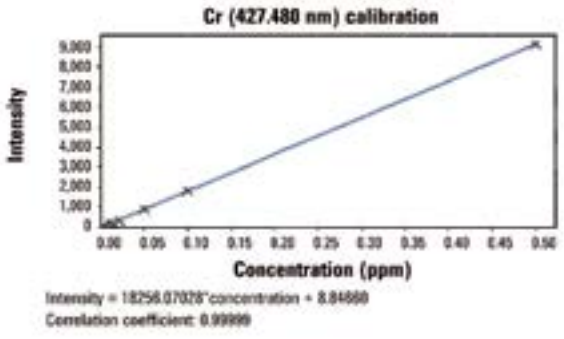

Figure 1. Cr calibration graph

Method detection limit (MDL)

The MDL is defined as three times the standard deviation (3σ) of the measured reagent blank concentration, read back consecutively 11 times.

The lower quantitative limit or limit of quantitation (LOQ) is typically defined as 3.33 x MDL (or 10σ).

The determined MDL and LOQ are reported in Table 4 and easily meet the required limits of 2 mg/kg for Cr in gelatin capsules as defined by the Chinese Pharmacopoeia (2010 version).

Table 4. MDL and LOQ for Cr using the Agilent 4100 MP-AES

	Concentration (mg/kg)
MDL (3σ)	0.12
LOQ (10σ)	0.40

Analysis of samples and spike recovery

Five gelatin capsules were randomly acquired and analyzed for Cr content using the described method.

Capsules C, D, and E were spiked post-digestion with 2.5 mg/kg (50 µg/L) of Cr and the recovery for each was measured. Recoveries were within 10% of the spike value, confirming the absence of matrix effects.

Table 5 shows the measured concentrations and spike recovery for Cr in a variety of Chinese gelatin capsules.

Table 5. Measured concentrations and spike recovery for Cr in a variety of Chinese gelatin capsules.

Sample	Measured Cr concentration in sample (mg/kg)	Measured Cr concentration in spiked sample (mg/kg)	Spike recovery (2.5 mg/kg spike) (mg/kg and %)
Capsule A Artificial Calculus Bovis	1.16	---	---
Capsule B Norfloxacin	<0.40	---	---
Capsule C Amoxicillin	<0.40	2.43	2.43 (97%)
Capsule D Pain relief remedy promoting blood circulation	<0.40	2.30	2.30 (92%)
Capsule E Pain relief remedy promoting blood circulation	0.95	3.48*	2.53 (101%)

*Including sample concentration

Conclusion

This application note demonstrates the successful digestion of gelatin pharmaceutical capsules using microwave digestion and the determination of chromium using the Agilent 4100 MP-AES. A method detection limit of 0.12 mg/kg was achieved, more than an order of magnitude below the maximum allowable limit for consumption of 2 mg/kg, as defined by the Chinese Pharmacopeia.

The nitrogen-based plasma of the Agilent 4100 MP-AES exhibits a high tolerance to difficult sample matrices, greater operator safety and significantly lower operating costs. MP-AES is a suitable alternative to comparable spectroscopy techniques including flame AAS that require the use of expensive and flammable gases such as acetylene.

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Agilent Technologies

Direct determination of Cu, Fe, Mn, P, Pb and Ti in HF acid-digested soils using the Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer

Application note

Agriculture

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Introduction

Accurate elemental analysis of soils is extremely important for numerous reasons. Lead and cadmium are known for their adverse health and environmental effects. Phosphorus, copper, iron, magnesium are considered important macro and micro nutrients for plants and thus, these elements are of interest for agricultural science, crop selection and soil remediation studies. Titanium minerals in soil are also used as weathering indicators [1].

Laboratories that analyze soil and rock samples must use hydrofluoric acid (HF) during sample preparation to ensure complete dissolution, especially where silicate based minerals may be present. Standard glass sample introduction systems are not suitable for the introduction of HF digests unless the samples are neutralized prior to analysis as the free HF attacks and degrades the glass and quartz components.

Unfortunately, the HF neutralization step reduces laboratory efficiency and introduces a potential source of contamination. Therefore, laboratories that routinely analyze samples prepared using HF digests prefer to work with

inert sample introduction components allowing HF digests to be run without the neutralization step.

Agilent has developed an inert torch for the 4200 MP-AES to facilitate the analysis of HF digests without prior neutralization (Figure 1). The inert MP-AES torch features an inert alumina injector. When used in conjunction with the inert double-pass spray chamber and an inert nebulizer, such as the OneNeb nebulizer, it provides a complete inert sample introduction system for use with HF digests. This expands the application range of the Agilent 4200 MP-AES to include the analysis of challenging geochemical samples.

In this study, the concentrations of Cu, Fe, Mn, P, Pb and Ti in a range of soil-based Standard Reference Materials (SRMs) digested using aqua regia and HF have been determined using the 4200 MP-AES and an inert sample introduction system, including the inert MP-AES torch (shown in Figure 1).

Figure 1. The inert MP-AES torch

Experimental

Instrumentation

The 4200 MP-AES is a fast sequential emission based multi-element analytical technique that uses a microwave-induced nitrogen-based plasma for sample excitation. This eliminates expensive and hazardous gases such as acetylene, increasing safety, and allowing unattended operation of the instrument, even in remote locations. Nitrogen can be supplied from bottled gas, Dewar or via the Agilent 4107 Nitrogen Generator (with air supplied from an air compressor). For this application, Dewar nitrogen was used to run the MP-AES.

The sample introduction system used for the analysis of HF-digested soil samples featured inert components including an inert double pass spray chamber, the inert MP-AES torch and the inert OneNeb nebulizer.

The instrument was controlled by the powerful and easy-to-use MP Expert software. The MP-AES features continuous wavelength coverage and MP Expert features an extensive wavelength database that allows the selection of wavelengths that are appropriate for the concentration range required for the analysis and which are relatively free of interferences.

Table 1. Agilent 4200 MP-AES operating conditions

Parameter	Setting/setup
Torch	Inert torch with alumina injector
Nebulizer	OneNeb inert nebulizer
Nebulizer flow	
	0.4 L/min for P
	0.6 L/min for Fe, Ti, Cu and Y
	0.9 L/min for Mn and Pb
Spray chamber	Inert double-pass spray chamber
Sample tubing	Solvaflex pump tubing with orange-green tabs
Internal Std tubing	Solvaflex pump tubing with orange-green tabs
Waste tubing	Solvaflex pump tubing with blue-blue tabs
Pump speed	10 rpm
Number of replicates	3
Read time	5 s for Pb
	3 s for P
	1 s for all others
Stabilization time	10 s
Uptake time	45 s (fast pump)
Rinse time	120 s (fast pump)

Standard Reference Materials

Three soil-based SRMs from the National Institute of Standard and Technology (NIST) were analyzed to validate the method used in this study (refer to Table 2) All were sourced from Graham B. Jackson (Aust) Pty Ltd and were used on an as-received basis.

Table 2. Soil-based standard reference materials and their certified concentrations, as used in this study.

	Certified concentration in mg/kg					
Reference Material	**Cu**	**Fe**	**Mn**	**P**	**Pb**	**Ti**
NIST SRM 2710a Montana I Soil	3420	43200	2140	1050	5520	3110
NIST SRM 2711a Montana II Soil	140	28200	675	842	1400	3170
NIST SRM 2709a San Joaquin Soil	33.9*	33600	529	688	17.3	3360

* reference value

Preparation of calibration standards and samples

Sample preparation included a HNO_3–HCl-HF digestion with a nominal sample weight of 0.5 g. The weighed sample was placed into an inert (PTFE) reaction vessel. In order to ensure a homogeneous reaction with the acid mix, 2 mL of de-ionized water was first added to moisten the sample. Subsequently, 2 mL of nitric acid 69% (Merck), 6 mL hydrochloric acid 37% (Merck) and 2 mL hydrofluoric acid 48% (Merck) was added. The samples were digested using the Milestone UltraWave microwave digestion system. The Single Reaction Chamber of the microwave digestion system was pressurized using a nitrogen gas pressure of 40 bar. The samples were made up to a volume of 40 mL using 18 MΩ de-ionized water. Samples were prepared in triplicate.

The temperature program used for the microwave digestion process is shown in Table 3.

Table 3. Parameters for microwave digestion (where t is the time and T1 and T2 are the initial and final vessel temperatures)

Step	t (min)	T1 (°C)	T2 (°C)
1	10	Ambient	150
2	5	150	150
3	10	150	230
4	10	230	230

Calibration standards were prepared from Agilent aqueous single element certified reference materials. Multi-element calibration standards were prepared by diluting the single element stock solutions using an aqueous solution of 20% aqua regia and 5% HF in 18 MΩ de-ionized water. Phosphorus standards were prepared separately due to spectral interferences from Cu, Fe and Mn. The diluent solution, containing 20% aqua regia / 5% hydrofluoric acid in 18 MΩ de-ionized water, was used to match the acid matrix of the digests. The calibration range was determined based on the expected concentration of the analytes in the completed digests of the SRMs. Ten calibration standards were used as shown in Table 4.

Table 4. Calibration standards

Solution	Cu	Fe	Mn	Pb	Ti	P
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Digestion Blank	0	0	0	0	0	0
Cal Std 1	4.0	20	8.0	1.0	4.0	-
Cal Std 2	10	50	20	2.5	10	-
Cal Std 3	20	100	40	5.0	20	-
Cal Std 4	60	300	120	15	60	-
Cal Std 5	80	400	160	20	80	-
Cal Std 6	120	600	240	30	120	-
Cal Std 7	240	1200	480	60	240	-
Cal Std 8	-	-	-	-	-	5.0
Cal Std 9	-	-	-	-	-	20
Cal Std 10	-	-	-	-	-	50

Wavelength selection, background and interference correction

Table 5 lists the emission lines selected for analysis, together with the background and interference correction methods used. The selected wavelengths provide minimal spectral interferences, and wide dynamic range, eliminating time-consuming sample dilutions and re-analysis. An internal standard solution of 10 mg/L Yttrium in 2% HNO_3 was delivered on-line using orange/green pump tubing with a Y-connector used to combine the flow with the sample prior to nebulization.

Table 5. Line selection, background and interference correction methods for each element

Element	Wavelength (nm)	Type	Back-ground/ Interference Correction	Interferents
Cu	324.754	Analyte	FLIC	Fe, Mn, Ni, Ti
Fe	248.327	Analyte	FLIC	Co
Mn	403.307	Analyte	FLIC	Co, Fe, V
P	213.618	Analyte	FLIC	Cu, Fe, Mn, Ni, Zn
Pb	405.781	Analyte	FLIC	Co, Fe, Mn, Ti, V
Ti	308.804	Analyte	FLIC	Co
Y	437.494	Internal Standard	Auto	-

Most soil samples contain a wide range of elements at varying concentrations - this can result in some spectral interferences. The MP Expert software has an extensive wavelength database that helps the analyst to choose the best analytical wavelengths, based on intensity and the potential for spectral interferences. When there are interferences and there are no other lines that either provide the required sensitivity or are free of interferences, Agilent's Fast Linear Interference Correction (FLIC)[2] can be used to apply correction. FLIC can be used when multiple, partly overlapping spectral components are present in the spectral window, or if there is only a single component present. FLIC also provides you with the flexibility to correct for structured background. FLIC models are constructed using pure solutions for the blank, analyte and the expected interferences in the sample. The Agilent MP Expert software estimates the amount of each model required to minimize the sum of squared differences between the unknown spectrum and the scaled sum of the models for the blank, analyte and expected interferences. This modeling provides accurate and automatic correction for the interferences identified in your sample spectra.

In this study, FLIC proved to be the right tool to resolve the interferences encountered in the reference materials analyzed. Table 6 lists the solutions used to build the FLIC models for the soil SRMs in this study. This is one example of how FLIC enables the user to analyze challenging samples with interferences. Measuring the element lead (Pb) represents a challenge since it is usually expected in low concentration in soil samples. Soil samples represent a very complex matrix with multiple potential interferences (Table 5). The wavelength database in the MP Expert software assists the user to choose the appropriate interferent elements. Using FLIC, it is possible to build correction models that can resolve the spectral interferences enabling the user to achieve accurate results.

The Pb content in the SRMs selected for this study ranged from a low of 20 mg/kg to more than 5000 mg/kg. To be able to analyze the samples with low Pb concentration, the most sensitive emission line was selected for analysis (405.781 nm). However in the vicinity of this emission line, a number of interferent elements were observed (Figure 2), with some of them present in the soil SRMs at percent (%) levels.

Figure 2 shows the signal for Pb at 405.781 nm with the interferent elements modeled using FLIC. Cobalt provides an interfering signal at 405.818 nm (green trace). Additionally, there are interferences from iron, which is present at very high levels in the soil SRMs (2.8 - 4.3 % w/w), over the wavelength range from 405.734 to 405.875 nm (purple trace). It was also found that V, which has a signal at 405.707 nm (yellow trace) and Ti signals at 405.762 and 405.814 nm (blue trace), were also introducing interferences at the Pb 405.781 nm wavelength. Finally Mn, which is present in the sample at moderately high levels, was also introducing an interferent signal at 405.795 nm (dark green trace).

Despite the interferences at the Pb 405.781 nm wavelength, FLIC was able to accurately model this complex matrix and achieve good results with excellent recoveries for Pb across a concentration range of two orders of magnitude.

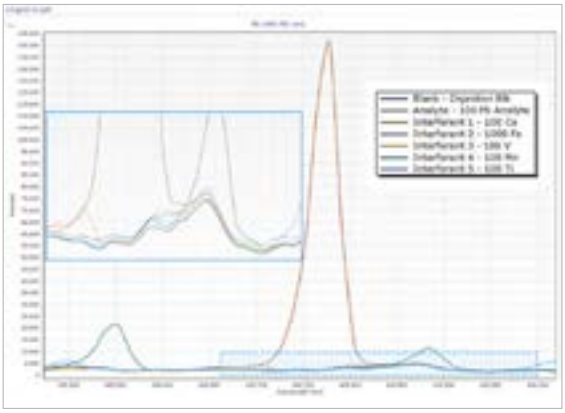

Figure 2. Spectral interferences for Pb 405.781 nm resolved using FLIC

Results and discussion

Method DLs

Method detection limits (MDL) were determined by running the full calibration, including FLIC analytes and interferents—then running 10 replicates of a digested acid blank 10 times. The MDL is defined as 3 times the standard deviation (S) of the concentration reading for each element.

The limit of quantification (LOQ) for this analysis was estimated as 10 times the standard deviation of the concentration readings multiplied by 80. This value (of 80) was selected as this was the total dilution factor used during sample preparation.

Table 7. Method detection limits and estimated limit of quantification

	Cu	Fe	Mn	P	Pb	Ti
MDL in mg/L in solution	0.0009	0.03	0.0005	0.119	0.010	0.018
LOQ in mg/L in solid	0.2	7.0	0.1	31.7	2.7	4.7

Long term stability

To check instrument stability during a long term measurement, a sample of NIST SRM 2710a Montana I soil digest was analyzed every 12 minutes over 8 hours of continuous measurement. A periodic calibration re-slope, which included the blank and one standard, was performed every 2.5 hours. Excellent stability was achieved over this long term measurement with all elements in the method having average recoveries within ±10% and the long term measurement precision over the full 8 hours was less than 5% RSD (Table 8). Further studies performed with the same sample type have shown that the long term stability could be improved by using a humidifier for the nebulizer gas flow. With the humidifier, the long term measurement precision over the full 8 hours was reduced to less than 3% RSD for all elements.

Table 6. FLIC sequence matrix (the numbers in parenthesis represent the concentration of the solutions in mg/L). MB = matrix blank

		Interf-1	Interf-2	Interf-3	Interf-4	Interf-5	Interf-6	Interf-7	Interf-8
Blank	Analyte	Co	Cu	Fe	Mn	Ni	Ti	V	Zn
MB	Cu (100)	-	-	Fe (1000)	Mn (100)	Ni (100)	Ti (100)	-	-
MB	Fe (100)	Co (100)	-	-	-	-	-	-	-
MB	Mn (100)	Co (100)	-	Fe (1000)	-	-	-	V (100)	-
MB	P (100)	-	Cu (100)	Fe (1000)	Mn (100)	Ni (100)	-	-	Zn (100)
MB	Pb (100)	Co (100)	-	Fe (1000)	Mn (100)	-	Ti (100)	V (100)	-
MB	Ti (100)	Co (100)	-	-	-	-	-	-	-

Table 8. Long-term precision for 8 hours continuous measurement of the NIST SRM 2710a Montana I soil digest

Precision (%RSD)					
Cu	Fe	Mn	P	Pb	Ti
3.2	2.8	3.2	4.2	2.2	2.0

Spike recoveries

An aliquot of acid blank was spiked with the analytes of interest at concentrations representative of ~40% of the concentration in the 2710a Montana I soil. The recoveries for the spiked matrix blank are listed in Table 9. An aliquot of the Montana I soil digest was also spiked with the analytes of interest at ~40% of the expected concentration in the soil. The recoveries for the spiked soil digest sample are listed in Table 10.

Table 9. Spike recoveries: Matrix Blank + 40% spike

	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	P (mg/L)	Pb (mg/L)	Ti (mg/L)
Spike conc	16	200	10	5	28	16
Measured	14.9	188	9.9	4.7	27.7	15.6
% Recovery	93.3	94.1	99.1	93.0	98.9	97.3

Table 10. Spike recoveries: NIST SRM 2710a Montana I Soil + 40% spike

	[Cu mg/L)	Fe (mg/L)	Mn (mg/L)	P (mg/L)	Pb (mg/L)	Ti (mg/L)
Spike conc	16	200	10	5	28	16
Measured	14.5	189	10.1	5.7	26.8	13.7
% Recovery	90.3	94.6	101	114	95.8	85.6

Recoveries of the soil based SRMs

The recoveries for the elements determined in the SRMs included in this study were all within the range of 100 ± 10 % which highlights the suitability of this method for the different soil matrices covered by this study (Tables 11-13). These results are the average of three separate digestions made in triplicate, measured using two different instruments with two different inert MP-AES torches. The results also demonstrate the wide dynamic range capability of the Agilent 4200 MP-AES, as elements were determined over a wide concentration range from ppm to % level in a single reading.

Table 11. Recoveries for NIST SRM 2710a Montana I Soil

Element (λ, nm)	Certified (mg/kg)	Measured (mg/kg)	Uncertainity (mg/kg) U^{95**}	Std Dev (n=9)	Recovery (%)
Cu (324.754)	3420±50	3435	53	85.5	100
Fe (248.327)	43200±800	42527	461	743.3	98
Mn (403.307)	2140±60	2254	38	60.8	105
P (213.618)	1050±40	1022	62	99.6	97
Pb (405.781)	5520±30	5395	185	297.8	98
Ti (308.804)	3110±70	2955	57	91.4	95

Table 12. Recoveries for NIST SRM 2711a Montana II soil

Element (λ, nm)	Certified (mg/kg)	Measured (mg/kg)	Uncertainity (mg/kg) U^{95**}	Std Dev (n=9)	Recovery (%)
Cu (324.754)	140±2	147	2.3	3.7	105
Fe (248.327)	28200±400	28640	366.3	591.0	102
Mn (403.307)	675±18	716	14.1	22.7	106
P (213.618)	842±511	804	52.3	84.4	96
Pb (405.781)	1400±10	1420	57.6	93.0	101
Ti (308.804)	3170±80	3061	86.3	139.2	97

Table 13. Recoveries for NIST SRM 2709a San Joaquin soil

Element (λ, nm)	Certified (mg/kg)	Measured (mg/kg)	Uncertainity (mg/kg) U^{95**}	Std Dev (n=9)	Recovery (%)
Cu (324.754)	33.9±0.5*	34.3	0.7	1.1	101
Fe (248.327)	33600±700	32941	689.0	1112	98
Mn (403.307)	529±18	550	9.5	15	104
P (213.618)	688±13	633	47.3	76	92
Pb (405.781)	17.3±0.1	18	1.0	1.6	106
Ti (308.804)	3360±70	3189	57.5	93	95

*These values have not been certified but are provided for reference
** The uncertainty is calculated at the 95% confidence interval using a t-distribution ($tS/n^{½}$); conditions: t(8)=1.86

Recoveries of the soil based SRMs without HF

HF is needed in the digestion process to ensure complete dissolution of titanium in the soil samples. To demonstrate the effectiveness of HF in achieving complete digestion, a set of samples were digested using only HCl-HNO_3 and analyzed. The recoveries for titanium were compared against those obtained using the HF digest, from a single digest prepared in triplicate at the same time. As expected the recoveries were quite poor when using only aqua-regia (Figure 3).

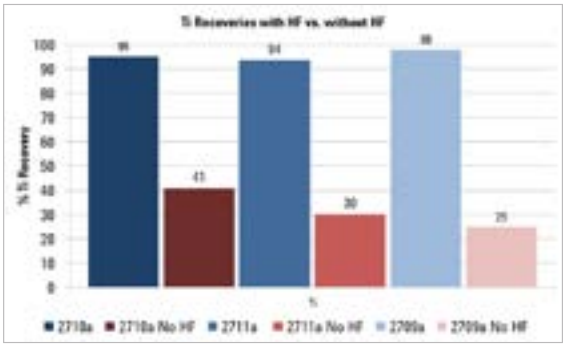

Figure 3. Recoveries for titanium in 3 different soil based NIST SRMs, comparing digests prepared with aqua regia only (show as red columns) with those using HF + aqua regia (shown as blue columns).

Conclusions

The results from analysis of the soil based SRMs included in this study demonstrate that the Agilent 4200 MP-AES is an excellent technique for the analysis of soils and challenging geochemical samples. The wide dynamic range capability was demonstrated as elements were determined over a wide concentration range from ppm to % level in the same sample, in a single reading, with excellent recoveries. When equipped with an inert sample introduction system, comprising an inert double pass spray chamber, the inert MP-AES torch and the inert OneNeb nebulizer, it is possible to analyze HF digests directly without a prior neutralization step. This eliminates one sample preparation step, increasing efficiency and minimizes potential sources of sample contamination.

Despite the numerous interferences, FLIC correction algorithm was able to model the complex interferent signals and produce good results for all elements with excellent recoveries across a concentration range of two orders of magnitude. The FLIC correction algorithm proved to be the right tool to resolve the interferences encountered in the reference materials analyzed.

References

1. Aide M. et al. Soil Science 168(3) (2003) 200–221

2. Agilent MP Expert Software, Technical Overview. Agilent Publication number 5990-8975EN

www.agilent.com/chem/4210mp-aes

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Determination of exchangeable cations in soil extracts using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer

Application note

Agriculture

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Introduction

Accurate, routine testing of nutrients in soil samples is critical to understanding its potential fertility. Many of the nutrients that are vital to plants are exchangeable cations. These are ions loosely attached to and/or adsorbed onto clay particles and organic matter in soil that may become available to plants. Determination of these cations is of great interest for agronomic diagnostic and soil sustainability, enabling more accurate assessment and management of nutrient requirements [1, 2]. If the results indicate there is a nutrient imbalance, then this can be corrected for by the application of a suitably formulated fertilizer.

Food & Agriculture Applications

This application note describes an analytical method for the determination of Ca, K, Mg, Mn and Na in soils using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). A chemical extraction with 1 M ammonium acetate is recommended (standard NF X 31-108) [1, 2, 3]. In this work, results obtained with MP-AES are compared to those obtained by other well-proven, validated techniques flame atomic absorption spectrometry (FAAS) and inductively coupled plasma-optical emission spectrometry (ICP-OES), and with inter-laboratory results to demonstrate the reliability and accuracy of MP-AES data.

Which measurement technique is right for you?

There are many factors to be taken into account when selecting the right analytical technique. In many cases several techniques will provide adequate detection range, so the technique of choice will depend on factors such as sample throughput requirements, ease-of-use, infrastructure required, and on-going operating costs. In the case of this application, it has been more common for smaller laboratories with low sample throughput requirements to use FAAS, while some larger laboratories (with higher sample throughput requirements) may use ICP-OES.

The 4100 MP-AES fits between FAAS and ICP-OES in many aspects such as detection power, dynamic range, and speed of analysis. For these key performance metrics, the MP-AES offers a unique alternative to both FAAS and ICP-OES.

There are also some clear differentiating benefits of the MP-AES technology over these more traditional options. By eliminating the need for on-going gas resupply, the MP-AES offers significantly reduced on-going operating costs over both FAAS and ICP-OES — and avoids flammable gases (required for FAAS), hence enhancing safety and allowing unattended, overnight operation. The reduced infrastructure required for MP-AES also makes it well-suited to remote sites where supply of gases can be difficult and/or expensive. These features make the MP-AES an attractive technique for many small to medium size agricultural laboratories, particularly those at remote locations, and for an increasing number of laboratories requiring the lowest possible on-going operating costs.

Experimental

Instrumentation

The 4100 MP-AES revolutionizes the way analysts conduct multi-elemental analysis. Using a microwave plasma that is based on nitrogen, supplied from a compressed air supply and the Agilent 4107 Nitrogen Generator, the 4100 MP-AES does not require flammable or expensive gases such as acetylene, nitrous oxide or argon. This improves lab safety, results in a significant reduction in operating costs and allows installation in mobile labs or remote locations where gas supplies may not be available.

Additionally, the 4100 MP-AES has been designed to improve the analytical performance and productivity when compared with FAAS, with good sensitivity and detection limits down to sub ppb levels over a wide linear range.

Instrument operating conditions are listed in Table 1.

Table 1. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	OneNeb
Spray chamber	Glass cyclonic single-pass
Sample tubing	White-white
CsCl tubing	Orange-yellow
Waste tubing	Blue-blue
Read time	3 s
Number of replicates	3
Stabilization time	15 s
Fast pump during sample uptake	Yes
Pump speed	15 rpm

The analysis of soil samples was also carried out by ICP-OES and FAAS. Conditions of analysis are as described in Table 2.

Table 2. Global conditions of analysis

Instrument	Dilution	Comments
Agilent 4100 MP-AES	On-line with CsCl 1.5%	OneNeb nebulizer
Agilent 280 FS AAS	SIPS 20. Dilution factor set by element	CsCl as modifier for Na and K, La/CsCl as modifier for Mg
Agilent 725 ICP-OES	No dilution	OneNeb nebulizer

Material

Soil samples were provided (air-dried and sieved <2 mm) by the French inter-laboratory comparisons organization BIPEA (Inter-professional Bureau of Study and Analysis, France). All samples have been recently analyzed in proficiency testing, so that the reference values and standard deviations for CaO, K_2O, MgO and Na_2O concentrations in ammonium acetate were known. Note: manganese was not included in the testing scheme but has been included in this investigation.

The reference numbers of the soil samples used were 403, 418, 421 and 423.

Sample preparation

As described in the standard NF X 31-108, 1 M ammonium acetate adjusted to pH 7, was used as extractant. The total concentration of dissolved salt was 77 g/L.

For each soil, 50 mL of 1 M ammonium acetate was added to 2.5 g of soil. The mixture was shaken by rotation in a room at 20 °C ±2 °C over 1 hour. After extraction, the samples were filtered using a filter paper and the clear solutions were analyzed immediately.

Standard preparation

Four multi-element standard solutions were prepared in 1 M ammonium acetate. Table 3 provides details of the calibration concentration range for each analyte. Single element stock solutions from Merck Germany were used. Table 4 displays selected wavelengths and calibration parameters used for analysis.

Cesium chloride was used as an ionization buffer. This was added on-line via a 'Y' piece to avoid manual spiking of standards and samples.

Table 3. Calibration standards used for soil extraction analysis (mg/L)

	Ca	K	Mg	Mn	Na
Blank	0	0	0	0	0
Standard 1	100	5	5	1.0	0.5
Standard 2	200	10	10	2.0	1.0
Standard 3	300	15	15	3.0	2.0
Standard 4	600	30	30	6.0	4.0

Table 4. Agilent 4100 MP-AES wavelengths and calibration parameters selected for analysis

Element	Wavelength (nm)	Read time (s)	Nebulizer pressure (kPa)	Background correction
Ca	430.253	3	240	Auto
K	769.897	3	240	Auto
Mg	383.829	3	240	Auto
Mn	403.076	3	240	Auto
Na	588.995	3	240	Auto

Results

Calibration

The calibration curves for Ca, K, Mg, Mn and Na on the MP-AES are displayed in Figure 1. Results show good linearity. This highlights the better linear dynamic range achieved with the 4100 MP-AES as compared to FAAS. Less sample dilutions are then needed when using MP-AES avoiding sample contamination and enhancing productivity.

Sample analysis

The accuracy of the results obtained by MP-AES was evaluated by two methods: i) comparison of the MP-AES results with results obtained with another analytical technique (FAAS and/or ICP-OES) and ii) calculation of z-scores for the MP-AES results with data from the inter-laboratory test (reference results and corresponding standard deviations).

Food & Agriculture Applications

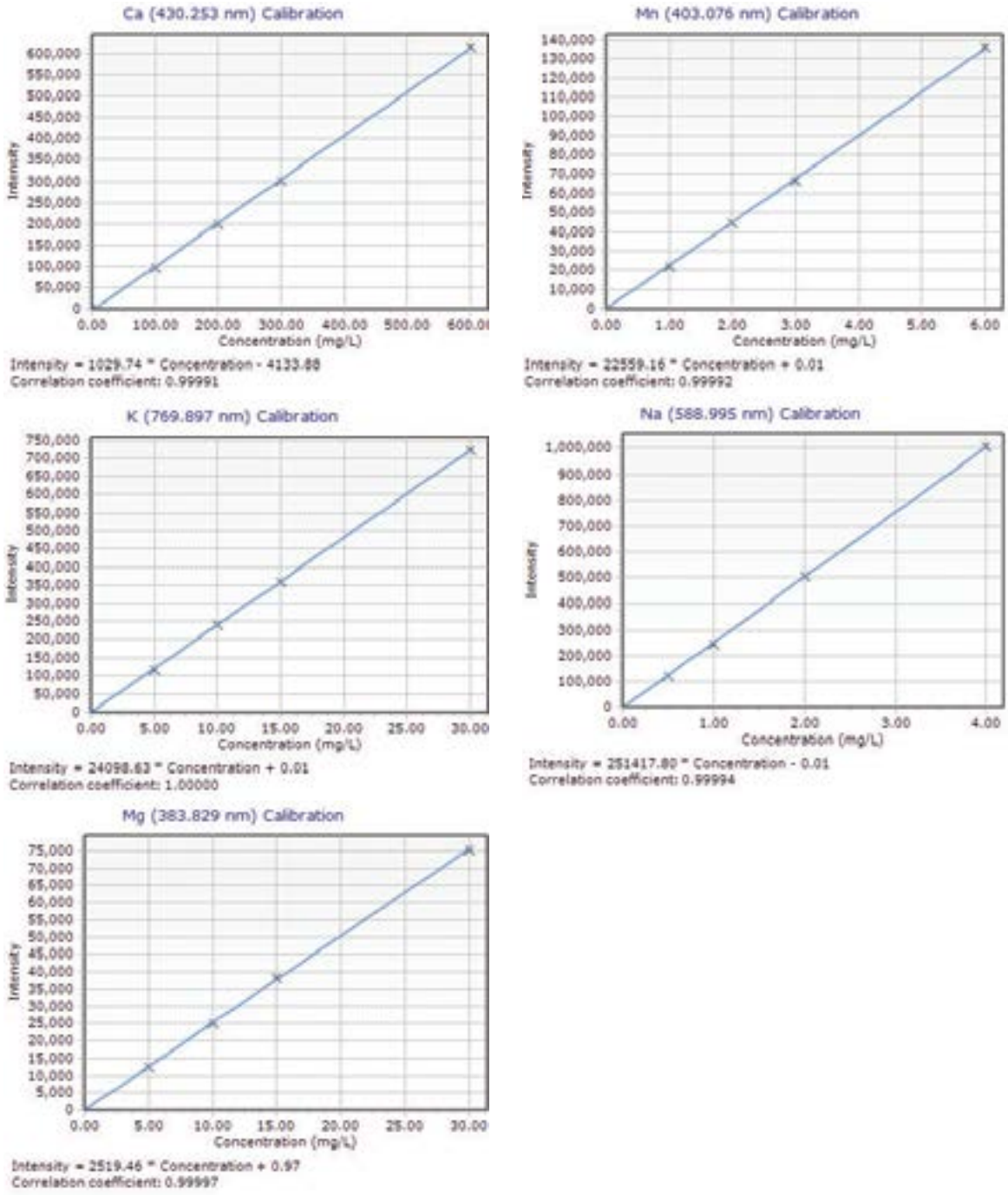

Figure 1. Typical MP-AES calibration curves for Ca, Mn, K, Na and Mg

Comparison of MP-AES with ICP-OES and/or FAAS
Figures 2 to 6 show for all cations an excellent agreement between the 4100 MP-AES results and those from other spectrometric techniques. The correlation of the analytical results between the different techniques was made and linear regressions are observed: coefficients of determination are $0.995 < R^2 < 0.999$ and the slopes are between 0.969 and 1.043 (Table 5).

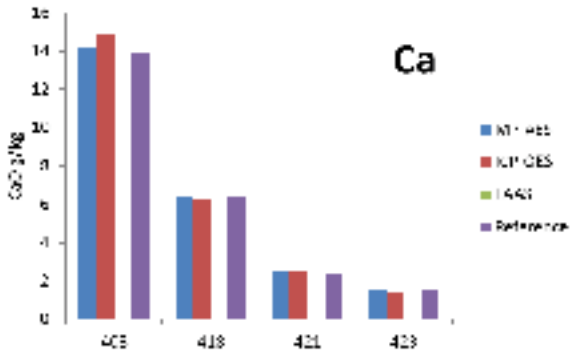

Figure 2. Reference results and Ca concentrations measured in soil extracts by MP-AES and ICP-OES (FAAS not determined)

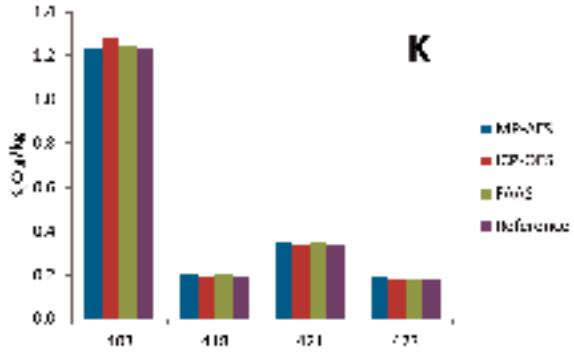

Figure 3. Reference results and K concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

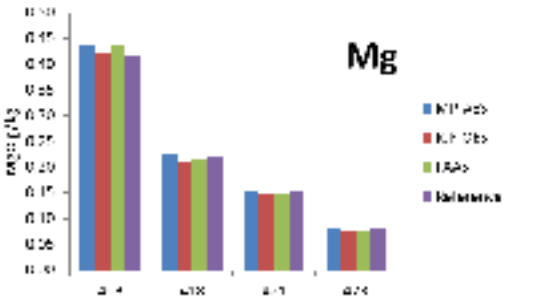

Figure 4. Reference results and Mg concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

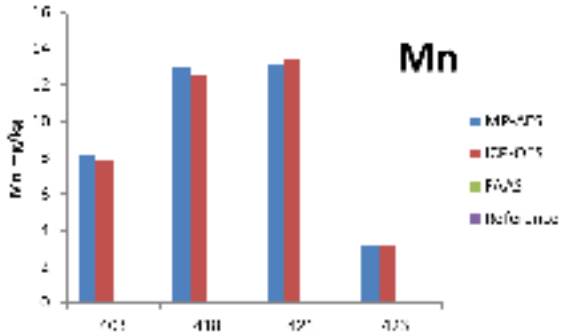

Figure 5. Mn concentrations measured in soil extracts by MP-AES and ICP-OES (FAAS not determined and no reference results available)

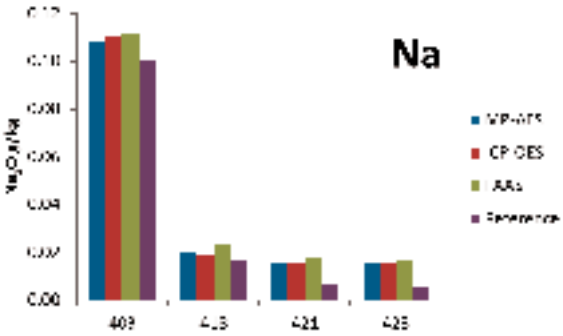

Figure 6. Reference results and Na concentrations measured in soil extracts by MP-AES, ICP-OES and FAAS

Bibliography

1. Matula, J. (2009). A relationship between multi-nutrient soil tests (Mehlich 3, ammonium acetate, and water extraction) and bioavailability of nutrients from soils for barley. *Plant Soil Environ., 55*(4), 173–180.

2. Kowalenko, C. G. (2004). Determining nutrients available in soils, in 'Advanced silage corn management book, a production guide for coastal British Columbia and the Pacific Northwest'. Ed. Bittman, S. & Kowalenko, C.G.

3. AFNOR - NF X 31-108 (2002). Soil quality — Determination of ammonium acetate extractable Ca++, Mg++, K+ and Na+ cations — Agitation method.

www.agilent.com/chem/4210mp-aes

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Geochemistry applications

Revolutionize the way you do your business. With no ongoing-gas requirements, you can locate the Agilent 4210 MP-AES where your samples are.

- The Agilent 4210 MP-AES expands your application range. With no flammable gases and no cylinder handling hazards, the Agilent 4210 MP-AES is ideal for remote field placement.
- Slash your operating costs — replacing your flame AA with the Agilent 4210 MP-AES can pay for itself in a matter of months, based on gas savings alone
- Improve your productivity — with no need for ongoing gas supply, remote sites and mobile laboratories will never again have to deal with the issue of sourcing gas, or having gas delivered to a remote location
- Accuracy even with difficult samples — vertical plasma torch provides excellent performance for tough samples with axial viewing for the best sensitivity
- The optional inert MP-AES torch enables direct measurement of metals in ore digests prepared using HF acid mixtures, eliminating the inefficient neutralization step
- The optional AVS 4 switching valve reduces sample load on sample introduction system, minimizing exposure to aggressive chemicals and harsh samples, further reducing costs by increasing life-time of consumables.

Rapid determination of gold in geological samples using the Agilent 4210 MP-AES

Application note

Metals, mining, geochemistry

Author

Kayla Coombs

Agilent Technologies
Australia

Introduction

The accurate and repeatable determination of gold in geological samples is vital for companies involved in precious metal production and the laboratories that support them. With large numbers of samples to be analyzed, the cost-per-sample and analysis times are also important considerations when selecting the most suitable analytical technique for the application.

Geological samples that contain precious metals are typically prepared using the fire assay process and analyzed using flame atomic absorption

spectrometry (FAAS) or inductively coupled plasma optical emission spectrometry (ICP-OES). FAAS requires acetylene and nitrous oxide gases which are expensive and can be difficult to source in remote mining locations. In contrast, microwave plasma atomic emission spectrometers, such as the Agilent 4210 MP-AES, use a nitrogen-based plasma that can be sustained using a nitrogen Dewar or nitrogen extracted from air using a nitrogen generator. Eliminating the need for costly and flammable gases ensures more cost efficient and safer analysis compared to FAAS. Furthermore, the hotter plasma excitation source (5000 K) of MP-AES expands the application range of the technique by providing higher matrix tolerance, wider linear dynamic range and lower detection limits than FAAS.

The 4210 MP-AES combines the intuitive MP Expert software, easy-fit torch, and a fully integrated Advanced Valve System (AVS 4) switching valve to simplify instrument setup, method development and analytical performance. These innovative features ensure that samples can be analyzed quickly and accurately, improving productivity and data quality, while keeping operating costs low.

This application note describes the analysis of gold in geological samples prepared by fire assay using an Agilent 4210 MP-AES fitted with an AVS 4 switching valve.

Experimental

Instrumentation

All measurements were performed using the Agilent 4210 MP-AES with a fully integrated AVS 4 four port switching valve and configured with an SPS 4 autosampler and humidifier accessory. The instrument was fitted with a 5 channel peristaltic pump to allow a modified pump tubing configuration for faster sample uptake. The sample introduction system consisted of a Meinhard nebulizer, single pass glass cyclonic spray chamber, and easy-fit torch. Once in place, no further realignment of the torch was required.

The AVS 4, shown in Figure 1, is fully integrated into the 4210 MP-AES instrument hardware and controlled through the MP Expert software for optimum timing and ease-of-use. The valve quickly switches between rinse and sample. This minimizes exposure of sample introduction components to high matrix samples, prolonging the lifetime of consumable items.

Figure 1. Agilent 4210 MP-AES with Agilent Advanced Valve System (AVS 4) four port switching valve

The operating parameters used for the 4210 MP-AES and AVS 4 switching valve are shown in Tables 1 and 2. Read time was decreased to 1 s for maximum sample throughput and the ideal nebulizer flow was easily determined using the Optimize Nebulizer Flow tool in the MP Expert software. All other method parameters used default settings.

To speed up sample delivery to the plasma, the flow rate of sample through the autosampler probe was increased based on the "rapid flow" concept—where the sample flow rate from the autosampler to the peristaltic pump is increased. To increase the sample flow rate, without overloading the nebulizer, an additional sample peristaltic pump tube was introduced to the system via a T-piece inserted between the end of the autosampler line and the start of the sample peristaltic pump tubing so that sample would flow through two sample perstaltic pump tubings instead of one. One of the peristaltic pump tubes was directed to the AVS 4 switching valve (to go to the nebulizer), and the other to waste, which avoided overloading the nebulizer with sample (Figure 2). By having sample flow through two pump tubings, the sample flow rate (through the autosampler probe up to the point where the T-piece was inserted) was increased, thus reducing sample uptake time by 40%.

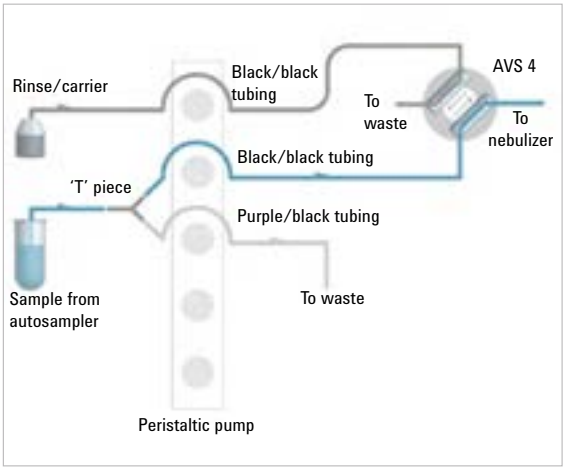

Figure 2. The "rapid flow" concept setup to increase the sample flow rate.

Table 1. Agilent 4210 MP-AES instrument and method parameters.

Parameter	Setting
Element	Au
Wavelength (nm)	267.595
Read time (s)	1
Replicates	3
Pump speed (rpm)	15
Fast pump during uptake and rinse (rpm)	80
Nebulizer flow (L/min)	0.85
Viewing position (mm)	0
Nebulizer	Meinhard
Spray chamber	Single pass glass cyclonic
Torch	Easy-fit torch
Sample pump tubing	Black/black (to AVS 4) Purple/black (to waste)
Carrier pump tubing	Black/black
Waste pump tubing	Blue/blue
Background correction	Auto

Table 2. Agilent AVS 4 settings.

Parameter	Setting
Uptake delay (s)	9
Switch delay (s)	7
Rinse time (s)	5
Stabilization time (s)	5

Samples and sample preparation

Six geological samples, two gold certified reference materials (CRMs) and a custom reference material (RM) were used in this study: SL76 and OxP116 (Rocklabs Reference Materials, New Zealand) and BP-13 (customer reference material—not commercially available). All samples and CRMs were prepared by a third party laboratory using a standard fire assay procedure. Ultrapure de-ionized water (18 MΩ resistivity, Millipore) and analytical grade hydrochloric acid (37% m/v, fuming) and nitric acid (69% m/v) were used for the preparation of all CRMs and samples. The final acid concentration of all solutions was 30% aqua regia.

Calibration standards of 2.5, 5, 10, 20, 50 and 100 mg/L were prepared from a 1000 mg/L Au single element standard. Standards were also prepared in 30% (v/v) aqua regia.

Calibration linearity

Au 267.595 nm was calibrated from 1 ppm up to 100 ppm for this method, with a correlation coefficient of greater than 0.999. This wide linear dynamic range allowed accurate determination of Au in geological samples from 1 ppm to over 60 ppm without the need for time consuming dilution and re-analysis of samples.

Results and discussion

Method detection limits

The procedure for determining the method detection limit (MDL) was based upon 40 CFR 136 Appendix B [1]. MDLs were calculated as three times the average standard deviation of ten replicate readings of a 150 µg/L solution measured after calibration with a 150 µg/L standard. The MDL was determined three times on two different instruments to give a total of six runs. The average of these six MDL measurements is given in Table 3.

Table 3. Agilent 4210 MP-AES method detection limit for Au 267.595 nm.

Element and wavelength (nm)	Average MDL (µg/L), n = 6
Au 267.595	7.2

Reference Material recoveries
To validate the method, various samples and CRMs were analyzed in triplicate using the 4210 MP-AES. The average Au value is presented in Table 4, with comparative results from FAAS analysis and certified values (in solution) for the three CRMs. There was no significant difference between the results obtained using FAAS and MP-AES, and the CRM recoveries were within ±10% of the certified value.

Using the AVS 4 switching valve, and modified pump tubing setup, the method was optimized to give a sample-to-sample analysis time of less than 30 seconds.

Long term stability
Three fire assay samples and one CRM were measured continuously for 3 hours without re-slope or recalibration to demonstrate the long term stability of the 4210 MP-AES.

Figure 4 shows the stability plot of the samples and CRM which were measured every 10 samples. All samples demonstrated excellent long term precision with a %RSD of less than 2% over the 3-hour analysis period (Table 5). This demonstrates the exceptional reliability and stability of the 4210 MP-AES with the AVS 4 switching valve for this analysis.

As the AVS 4 directs sample away from the sample introduction system during uptake and rinse, exposure to the matrix present in the samples is minimized resulting in increased lifetime of consumables, such as the nebulizer, spray chamber and torch. This means more high-matrix samples, such as these geological digests, can be analyzed before consumables need to be replaced, which decreases ongoing instrument running costs.

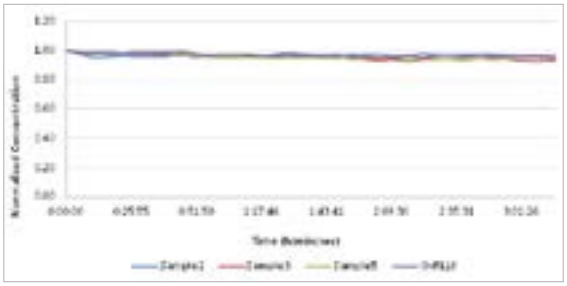

Figure 4. Normalized concentration of Au in geological samples measured over 3 hours.

Table 4. Comparative Au recovery results for samples and CRMs in solution obtained using MP-AES and FAAS.

Sample/Reference Material	Gold Certified Value (mg/L)	FAAS Measured Value (mg/L)	FAAS Recovery (%)	MP-AES Measured Value (mg/L)	MP-AES Recovery (%)	Difference between FAAS & MP-AES results (%)
Sample 1	-	4.180	-	4.495	-	8%
Sample 2	-	1.089	-	1.157	-	6%
Sample 3	-	17.19	-	17.87	-	4%
Sample 4	-	62.80	-	62.76	-	0%
Sample 5	-	28.18	-	28.90	-	3%
Sample 6	-	1.663	-	1.786	-	7%
SL76	17.88	18.33	103	18.52	104	1%
BP-13	1.074	1.089	101	1.156	108	6%
OxP116	44.85	44.99	100	44.95	100	0%

Table 5. Long term stability %RSD results for Au in four geological samples.

Solution	Average Concentration (mg/L)	%RSD over 3 hours
Sample 2	1.171	0.9
Sample 3	17.21	1.9
Sample 5	28.27	1.8
OxP116	44.53	1.3

Conclusions

The Agilent 4210 MP-AES is a high performance, safe and cost effective alternative to FAAS for the analysis of Au in geochemical samples. In this study, the easy-to-use AVS 4 switching valve system minimized the exposure of the sample introduction components to high matrix fire assay samples, offering further long term cost savings for labs conducting routine geochemical analysis.

The 4210 MP-AES with AVS 4 switching valve showed:

- Rapid analysis capabilities with a sample-to-sample analysis time of less than 30 seconds.
- An impressive linear dynamic range allowing the determination of Au over a wide concentration range without the need for time consuming dilutions.
- High analytical performance with a method detection limit of 7.2 ppb and CRM recoveries within ± 10% of certified values.
- Measured concentrations were within 10% of those determined with FAAS for all samples and CRMs analyzed.
- Excellent long term stability with %RSD values for four different samples below 2% over three hours.

References

1. US Environmental Protection Agency, 40 CFR Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11, July 2011, https://www.gpo.gov/fdsys/granule/CFR-2011-title40-vol23/CFR-2011-title40-vol23-part136-appB/content-detail.html

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Agilent Technologies

Direct determination of Al, B, Co, Cr, Mo, Ti, V and Zr in HF acid-digested nickel alloy using the Agilent 4210 Microwave Plasma-Atomic Emission Spectrometer

Application note

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Introduction

Nickel alloys are used when good high- and low-temperature strength and corrosion resistance are needed. Typical industrial applications are for fabrication of chemical and petrochemical process vessels and gas turbine parts. The aerospace and military industries are also important users of nickel based alloys, which are frequently used in the manufacture of jet engine parts including turbine blades. The additive elements in the nickel alloy and their concentrations are carefully selected in order to obtain the desired material properties. For example, titanium (Ti) is added to improve corrosion resistance and increase the strength-to-density ratio of the alloy.

It is also known that low concentrations of boron (B) and zirconium (Zr) improve material hardness [1, 2]. A slight change in composition can adversely affect the properties of the alloy. Therefore, accurate elemental analysis of nickel alloys is extremely important from the metallurgical and engineering point of view.

Elemental analysis of nickel alloys can be performed using non-destructive techniques such as X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) or arc spark emission spectrometry. However, some of these techniques are limited to analysis of only the exposed surface of the material. In order to analyze the total content in the bulk material, the whole sample must be dissolved (digested) in an acid mix and the resulting digest can then be analyzed using a suitable spectroscopic method such as ICP-OES and more recently MP-AES. In this study, a method to determine the concentrations of Al, B, Co, Cr, Mo, Ti, V and Zr in a nickel alloy using the Agilent 4210 MP-AES, is presented.

Figure 1. Easy-fit inert torch for 4200/4210 MP-AES

Hydrofluoric (HF) acid must be employed during sample preparation to ensure complete dissolution of alloys containing elements such as Ti, Zr, Hf, Nb, Ta, Mo, W, Ge, Sn or Sb. Sample digests prepared in HF cannot be analyzed directly using standard glass and quartz sample introduction systems as the free HF attacks and degrades the glass and quartz components. To prevent degradation, the residual HF needs to be neutralized by adding boric acid (H_3BO_3), prior to analysis. This neutralization process adds another sample preparation step, reducing laboratory efficiency and introducing a potential source of contamination. This preparation process is also not suitable if boron is one of the analytes of interest, as in this particular case.

Therefore, laboratories performing this type of analysis prefer to use an inert sample introduction system, to allow direct analysis of the HF digests without needing a pre-analysis neutralization step [3]. For this application the inert torch for the 4200/4210 series MP-AES was used in conjunction with an inert double-pass spray chamber and the inert OneNeb Series 2 nebulizer, to facilitate the direct analysis of HF digests without prior neutralization.

Experimental

Instrumentation

The 4210 MP-AES is a fast sequential, emission based multi-element analytical technique that uses a microwave-induced plasma for sample excitation. The MP-AES technique utilizes a nitrogen based plasma. This eliminates the need for expensive and hazardous gases such as acetylene, increasing safety, and enabling unattended operation of the instrument, even in remote locations. Nitrogen can be supplied from bottled gas, a Dewar or the Agilent 4107 Nitrogen Generator (with air supplied from an air compressor). For this application, Dewar nitrogen was used to run the MP-AES.

The sample introduction system used featured inert components including an inert double pass spray chamber, the inert MP-AES torch (Figure 1) and the inert OneNeb Series 2 nebulizer. The Agilent nebulizer gas humidifier accessory was fitted to improve long term stability and reduce deposition in the nebulizer from Total Dissolved Solids (TDS) in the digest.

The instrument was controlled by the powerful and easy-to-use MP Expert software. The MP-AES features continuous wavelength coverage that allows the selection of wavelengths that are appropriate for the concentration range required for the analysis and which are relatively free of interferences. Table 1 lists instrument operating conditions used in the method.

Table 1. Agilent 4210 MP-AES operating conditions.

Instrument parameter	Setting
Torch	Easy fit inert torch with alumina injector
Nebulizer	OneNeb Series 2 inert nebulizer
Nebulizer flow	Individually optimized for each element, see Table 5
Nebulizer gas humidifier	Fitted
Spray chamber	Inert double-pass spray chamber
Sample & internal std tubing	Orange/green Solvaflex
Waste tubing	Blue/blue Solvaflex
Pump speed (rpm)	15
Number of replicates	3
Analytes	Al, B, Co, Cr, Mo, Ti, V, Zr (Lu as internal Std)
Read time (s)	B: 5, Lu: 3, Zr: 10, Al, Co, Cr, Mo, Ti & V: 1
Stabilization time (s)	15
Uptake time (s)	30 (fast pump)
Rinse time (s)	75 (fast pump)

Standard Reference Material

A certified reference material (IN 100 alloy–cast; (BCS/SS-CRM No. 345)) from the Bureau of Analysed Samples Ltd was analyzed to validate the method presented in this study. IN 100 alloy is a nickel based alloy that provides high rupture strength at high temperatures. IN 100 alloy has a high concentration of Al and Ti which makes this material particularly attractive on a strength to density basis. The alloy has been successfully utilized in a variety of shapes from turbine blades, vanes and nozzles to integral wheels [4]. Table 2 highlights the certified concentrations of the IN 100 alloy. The IN 100 nickel alloy was sourced from Graham B. Jackson. (Aust) Ltd. and used on an as-received basis.

Table 2. Certified concentrations for the IN 100 nickel based alloy CRM used in this study

IN 100 alloy (BCS/SS-CRM No. 345) Certified concentrations in weight %			
Al	5.58 ± 0.07	Mo	3.01 ± 0.06
B	0.019 ± 0.003	Ti	4.74 ± 0.06
Co	14.71 ± 0.07	V	1.00 ± 0.04
Cr	9.95 ± 0.08	Zr	0.044 ± 0.001

Preparation of calibration standards and samples

The sample preparation procedure used a HNO_3-HCl-HF digestion based on a nominal sample weight of approximately 0.15 g. The sample was accurately weighed and placed directly into the inert (PTFE) reaction vial. 3 mL of nitric acid 69% (Merck) and 9 mL of hydrochloric acid 37% (Merck) were added to the vial and thoroughly mixed. Subsequently, 2 mL of hydrofluoric acid 48% (Merck) were added in two portions. The samples were digested using the Milestone UltraWave Single Reaction Chamber (SRC) microwave digestion system which serves both as a microwave cavity and reaction vessel, that assures high temperature capabilities. Sealing of the vials was not required since the Single Reaction Chamber was pressurized using a nitrogen gas pressure of 45 bar. The digests were made up to a volume of 40 mL using 18 MΩ de-ionized water. Samples were prepared, at least, in triplicate. The temperature program used for the microwave digestion process is shown in Table 3.

Table 3. Parameters used for microwave digestion (where t is the time and T1 and T2 are the programmed initial and final vessel temperatures)

Step	t (min)	T1 (°C)	T2 (°C)	Power (W)
1	25	Ambient	250	1500
2	25	250	250	1500

Calibration standards were prepared from Agilent aqueous single element certified reference materials. In order to match the acid matrix of the digests, all calibration standards were diluted with a solution containing 20% aqua regia / 5% HF in 18 MΩ de-ionized water. The calibration range was determined based on the expected concentration of the elements in the completed digest of the IN 100 nickel alloy used. The calibration standards and the concentrations used are shown in Table 4.

Table 4. Calibration standards used in this study.

Solution	Analyte and Standard Concentrations (mg/L)							
	Al	B	Co	Cr	Mo	Ti	V	Zr
Calibration Blank	0	0	0	0	0	0	0	0
Standard 1	24		48	40		20	6	0.8
Standard 2	72		144	120		60	18	2.4
Standard 3	144		288	240		120	36	4.8
Standard 4	288		576	480		240	72	9.6
Standard 5					50			
Standard 6					100			
Standard 7					200			
Standard 8		1.5						
Standard 9		2.5						
Standard 10		5						
Standard 11		8						

Wavelength selection, background and interference correction

Table 5 lists the emission lines selected for analysis, together with the background and interference correction methods used. The selected wavelengths provide minimal spectral interferences, and wide dynamic range, eliminating time-consuming sample dilutions and re-analysis.

An internal standard (Istd) solution of 50 mg/L lutetium solution in 2% HNO_3 was used. The internal standard was delivered on-line using a Y-connector to combine this solution with the sample prior to nebulization.

When analyzing metal alloys, there can be a wide range of elements present at varying concentrations from hundreds of ppm to % levels, which can result in numerous spectral interferences. The MP Expert software has an extensive wavelength database that helps the analyst to choose the best analytical wavelengths, based on intensity and the potential for spectral interferences. When interferences are present and there are no other lines that either provide the required sensitivity or are free of interferences, Agilent's Fast Linear Interference Correction (FLIC) [5], can be used to apply correction.

FLIC can be used when multiple, partly overlapping spectral components are present in the spectral window, or if there is only a single component present. FLIC also provides the flexibility to correct for structured background. FLIC models are constructed using pure solutions for the blank, element of interest and the expected interfering element(s) within the sample. This modeling provides accurate and automatic correction for interferences identified in your sample spectra.

In this study, FLIC proved effective for resolving interferences encountered in the reference material analyzed. The blank, analyte and interferent solutions used to develop the FLIC models are displayed in Table 6.

Table 5. Line selection, nebulizer flow, background and interference correction methods for each element

Element	Wavelength (nm)	Nebulizer Flow (L/min)	Background/Interference Correction	Interferent(s)	Calibration fit	Calibration Correlation coefficient
Al	394.401	0.35	Auto		Linear	0.999
B	249.772	0.45	FLIC + IStd	Ni	Rational	0.997
Co	344.917	0.35	Auto		Linear	0.999
Cr	435.177	0.45	FLIC+ IStd	V	Linear	0.999
Mo	553.305	0.45	Auto		Linear	0.999
Ti	453.324	0.35	Auto		Linear	0.999
V	327.612	0.80	Auto+ IStd		Linear	0.999
Zr	383.676	0.40	FLIC + IStd	Ti, V, Ni	Linear	0.999
Lu	261.542	0.45	Auto	Used as Internal Standard		

Table 6. FLIC sequence matrix listing the solutions used to develop the FLIC models (interferent solution concentration in mg/L shown in parentheses)

Element & wavelength (nm)	Blank solution	Analyte solution	Interferent solution 1	Interferent solution 2
B 249.772	Calibration Blank	B (10)	Ni (10000)	
Cr 435.177	Calibration Blank	Cr (1000)	V (1000)	
Zr 383.676	Calibration Blank	Zr (100)	Ti (1000)	V (1000)

The determination of chromium in the IN 100 alloy CRM provides a good example of how FLIC modelling enables the user to remove interferences when determining challenging samples where interferences are present. The chromium concentration in the IN 100 alloy is high. For that reason, the Cr 435.177 nm wavelength was selected for analysis as it is a fairly insensitive line and almost free of interferences, except for the nearby V(I) signal at 435.287 nm. Figure 2 shows the signal for Cr 435.177 nm (red trace) with the interfering element (V) modeled using FLIC (green trace) enabling the user to determine Cr in the sample directly.

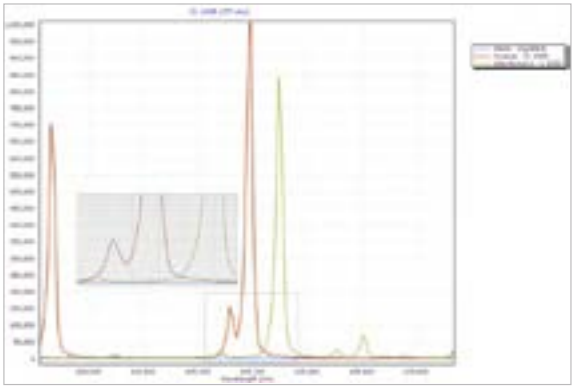

Figure 2. Spectral interferences for Cr at the 435.177 nm wavelength, resolved using FLIC

Results and discussion

Method Detection Limits

Method Detection Limits (MDLs) were determined by running the digested acid blank 10 times under the method conditions after calibration. The MDL is defined as 3 times the standard deviation (S) of the concentration readings for each element. The Limit of Quantification (LOQ) for this analysis was estimated as 10 times the standard deviation of the concentration readings, multiplied by the average dilution factor used during sample preparation (267x).

Table 7. Method detection limits and estimated limit of quantification

	Element and Wavelength (nm)							
	Al 394.401	B 249.772	Co 344.917	Cr 435.177	Mo 553.305	T 453.324	V 327.612	Zr 383.676
MDL in solution (mg/L)	0.007	0.003	0.10	0.02	0.03	0.03	0.03	0.004
LOQ in the solid sample (mg/kg)	6.2	2.8	89	20	24	26	23	3.5

Long term stability

To check instrument stability during a long term measurement, the digested IN 100 nickel alloy sample was analyzed every 4 minutes over 8 hours of continuous measurement. A periodic calibration reslope, which included the blank and one standard (Standard 3), was performed every 3 hours. Excellent long term stability was achieved over 8 hours of operation with all elements in the method having average recoveries within ±10% of certified values (Figure 3) with a long term measurement precision of less than 5% RSD (Table 8).

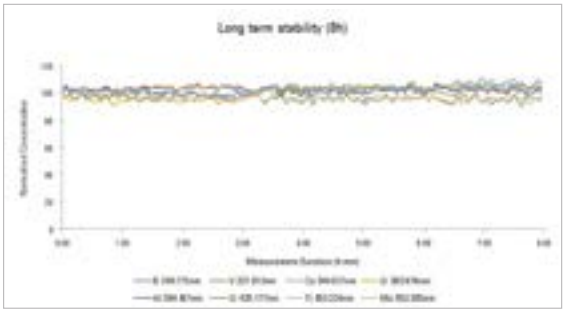

Figure 3. Long term stability for continuous measurement of the IN 100 nickel alloy CRM over 8 hours

Recoveries for the IN 100 nickel alloy CRM

The recoveries for all elements determined in the IN 100 nickel alloy CRM were within ± 10% of the certified values, highlighting the suitability of this method for determining nickel based alloys (Table 9). These results are the average of three separate sets of digestions, made at least in triplicate, analyzed twice. The results also demonstrate the wide dynamic range capability of the Agilent 4210 MP-AES, as elements were determined over a wide concentration range from ppm to % level in a single reading, without dilution.

Recoveries for the IN 100 nickel alloy CRM without HF

HF acid is needed in the digestion process to ensure complete dissolution and good recovery for Ti, Mo and Zr in the IN 100 nickel alloy CRM. To demonstrate the effectiveness of HF in achieving complete digestion, two IN 100 nickel alloy CRM samples were digested using only HCl-HNO_3 and analyzed. The recoveries for the elements analyzed were compared against those obtained with HF present in the acid mix. As expected, the recoveries were quite poor for Mo, Ti and Zr when using only an aqua-regia digest (Figure 4).

Table 8. Long-term precision for 8 hours continuous measurement of the IN 100 nickel alloy CRM.

Element & wavelength (nm)	Al 394.401 nm	B 249.772 nm	Co 344.917 nm	Cr 435.117 nm	Mo 553.305 nm	Ti 453.324 nm	V 327.612 nm	Zr 383.676 nm
Precision (%RSD)	2.1	1.3	3.1	2.2	2.1	3.0	1.7	4.5

Table 9. Recoveries and calculated uncertainties for elements determined in the IN 100 nickel alloy CRM

Element and wavelength (nm)	**Certified Concentration (weight %)**	**Certified Uncertainty * (weight %)**	**Measured Concentration (weight %)**	**Calculated Uncertainty* n=22 (weight %)**	**Recovery (%)**
Al 394.401 nm	5.58	0.07	5.33	0.12	95.4
B 249.772 nm	0.019	0.003	0.020	0.0003	105.4
Co 344.917 nm	14.71	0.07	15.52	0.20	105.5
Cr 435.177 nm	9.95	0.08	10.68	0.14	107.4
Mo 553.305 nm	3.01	0.06	3.01	0.05	100.0
Ti 453.324 nm	4.74	0.06	4.55	0.08	96.0
V 327.612 nm	1.00	0.04	0.95	0.01	95.0
Zr 383.676 nm	0.044	0.001	0.041	0.001	93.1

* This value represents the half width confidence interval C(95%), which is calculated as t x S_m / √(n), where "t" is the appropriate two sided Student's t value at the 95% confidence level, and S_m is the standard deviation (of the intralaboratory means for the CRM, or the replicate readings for the IN 100 alloy sample determinations).

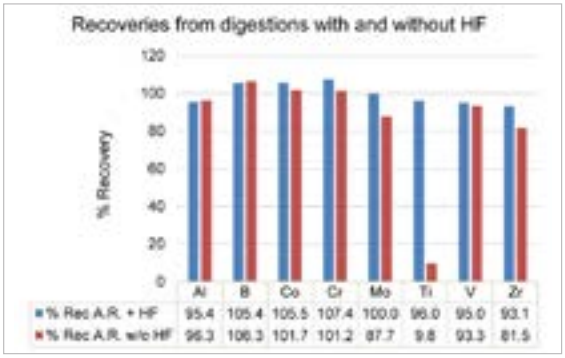

Figure 4. Recoveries for selected elements in the IN 100 nickel alloy CRM, comparing digests prepared with aqua-regia only (red) and using HF + aqua-regia (blue).

Conclusions

The results from analysis of the IN 100 nickel alloy CRM demonstrate that the Agilent 4210 MP-AES is an excellent technique for the analysis of challenging metallurgical samples. The wide dynamic range capability was demonstrated as elements were determined over a wide concentration range from hundreds of ppm to % level in the same sample, without any pre-analysis dilution, in a single reading with excellent recoveries. Good long term stability was also demonstrated for continuous measurement of the IN 100 nickel alloy CRM over a period of 8 hours. FLIC was able to successfully model the complex interferent signals and apply correction, ensuring good results for all elements with excellent recoveries across a concentration range of three orders of magnitude.

References

1. R.F. Decker and J.W. Freeman, Mechanism of beneficial effects of boron and zirconium on creep-rupture properties of a complex heat resistant alloy, 1958, National Advisory Committee for Aeronautic Technical Note 4286, (Accessed online July 2016 at: http://naca.central.cranfield.ac.uk/reports/1958/naca-tn-4286.pdf)

2. P. Kontis et al, On the effect of boron on grain boundary character in a new polycrystalline superalloy, *Acta Materialia,* 2016 ,103, pp. 688–699

3. D. McDonald and A. Amorin, Direct determination of Cu, Fe, Mn, P, Pb and Ti in HF acid-digested soils using the Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer, Agilent publication, 2015, 5991-5991EN.

4. Engineering Properties of IN-100 Alloy, Nickel Institute (Accessed online July 2016 at: https://www.nickelinstitute.org/en/TechnicalLiterature/INCO%20Series/0483_IN_100_Alloy_EngineeringProperties.aspx).

5. Agilent MP Expert Software, Agilent Publication, 2011, 5990-8975EN.

www.agilent.com/chem/4210mp-aes

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Determination of major and minor elements in geological samples using the 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES)

Application note

Mining, geochemistry, and metals

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Introduction

The development of atomic spectrometric methodologies for geochemical sample analysis presents many challenges to commercial laboratories. The range of concentrations in geochemical analysis varies from major elements that are present at percent levels, to trace elements that are present at sub-ppm levels. For example, Cu can be present at percent levels for target drillings, ppm levels in explorations and sub-ppm levels in selective leaches. In addition to the wide working range required for the analysis, high levels of total dissolved solids, spectral interferences due to emission line overlaps and non-spectral interferences due to easily ionizable elements (EIE) present challenges even to the experienced analytical chemist. Flame Atomic Absorption Spectrometry (FAAS) has long been the instrument of choice

for geochemical analysis but with current trends in the market for lower detection limits, lower cost of analysis, improved ease of use and improved safety, the Agilent 4200 MP-AES is the ideal replacement for FAAS.

With the introduction of the 4200 MP-AES, the application range of the MP-AES has expanded to include challenging geochemical samples. The second generation 4200 MP-AES features an advanced microwave cavity and a torch designed to handle samples with high dissolved solids with better detection limits and increased working range than FAAS. The MP-AES runs off nitrogen, eliminating expensive and hazardous gases such as acetylene, increasing safety, and allowing for unattended operation of the instrument, even in remote locations.

The simplicity of the instrumentation and the user friendly MP Expert software facilitates easy instrument setup and method development with minimal training, even for novice laboratory technicians. This application note presents the base metals (Ag, Cu, Ni, Pb and Zn) results for geochemical certified reference materials analyzed by the 4200 MP-AES.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES. Dewar nitrogen was used to run the MP-AES. Nitrogen can be supplied using either bottled gas or an Agilent 4107 Nitrogen Generator. The nitrogen generator alleviates the difficulties in sourcing gases in remote locations or in metropolitan areas where supply of analytical grade gases is difficult. A multi-purpose sample introduction system configuration was used with an inert OneNeb nebulizer and a double pass glass cyclonic spray chamber, orange/green pump tubing and a pump speed of 10 rpm. This setup provided a well-controlled matrix loading to the plasma without sacrificing detection limits. The nebulizer gas flow is mass flow controlled, providing short and long-term sample nebulization stability during the high total dissolved solid sample analysis. The instrument operates in a fast sequential mode and with the peltier cooled CCD detector, background and spectral interferences can be simultaneously corrected easily and accurately using MP Expert software. The method parameters are given in Table 1.

Table 1. Method parameters used in the analysis

Parameter	Value
Nebulizer	OneNeb
Nebulizer flow rate	0.4 L/min
Spay chamber	Double pass glass cyclonic
Pump rate	10 rpm
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue
Internal standard pump tubing	Orange/green
Autosampler	Agilent SPS 3
Read time	5 seconds for Ag, 3 seconds for all others
Number of replicates	3
Fast pump during uptake	On
Sample uptake delay	30 seconds
Rinse time	120 seconds
Stabilization time	20 seconds
Background correction	Auto
Gas source	Dewar N_2

Geochemistry Applications

Sample and calibration standard preparation
Two reference materials (GeoStats Pty Ltd) were analyzed to validate the method: GBM398-4 Low grade Cu/Pb/Zn with Laterite; and GBM908-14 Cu-Zn-Pb Sulphide Ore. The sample preparation procedure was a HNO_3-HCl-$HClO_4$-HF four-acid digestion with 0.4g of nominal sample weight. The mixture was taken to near dryness and after cooling, the digest was brought to a 100 mL final volume with 30% HCl solution. This represents a 250x nominal sample dilution. This four-acid digestion procedure provides near total digestion of samples for the analysis.

All calibration standards solutions were prepared in 6% HNO_3 and 19% HCl.

Wavelength selection and background correction
Table 2 gives the emission line selection, background and interference correction methods used. The selected wavelengths provide minimal spectral interferences, and wide dynamic range, eliminating time-consuming sample dilutions and reanalysis. An internal standard solution of 10 mg/L lutetium was delivered using orange/green tubing and a Y-connector was used to connect the sample tubing. Lutetium was selected as the internal standard element because it is rarely present in geochemical samples. The acceptance criteria for the calibration curve was a correlation coefficient greater than 0.999, and less than 10% calibration fit error on each standard. A linear curve fit was used for all wavelengths.

Spectral interference corrections
Geological samples can contain a wide range of elements at varying concentrations which can result in spectral interferences. The 4200 MP-AES has continuous wavelength coverage across the available wavelength range and the MP Expert software contains an extensive wavelength database that helps to choose analytical wavelengths and identify possible interferences. A combination of Agilent Fast Linear Interference Correction (FLIC) and conventional inter-element corrections (IECs) were used for the samples analyzed in this matrix. FLIC is an advanced and easy to implement background correction method that corrects for spectral interferences as well.

Multiple line interferences on Ag 328.068 nm were corrected by using conventional inter-element correction (IEC). The IEC factors were developed using easy to use steps built into the MP Expert software. This involved using a 1 mg/L single element silver standard, and 100 and 1000 ppm single element interferent standards to generate the IEC factors. The concentration of interferent standards were selected to reflect the concentration of interferents in the samples.

Table 2. Analyte line selection, background, and interference correction methods

Element	Wavelength (nm)	Type	Background Correction	Interference Correction	Possible Interferences
Ni	305.082	Analyte	Auto		La
Ag	328.068	Analyte	Auto	IEC	Cu, Ti
Ti	334.940	IEC	Auto		
Pb	405.781	Analyte	Auto		La, Ti
Zn	481.053	Analyte		FLIC	La, Sr, and Ti
Cu	510.554	Analyte		FLIC	Al_2O_3 and La
Lu	547.669	IS		FLIC	Ni, Ti

FLIC models were used for Zn, Cu and Lu to correct spectral interferences from Al, Ti, La and Sr. For example, if aluminium is present in samples at percent levels, an aluminium oxide emission can interfere with the Cu 510.554 nm line. Creating a FLIC model with a high concentration aluminium interference model will correct for the spectral contribution to the Cu 510.554 nm line. Figure 2 depicts Ni and Ti interference on Lu as corrected by FLIC.

Table 3 gives the FLIC sequence matrix for running the blank and single element analyte and interferent standards.

If samples contain other elements that create spectral interferences on analyte lines, more IEC corrections can be generated, or further FLIC models can easily be created in MP Expert.

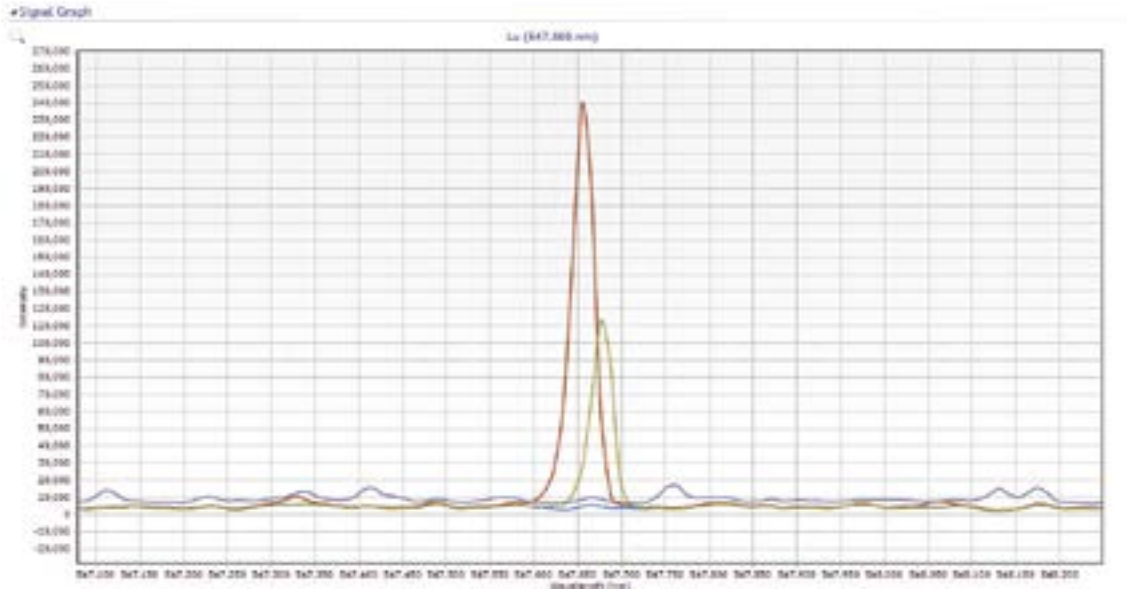


Figure 2. Ni and Ti interference on the Lu 547.669 nm line using FLIC with the blank (blue), Lu (red), Ni (green), and Ti (dark blue)

Table 3. FLIC sequence

Anayte (nm)	Blank	Analyte mg/L	Interferent 1 Al mg/L	Interferent 2 Ti mg/L	Interferent 3 La mg/L	Interferent 4 Sr mg/L	Interferent 5 Ni mg/L
Zn (481.053)	Cal Blank	10	x	100	100	100	x
Cu (510.554)	Cal Blank	10	1000	x	100	x	x
Lu (547.669)	Cal Blank	10	x	100	x	x	100

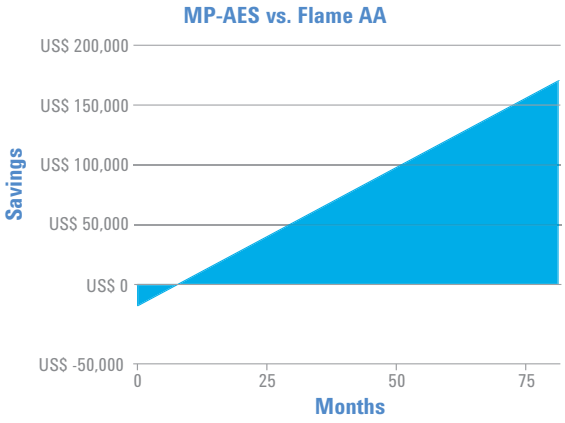
Results and Discussion

Results obtained on the MP-AES for the two reference materials are given in Table 4. Method detection limits (MDLs) were determined by analyzing 10 replicates of acid digested method blank under method conditions. The MP-AES results are within ±10% of certified concentrations (see Table 4).

The results show that the MP-AES is capable of measuring silver at low levels by using IEC to correct for spectral interferences. Elements such as Cu and Zn show excellent recoveries across a wide concentration range (0.39% to 2.37% for Cu, and 0.51% to 4.27% for Zn) demonstrating the capability of the MP-AES to measure samples over a wide dynamic range.

Cost savings with the 4200 MP-AES

The potential cost saving of using the 4200 MP-AES for this application was estimated by comparing an FAAS purchased with an air compressor and 1 year of consumables to an MP-AES purchased with air compressor, SPS 3, and 1 year of consumables. The analysis requirements were assumed to be 350 samples per week and 5 elements per sample. The calculation assumes that the FAAS is run without an autosampler and that all elements are analyzed with air/acetylene. In this example the results show an estimated cost saving over US $150,000 over a 7 year evaluation period. A global average gas cost was used in this calculation and results will vary from country to country.



This example is intended to help you compare the running costs and savings of the MP-AES vs. flame AA. The applied formulas and parameters are correct to the best of our knowledge, but we cannot guarantee the results. Savings may vary depending on factors such as local gas and electricity costs, operator costs, number and types of elements. For this calculation operator labor costs were set to US$25/hour and electricity costs were set to US$0.18 per kW.

Table 4. MDL and recoveries for reference materials determined by the 4200 MP-AES. All results shown for the solid sample.

			GBM398-4			GBM908-14		
Analyte	**Units**	**MDL**	**MP-AES**	**Certified**	**Recovery (%)**	**MP-AES**	**Certified**	**Recovery (%)**
Ag	mg/kg	1	45.8	48.7	94	298.7	303.7	98
Cu	wt %	0.002	0.37	0.39	95	2.30	2.37	97
Ni	wt %	0.002	0.39	0.41	97	-	nr	-
Pb	wt %	0.002	1.08	1.17	92	3.24	3.30	98
Zn	wt %	0.002	0.50	0.51	98	4.24	4.27	99

nr = not reported

Conclusion

The results of the analysis of geochemical reference materials obtained using the Agilent 4200 MP-AES indicate that MP-AES is an excellent technique for challenging geochemical sample analysis. The next generation waveguide and torch create a plasma that is capable of determining elements at ppm levels to percent levels in the sample. The continuous wavelength range and extensive wavelength database allow wavelengths to be selected that minimize spectral interferences and maximize the working range. In addition, spectral interferences were successfully corrected with the use of IECs and FLIC models.

By eliminating hazardous gases such as acetylene, the MP-AES greatly improves laboratory safety and provides significant reductions in running costs. The elimination of expensive hazardous gases also means that the MP-AES can run unattended and in remote locations.

www.agilent.com/chem/4210mp-aes

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New methodology for determination of gold and precious metals using the Agilent 4100 MP-AES

Application note

Geochemistry, metals and mining

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Introduction

The accurate and precise determination of gold and other precious metals (PMs) is a vital task for companies involved in PM production and the contract or service laboratories that support them. This might involve the processing of hundreds of samples typical of exploration and mining activities, or supplying the quality control assay of the final product from PM producers or recyclers. PMs are also produced as a by-product of copper or nickel processing.

Today's analysts have access to a range of elemental analytical techniques including flame and graphite furnace atomic absorption spectroscopy (AA), inductively coupled plasma optical emission spectroscopy (ICP-OES) and ICP mass spectroscopy (ICP-MS). The choice of method will depend on a number of factors, for example, the technology that is available, the skill of the operator, sample type, cost of analysis, sample throughput requirements and the objective of the analytical result.

Agilent has identified an increased need for multi-element determinations over a wide dynamic range at an attractive overall cost of analysis, taking into account instrument supplies, consumables, power and labor, and has developed a new instrument to meet this need.

The Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) (Figure 1) is a low-cost, highly automated technique that is suitable for the trace analysis of PMs in samples typically found in mining and exploration activities. As MP-AES relies on the generation of a microwave plasma using nitrogen, no flammable gases such as acetylene are required. This reduces running costs and improves lab safety. Nitrogen can be supplied from bottled gas or the Agilent 4107 Nitrogen Generator. This alleviates the difficulty and costs in sourcing gases such as acetylene, especially in remote locations.

Figure 1. Agilent 4100 MP-AES

This application note describes the analysis of PM samples prepared by fire assay using the Agilent 4100 MP-AES.

Experimental

Instrumentation

The Agilent 4100 MP-AES is a fast sequential multi-element analytical technique that has a microwave-induced nitrogen plasma at its heart. As a result running costs are significantly reduced as only nitrogen is required for plasma operation.

The 4100 MP-AES uses Agilent's unique Microwave Excitation Assembly to create a concentrated axial magnetic field around a conventional torch. This focuses and contains the microwave energy where it is needed to produce a toroidal plasma with a cooler central channel that is suitable for stable introduction of liquid samples using a conventional sample introduction system.

Samples and sample preparation

A series of samples that are normally analyzed by flame AA were prepared using fire assay. A 30 g rock sample was heated with flux to over 1,000 °C. The process yields a small silver sphere, which was then dissolved in 4 mL of 25% aqua regia. The 4100 MP-AES operating parameters were then optimized, as shown in Table 1.

Table 1. Agilent 4100 MP-AES operating parameters

Instrument parameter	Setting
Analytes (wavelength)	Au (267.595), Pt (265.945), Pd (363.470)
Nebulizer pressure	140–240 kPa
Read time	3 s
No. of replicates	3
Sample uptake delay	10 s
Stabilization time	5 s
Background correction	Auto

Method detection limits

Method Detection Limits (MDLs) for gold, platinum and palladium were determined by measuring two sets of ten method blanks twice, on non-consecutive days, using the conditions as defined in the analytical method. The MDL was calculated as the 3 sigma standard deviation of the twenty concentration results.

The MDLs listed in Table 2 are sufficiently low for this type of analysis.

Table 2. MDLs for Au, Pt and Pd in fire assay samples

Analyte	Wavelength (nm)	MDL (µg/L)
Au	267.595	4
Pt	265.945	13
Pd	363.470	0.7

Linear range

The concentration or working range of an analytical technique is the range of concentrations that can be measured accurately without the need to recalibrate or dilute the sample. The linear range for Au, Pt and Pd was investigated using the 4100 MP-AES. A series of standards was prepared at concentrations of 2, 7, 70, 90, 100, 110 and 120 mg/L, and analyzed using the 4100 MP-AES. The calibration graphs obtained are shown in Figures 2, 3 and 4. These show that the linearity for all three analytes was acceptable up to a concentration of 120 mg/L, which exceeds the requirements of the application.

Sample volume

The analysis of PMs is volume-sensitive. The typical total sample volume available for analysis is around 4 mL. By using an Agilent SPS 3 Sample Preparation System connected to the 4100 MP-AES, the method cycle time (sample to sample) was 55 s and the sample volume consumed during analysis was 1.8 mL.

Accuracy

In order to test the ability of the 4100 MP-AES to analyze PMs at variable concentrations, a batch of Certified Reference Materials (CRMs) was analyzed.

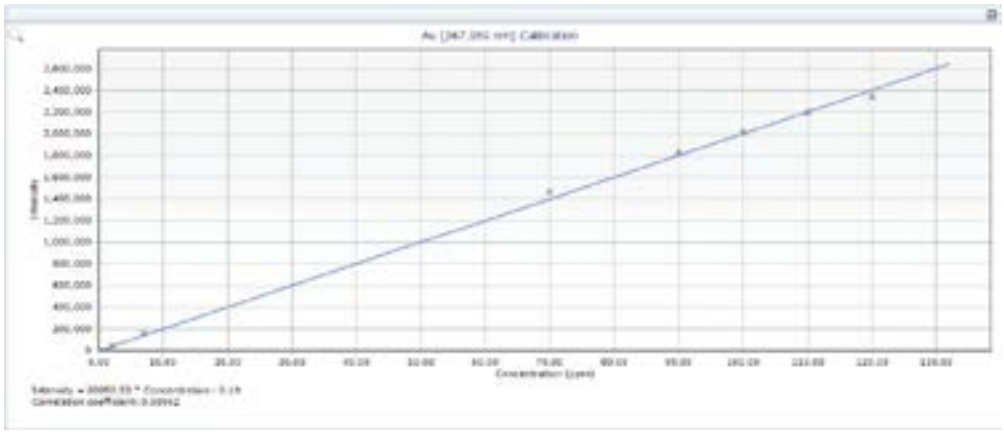

Figure 2 Calibration graph for Au at the 267.595 nm wavelength

Figure 3. Calibration graph for Pt at the 265.945 nm wavelength

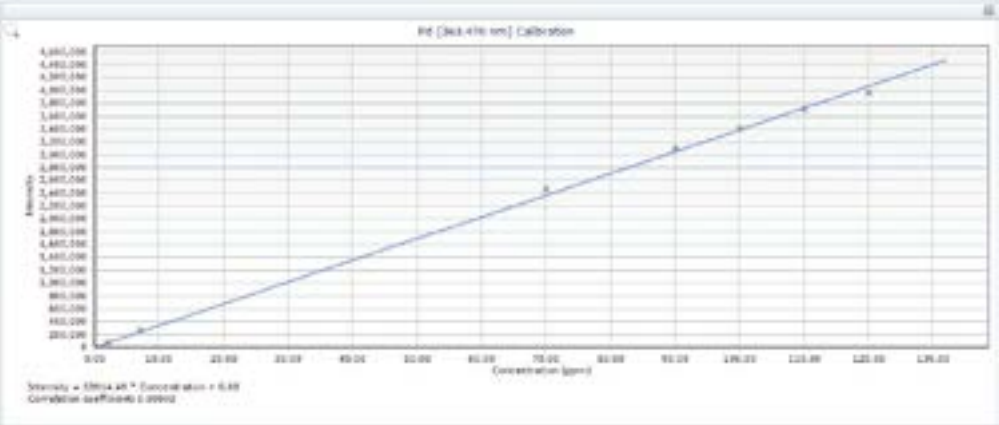

Figure 4. Calibration graph for Pd at the 363.469 nm wavelength

These were custom CRMs that had been professionally prepared from solid ore samples and certified through a round robin test process. They are not commercially available. The results listed in Table 4 show excellent agreement (accuracy) between the 4100 MP-AES measured results and the certified values.

Table 4. Results for Au, Pt and Pd obtained using the 4100 MP-AES compared to certified reference values

Gold	CRM certified value (mg/L)	MP-AES result (mg/L)
CRM 1	19.8	19.3
CRM 2	7.9	7.4
CRM 3	23.1	22.7
CRM 4	5.6	5.7
CRM 5	57.8	55.3
CRM 6	3.1	3.3
CRM 7	35.9	35.4
CRM 8	8.4	8.9

Platinum	CRM certified value (mg/L)	MP-AES result (mg/L)
CRM 6	0.74	0.75
CRM 7	35.6	35.9
CRM 8	9.0	9.5

Palladium	CRM certified value (mg/L)	MP-AES result (mg/L)
CRM 6	3.21	3.4
CRM 7	44.4	44.0
CRM 8	35.0	36.5

Recovery of unknown samples

A batch of unknown samples was analyzed for gold content using the 4100 MP-AES, and the results compared with the data obtained from analysis using conventional flame AA. The comparison can be seen in Table 5.

A typical spectrum of a sample containing approximately 40 ppm of gold can be seen in Figure 5. This demonstrates excellent signal to noise ratio with the flat baseline and the narrow emission peak confirming there are no spectral interferences.

Table 5. Results for gold in unknown samples, comparing the 4100 MP-AES with flame AA

Sample	MP-AES result (mg/L)	Flame AA result (mg/L)	Agreement with AA result (%)
1	0.09	0.09	100
2	0.85	0.84	101
3	5.3	5.1	104
4	13.7	14.4	95
5	20.8	21.8	95
6	4.3	4.1	105
7	1.0	1.0	100

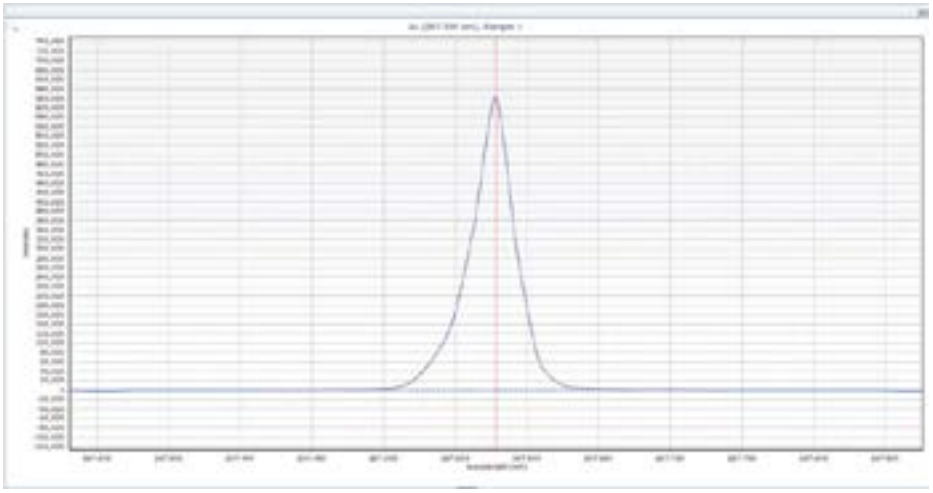

Figure 5. A typical PM sample spectrum for Au at the 267.595 nm wavelength

Conclusions

Following a thorough evaluation of the performance of the Agilent 4100 MP-AES, it is apparent that the 4100 MP-AES offers many advantages for the analysis of gold and other precious metals compared to conventional analysis techniques such as flame AA. The 4100 MP-AES offers superior sensitivity, an increased linear dynamic range and improved speed of analysis. In addition, the 4100 MP-AES more than doubles the measurement speed of conventional AA systems. It also offers exceptional accuracy as demonstrated by the excellent agreement with the certified values for several CRMs and real samples. Furthermore, the 4100 MP-AES has the lowest running costs of all of today's atomic spectroscopy techniques, due to reduced gas costs. Its use of non-combustible nitrogen also ensures that, unlike flame AA, the 4100 MP-AES can provide safer, multi-element unattended overnight operation.

The 4100 MP-AES also offers the option of installation at remote locations. This enables laboratories to analyze samples at the source rather than shipping the samples to a central laboratory for analysis, as is the current practice. In other instances where remote analysis is already performed using flame AA, the MP-AES provides the user with capability to analyze the samples in a safer environment, without the need for flammable gases such as acetylene.

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Determination of major and minor elements in geological samples using the 4100 MP-AES

Application note

Geochemistry, metals and mining

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Introduction

Establishing the elemental composition and grade of base metal ores is carried out at different stages of mining and processing. It is used in advanced exploration to confirm the feasibility of mining the ore, and in the assay of the ore concentrate. The determination of the concentration of base metals requires a technique with good accuracy and precision that is capable of generating and managing data from the analysis of large numbers of samples. Consequently, there are also very high expectations in terms of sample throughput and reliability.

In addition, ore-grade samples contain a range of concentrations. It would not be unusual to see high percentage level analytes present alongside low parts per million level analytes. A sample with 40% copper would not be unexpected, and as such, any analysis technique used needs to be able to cope with this range of concentrations.

Geochemistry Applications

Typically, the determination of major and minor elements in geological samples is performed using flame atomic absorption spectroscopy (FAAS) and/or inductively coupled plasma optical emission spectroscopy (ICP-OES). Agilent has developed a new instrument, the 4100 Microwave Plasma Atomic Emission Spectrometer (MP-AES), that out-performs FAAS in terms of analytical performance, and offers lower operating costs and unattended overnight operation. The 4100 MP-AES is a highly automated multi-element system with high matrix tolerance and high sample throughput. This ensures that challenging samples can be analyzed quickly and reliably with little operator training and minimal method development.

Experimental

Instrumentation

The 4100 MP-AES is a fast sequential multi-element analytical technique that uses a microwave-induced plasma to provide analysis of liquid sample using a conventional sample introduction system. As MP-AES relies on the generation of a microwave plasma using nitrogen, no flammable gases such as acetylene are required. This reduces running costs and improves lab safety. Nitrogen can be supplied from bottled gas or the Agilent 4107 Nitrogen Generator. This alleviates the difficulty and costs in sourcing gases such as acetylene, specially in remote locations.

The potential of the Agilent 4100 MP-AES for the analysis of ore-grade base metal samples was investigated following preparation of the samples by a four-acid digestion procedure.

Samples and sample preparation

Ore-grade samples require different digestion techniques to geochemical exploration samples in order to dissolve the high metal concentrations and retain them in solution. As a result, dilution factors are greater than with geochemical exploration samples, resulting in higher detection limits, and also higher upper limits.

The preparation method used involves taking 0.4 g of sample and performing a four-acid (HNO_3-$HClO_4$-HF-HCl) digestion. The process is completed by further addition of hydrochloric acid and deionized water, followed by cooling to room temperature. The resulting solution was diluted to 100 mL with de-ionized water resulting in a final matrix of 30% HCl. This represents a 250-fold sample dilution.

The 4100 MP-AES operating parameters were optimized as shown in Table 1.

Table 1. Agilent 4100 MP-AES operating parameters

Instrument parameter	Setting
Nebulizer pressure	80–240 kPa
Read time	3 s (10 s for Ag)
Stabilization time	15 s
Background correction	Auto

Results and discussion

Method detection limits (MDLs)

Method detection limits (MDLs) for silver, copper, molybdenum, nickel, lead, and zinc were determined. Table 2 shows that excellent MDLs can be obtained using the 4100 MP-AES.

Table 2. MDLs for digestions of ore-grade base metal samples

Analyte	Wavelength (nm)	MDL (ppm)
Ag	328.068	0.04
Cu	327.395	0.1
Mo	379.398	0.7
Ni	352.453	0.4
Pb	405.781	0.4
Zn	213.857	0.7

Quantitative analysis

A batch of base metal ore sample digests were prepared using the sample preparation method. These sample were analysed by the 4100 MP-AES using a blank and three matrix-matched standard solutions.

Accuracy

The results obtained by the 4100 MP-AES for Ag, Cu, Mo, Ni, Pb and Zn were plotted against the expected results — see Figures 1 to 7. The graphs show good correlation (accuracy) over the calibration range, up to ~4% for copper, indicating that MP-AES is a suitable technique for the application.

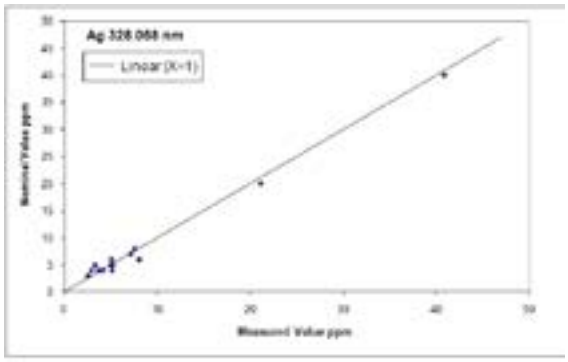

Figure 1. MP-AES measured results for Ag compared to nominal values

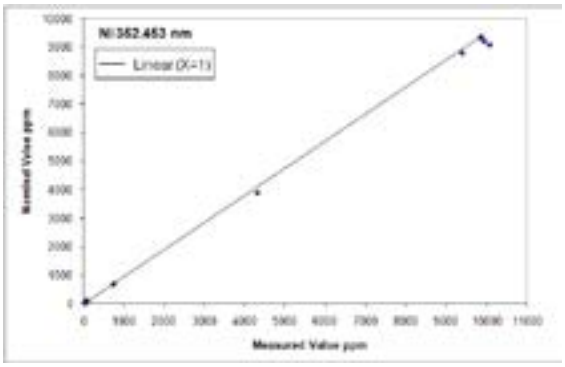

Figure 4. MP-AES measured results for Ni compared to nominal values

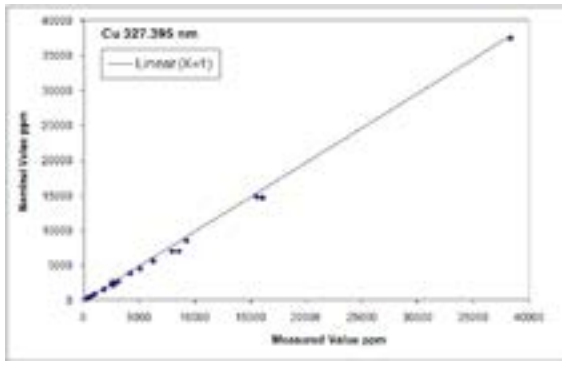

Figure 2. MP-AES measured results for Cu compared to nominal values

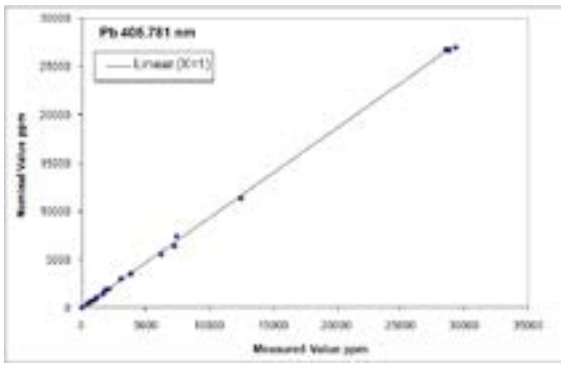

Figure 5. MP-AES measured results for Pb compared to nominal values

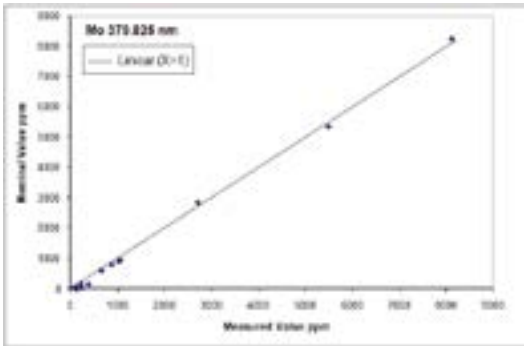

Figure 3. MP-AES measured results for Mo compared to nominal values

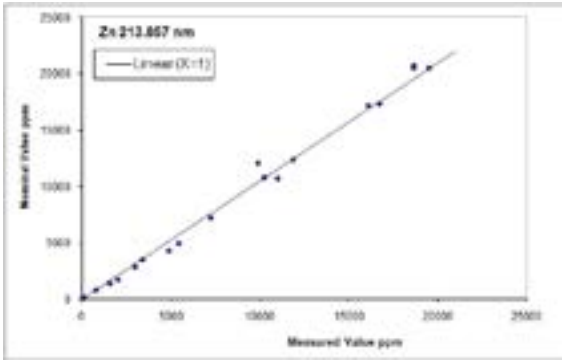

Figure 6. MP-AES measured results for Zn at the 213.857 nm wavelength compared to nominal values

Geochemistry Applications

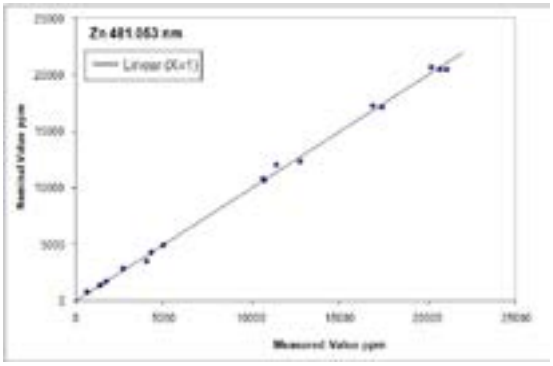

Figure 7. MP-AES measured results for Zn at the 481.053 nm wavelength compared to nominal values

Conclusions

A series of geological samples has been successfully analyzed using the Agilent 4100 MP-AES, following a sample preparation procedure that is commonly used to prepare base metal ores for analysis by geochemical laboratories. Quantitative results were obtained for 6 elements present in a batch of 23 base metal ore samples, with measured concentrations ranging from less than 1 ppm to 29%. The comparative results for Ag, Cu, Mo, Ni, Pb and Zn obtained using MP-AES show that the 4100 MP-AES is well suited to this application. It also offers additional benefits over comparative techniques such as flame AAS, through lower operating costs, improved safety and the ability to perform the analysis using unattended overnight operation.

Operating costs can be further reduced by directly generating nitrogen from compressed air using an Agilent 4107 Nitrogen Generator. This is particularly advantageous in areas where gas supplies are expensive, difficult to obtain or pose logistics challenges in transporting bulk cylinders to site. The 4100 MP-AES also offers the possibility of installations in remote locations. This enables laboratories to analyze samples locally at the source rather than transporting the samples to a central laboratory for analysis, as is the current practice. Furthermore, the Agilent 4100 MP-AES has the lowest operating costs of comparable techniques such as flame AA, and by using non-flammable gases, removes safety concerns associated with acetylene and nitrous oxide.

www.agilent.com/chem/4210mp-aes

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Environmental applications

Simplicity and accuracy make Agilent MP-AES the right choice for the analysis of a broad range of environmental matrices.

MP-AES enables you to make the right decisions for your waste disposal—ideal for QA/QC analysis of production streams and monitoring of metals content in solid and liquid waste.

- Simplify your analysis with auto optimization and auto background correction
- Measure your toughest samples accurately with a robust vertical plasma
- Achieve excellent long term precision for elevated salt-matrix samples using the humidifier accessory
- Reduce sample preparation of complex hydrofluoric (HF) acid digests using an inert sample introduction system that eliminates the need for a neutralization step, improving your productivity and efficiency
- Utilize the Automation Software Pack to assist with remote operation of the MP-AES when it is located near to the sample, away from your lab.

Elemental analysis of river sediment using the Agilent 4200 MP-AES

Application note

Environmental: Soils, sludges & sediments

Authors

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Introduction

The elemental profile of river sediments provides valuable insight into the health of a river, as well as the wider environment. Some elements that are essential for the ecology of the river at trace levels e.g. manganese, copper and zinc, can be toxic at high concentrations.

Traditionally, the concentration of elements in river sediments is determined via Flame Atomic Absorption Spectroscopy (FAAS). This technique has the drawback of requiring expensive and hazardous gases such as acetylene and nitrous oxide and also requires element-specific sample preparation that adds time and cost to the analysis.

The novel Agilent 4200 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) is the ideal alternative for laboratories looking to transition away from FAAS to a higher performance, lower cost and safer technique. MP-AES is a fast sequential, multielement analytical technique that uses a microwave-induced nitrogen-based plasma for sample excitation. The use of nitrogen eliminates the need for acetylene and nitrous oxide, which can

be generated from surrounding air, using a nitrogen generator. This makes it safer and allows unattended operation of the instrument, even for overnight runs.

This application demonstrates a simple, fast, low cost, and safe method to analyze major and minor elements in river sediment, with no compromise in data quality or ease of use. It describes a simple one step dilution sample preparation procedure and an analytical method that was used to analyze major elements, Ca, K, Mg, Na and Al, and minor elements, Fe, Zn, Cu, and Mn, in a river sediment certified reference material (CRM) using the Agilent 4200 MP-AES.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES fitted with a OneNeb nebulizer, double-pass glass cyclonic spray chamber and easy-fit torch. Nitrogen was supplied from a Dewar, but could also have been obtained via the Agilent 4107 Nitrogen Generator (with air supplied from an air compressor). An Agilent SPS 4 autosampler was used to deliver samples to the instrument, allowing the system to be operated unattended. Method parameters are given in Table 1.

Table 1. MP-AES method parameters

Instrument Parameter	Setting
Nebulizer	OneNeb
Nebulizer flow rate	Optimized
Spay chamber	Double pass glass cyclonic
Pump rate (rpm)	15
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue
Autosampler	Agilent SPS 4
Read time (s)	3 ; 2 for Na and K
Number of replicates	3
Fast pump during uptake	On
Sample uptake delay (s)	55
Rinse time (s)	45
Stabilization time (s)	10
Background correction	Auto
Gas source	Dewar nitrogen

Sample and sample preparation

River Sediment Solution B CRM (CRM-RS-B) purchased from High Purity Standards (Charleston, SC, USA) was used to validate the method. The CRM was prepared for analysis by diluting 1:10 with 2% HNO_3.

Calibration standards

Single element Reference Materials (Agilent Technologies) were used to prepare a set of multielement calibration standards. The Blank and standards were prepared in 2% HNO_3. No ionization buffers were required.

Wavelength selection and calibration range

Details of wavelength selection and nebulizer flow rate are given in Table 2. The Agilent 4200 MP-AES features continuous wavelength coverage and the MP Expert software includes an extensive wavelength database that allows the selection of wavelengths suited to the concentration range required for the analysis. All wavelengths were selected to provide the widest dynamic range while minimizing spectral interferences. For example, the less sensitive Mg 383.829 nm line was selected over the more sensitive Mg 285 nm line because it has a large linear dynamic range, meets the detection limit requirements of the application, and is free from spectral interferences.

Table 2. Selected wavelength and nebulizer flow for each element being determined

Element	Wavelength (nm)	Nebulizer Flow (L/min)
Zn	213.857	0.45
Fe	373.486	0.5
Ca	422.673	0.6
Cu	324.754	0.7
Mg	383.829	0.9
K	766.491	0.75
Mn	403.076	0.9
Al	394.401	0.95
Na	588.995	0.95

Results and discussion

Calibration

Each element was calibrated using a four point calibration. All calibration curves were linear, with a correlation coefficient greater than 0.999, and less than 10% calibration error on each calibration point. The calibration curve for Mg 383.829 nm (Figure 1) is a typical example, showing excellent linearity across the calibration range.

Table 3 summarizes the calibration standard concentration range and correlation coefficients for all 9 elements. Due to the wide working range of MP-AES, only one dilution of the sample was required to measure all of the elements of interest. Reducing the number of sample dilution steps improved productivity and reduced the risk of sample contamination and dilution errors. The wide dynamic range of MP-AES eliminates the need for the strategies commonly used on FAAS to determine elements present at high concentration, such as burner rotation or measuring elements in emission mode.

Table 3. Typical MP-AES calibration range

Element/ Wavelength (nm)	Std Conc. Range, mg/L	Linear Correlation Coefficient r
Ca 422.673	0-25	0.99992
Mg 383.829	0-25	0.99999
Na 588.995	0-20	0.99966
K 766.491	0-25	0.99991
Zn 213.857	0-10	0.99996
Fe 373.486	0-50	0.99998
Al 394.401	0-100	0.99994
Cu 324.754	0-5	1.00000
Mn 403.076	0-10	1.99991

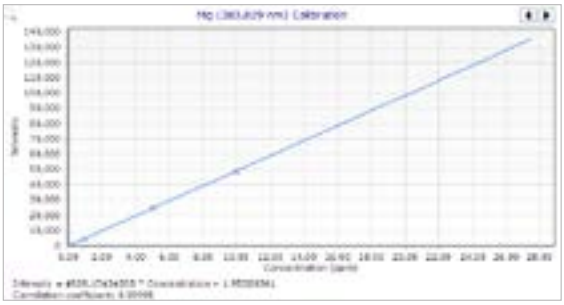

Figure 1. Calibration curve for Mg 383.829 nm

Sample analysis

The river sediment CRM-RS-B was measured three times using two separate MP-AES instruments. The mean concentration, standard deviation (SD), and recovery was calculated for each analyte, as shown in Table 4. All elements were determined in one sample measurement. The precision between the two instruments was excellent, as indicated by the low SD. The mean of the measured results was in good agreement with CRM values (99-107%).

The results demonstrate the ability of the 4200 MP-AES to measure low concentrations (Cu, Zn and Mn), in the presence of major elements (Fe, Ca, Mg, K, Al) and achieve excellent recoveries across a wide concentration range.

Element/ Wavelength (nm)	Measured conc. in solution-Instrument 1 (mg/L)	Measured conc. in solution-Instrument 2 (mg/L)	Mean (mg/L)	SD	Certified conc. (mg/L)	Recovery in solution (%)
Zn 213.857	4.94	5.12	5.03	0.124	5.0	100.7
Fe 373.486	429.6	406.7	418.2	16.2	400.0	104.5
Ca 422.673	305.6	302.4	304	2.28	300.0	101.0
Cu 324.754	1.06	1.08	1.07	0.020	1.00	107.0
Mg 383.829	125.1	121.9	123.5	2.25	120.0	102.9
K 766.491	204.0	204.8	204.4	0.51	200.0	102.2
Mn 403.076	6.08	6	6.04	0.055	6.0	100.7
Al 394.401	597.1	592.1	594.6	3.54	600.0	99.1
Na 588.995	53.2	53.3	53.3	0.015	50.0	106.5

Method Detection Limits

Three sigma Method Detection Limits (MDLs) were calculated from ten replicate measurements of the blank using a 3 second integration time. These MDLs were acquired using a set of conditions suitable for routine sample analysis rather than highly optimized conditions. Therefore, they are not the best possible detection limits but are more than sufficient for the method requirements.

The MDLs were measured three times on two separate instruments. The results shown in Table 5 are the average of the six measurements.

Table 5. Method Detection Limits in ppb (µg/L).

Element	Wavelength (nm)	Average MDL (µg/L), n=6
Zn	213.857	4.44
Fe	373.486	5.39
Ca	422.673	0.310
Cu	324.754	1.21
Mg	383.829	1.91
K	766.491	2.35
Mn	403.076	0.305
Al	394.401	0.452
Na	588.995	3.28

Long term stability

The river sediment CRM was analyzed every 10 samples over 12 hours of continuous measurement, as shown in Figure 2. Excellent stability was achieved over this long term measurement. Average recoveries for most elements were within ± 5%, and all elements in the method were within ± 10% of the certified value. The long term measurement precision over the full 12 hours was less than 2% RSD (Table 6), demonstrating the suitability of the 4200 MP-AES for routine measurement of metals in river sediment samples.

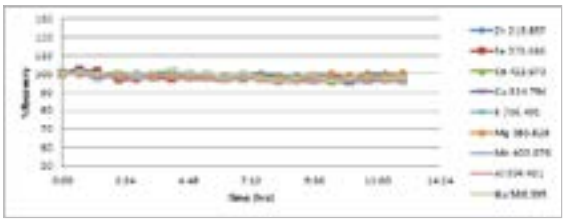

Figure 2. Long-term stability plot. <2.0% RSD over 12 hours analysis of river sediment sample

Table 6. Long-term precision and average recovery over 12 hours of continuous measurement of the river sediment CRM

Element/ Wavelength (nm)	%RSD	Average Recovery (%)
Zn 213.857	0.9	96.4
Fe 373.486	1.8	96.8
Ca 422.673	1.5	93.3
Cu 324.754	1.8	95.2
K 766.491	1.2	93.3
Mg 383.829	0.8	102.4
Mn 403.076	1.3	103.1
Al 394.401	1.6	99.6
Na 588.995	1.5	107.3

Potential cost savings with the 4200 MP-AES

The example given in Figure 3 allows comparison of the running costs and potential savings of the MP-AES compared to operating a FAAS.

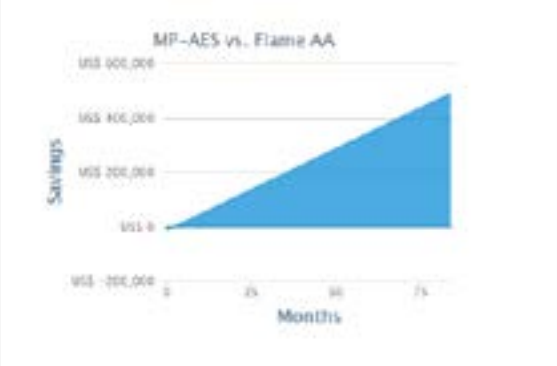

Figure 3. Potential cost savings with MP-AES compared to FAAS over time*

The lower operating costs of the MP-AES, compared to FAAS could deliver savings of close to USD500k over a 7-year evaluation period, as indicated in Figure 3. The cost-comparison was based on the following criteria:

- An FAAS fitted with an air compressor and 1 year of consumables, including acetylene gas
- An MP-AES fitted with an air compressor, SPS 4 autosampler and 1 year of consumables
- Nine elements measured under method conditions, all with air/acetylene flame.
- Based on the analysis of 300 samples per week

Conclusions

The Agilent 4200 MP-AES is suited to the analysis of major and trace elements in river sediments, as demonstrated in this study. The instrument's wide dynamic range ensured that only one dilution of the samples was required to measure the complete set of elements, increasing laboratory productivity and reducing the risk of errors. Excellent recoveries of the certified standard material were achieved, with good precision across two separate instruments.

The robust plasma and sample introduction system consisting of the OneNeb nebulizer and mass flow controlled nebulizer gas flow ensured excellent stability over 12 hours period—without the need to recalibrate. Automated wavelength selection reduced all potential chemical and ionization interferences, greatly simplifying method development.

MP-AES is an ideal replacement technique for FAAS for those labs looking to boost their productivity and realize significant cost benefits.

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*This example is intended to help you compare the running costs and savings of the MP-AES vs. flame AA. The applied formulas and parameters are correct to the best of our knowledge, but we cannot guarantee the results. Savings may vary depending on factors such as local gas and electricity costs, operator costs, number and types of elements.
For this calculation, operator labor costs were set to USD 25 per hour and electricity costs were set to USD 0.2 per kW.

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Analysis of domestic sludge using the Agilent 4200 MP-AES

Application note

Environmental

Authors

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Introduction

Managing the treatment and disposal of domestic sludge is an important activity and one that is highly regulated in many countries. After treatment, the effluent may be discharged leaving a mixture of water, organic solids and chemicals, nutrients, heavy metals, and inorganic ions. This sludge can be further treated and the resulting biosolids can then be applied to the land as a fertilizer, sent to landfill or incinerated. It is vital that the sludge or biosolids are tested and conform to regulatory levels in order to protect public health and the environment.

The United States federal biosolids rule is contained in 40 CFR Part 503. The European Union Sludge Directive 86/278/EEC is expected to be revised as several Member States have enacted and implemented stricter limit values for heavy metals and set requirements for other contaminants.

In this work, an Agilent 4200 MP-AES was used to determine major and minor elements in domestic sludge, following microwave digestion.

MP-AES is a fast sequential, multielement analytical technique that uses a microwave-induced nitrogen-based plasma for sample excitation. Without needing expensive and hazardous gases such as acetylene, MP-AES increases lab safety and allows unattended operation, even for overnight runs. Sample throughput can be further enhanced with the use of the high capacity autosampler, the Agilent SPS 4.

The 4200 MP-AES with MP Expert software uses a high number of automated parameters including pre-set methods, auto optimization, suggested wavelengths, and background correction. It has a simple yet powerful user interface and a reliable torch loader that automatically aligns the torch and connects gases for fast start up and reproducible performance.

This application note describes the sample preparation procedure and analytical method used to analyze Zn, Mn, Cr, Ca, Fe, Cu and Mg in a domestic sludge standard reference material (SRM) using the Agilent 4200 MP-AES.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES fitted with a OneNeb nebulizer, double-pass glass cyclonic spray chamber and easy-fit torch. Nitrogen can be supplied from bottled gas, Dewar or via the Agilent 4107 Nitrogen Generator (with air supplied from an air compressor). For this application, Dewar nitrogen was used. An Agilent SPS 4 autosampler was used to deliver samples to the instrument, allowing the system to be operated unattended. Method parameters are given in Table 1.

Table 1. MP-AES method parameters

Instrument Parameter	Setting
Nebulizer	OneNeb
Nebulizer flow rate	Optimized
Spay chamber	Double-pass cyclonic glass
Pump rate	15 rpm
Sample pump tubing	Orange/green
Waste pump tubing	Blue/blue
Read time (s)	3
Number of replicates	3
Fast pump during uptake	On
Sample uptake delay (s)	50
Rinse time (s)	45
Stabilization time (s)	10
Background correction	Auto
Gas source	Dewar nitrogen

Sample and sample preparation

Domestic Sludge SRM (SRM®- 2781, NIST, Gaithersburg, MD, US) was used to validate the accuracy of the method. Approximately 0.5 g of the SRM sample was accurately weighed into a microwave vessel followed by the addition of 6 mL HNO_3 and 2 mL H_2O_2. Acid digestion was performed in an UltraWAVE Single Reaction Chamber Microwave Digester. Heating conditions are given in Table 2. After cooling, the digested solution was transferred quantitatively to a volumetric flask and brought to a 50 mL volume with 18.2 MΩ deionized water. The final acid concentration was 12% HNO_3.

Table 2: Parameters used for microwave digestion

Parameter	Setting
Ramp (min)	10
Temp (°C)	150
Hold (min)	5
Ramp (min)	10
Temp (°C)	230
Hold (min)	10
Total (min)	30

Calibration standards

Single element stock solutions (Agilent Technologies) were used to prepare the multi-element calibration standards. One set of multi-element standards was used for the calibration. All working standards were prepared in 12% HNO_3 and HCl. No modifier or ionization buffers were required.

Wavelength selection and calibration range

Details of wavelength selection and nebulizer flow rate are given in Table 3. MP-AES features continuous wavelength coverage and the MP Expert software includes an extensive wavelength database that allows the selection of wavelengths suited to the concentration range required for the analysis. For example, in this application, the less sensitive Mg 383.829 nm line was selected over the more sensitive Mg 285 nm line because it has a large dynamic range, meets the detection limit requirements of the application, and is free from spectral interferences.

Table 3. Element, wavelength and nebulizer flow

Element	Wavelength (nm)	Nebulizer Flow (L/min)
Zn	213.857	0.45
Mn	403.449	0.9
Cr	425.433	0.9
Ca	445.478	0.5
Fe	373.486	0.5
Cu	324.754	0.7
Mg	383.829	0.9

Results and discussion

Calibration

In addition to minimizing spectral interferences, all wavelengths were selected to provide the widest dynamic range. Each element was calibrated using a three point calibration. All calibration curves were linear, except for Ca 455.478 nm, which was rational fit. The curves had a correlation factor greater than 0.999 and less than 10% calibration error on each calibration point. The calibration curve for Mg 383.829 nm (Figure 1) is a typical example, showing excellent linearity across the calibration range.

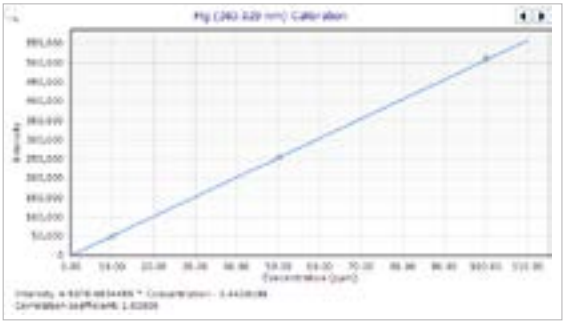

Figure 1. Calibration curve for Mg 383.829 nm.

Table 4 summarizes the calibration standard concentration range and correlation coefficients for all 7 elements. As the working range of MP-AES far exceeds that of FAAS, further dilution of the sample digest was not required to measure all of the elements of interest. Reducing the number of sample dilution steps improves productivity and reduces the risk of sample contamination.

Table 4. Calibration standard concentration range and correlation coefficients

Element / Wavelength (nm)	Standard Conc. Range (mg/L)	Linear Correlation Coefficient - r
Zn 213.857	0-10	0.99987
Mn 403.449	0-10	0.99994
Cr 425.433	0-10	0.99964
Ca 445.478	0-250	0.99999
Fe 373.486	0-250	0.99988
Cu 324.754	0-100	0.99998
Mg 383.829	0-100	1.00000

Sample analysis

Recoveries of the domestic sludge SRM are based on the average of 3 replicate digestions over separate analyses. The mean concentration, standard deviation (SD), and recovery was calculated for each analyte, as shown in Table 5. The results obtained with the method were in good agreement with the SRM values (96–103%), verifying the method.

Table 5. MP-AES recovery of elements in NIST 2781 domestic sludge SRM. Results are compared to the reference leach values.

Element/ Wavelength (nm)	Measured conc in sample (mg/L)	SD	Leachable mass fraction (mg/kg)	Recovery in sample (%)
Zn 213.857	1132.8	94.6	1120	101.1
Mn 403.449	768.3	21.7	745	103.1
Cr 425.433	142.9	3.68	143	99.9
Ca 445.478	35145.3	716.5	36440	96.4
Fe 373.486	25108.0	232.6	24300	103.3
Cu 324.754	599.1	15.3	601	99.7
Mg 383.829	4842.0	252.6	4850	99.8

Method Detection Limits

Method Detection Limits (MDL) were determined using three sigma of ten replicate measurements of the matrix blank solution, then multiplying by the dilution factor to calculate the MDL in the original sample. These MDLs were acquired using a method conditions suitable for routine sample analysis rather than highly optimized conditions. Consequently, they are not best-possible detection limits but are more than sufficient for the method requirements. The results are shown in Table 6.

Table 6. Method Detection Limits in the original sample (mg/kg).

Element	Wavelength (nm)	MDL (mg/kg)
Zn	213.857	0.25
Mn	403.449	0.03
Cr	425.433	0.03
Ca	445.478	1.03
Fe	373.486	0.88
Cu	324.754	0.43
Mg	383.829	0.20

Long term stability

The domestic sludge SRM was analyzed every 10 samples over 12 hours of continuous measurement. Excellent stability was achieved over this period as shown in Figure 2. Average recoveries for most elements were within ± 2%. The long term measurement precision over the full 12 hours was less than 2% RSD (Table 7), demonstrating the suitability of the 4200 MP-AES for routine measurement of metals in domestic sludge samples.

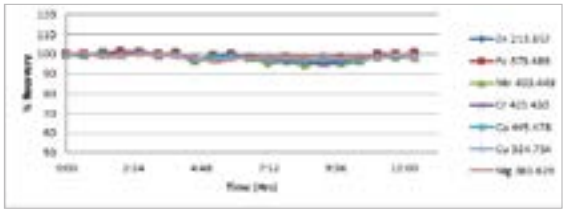

Figure 2. Long-term stability plot. <2.0% RSD over 12 hours analysis of domestic sludge SRM.

Table 7. Long-term precision and average recovery over 12 hours continuous measurement of the domestic sludge SRM.

Element/ Wavelength (nm)	%RSD	Average Recovery (%)
Zn 213.857	0.8	99.2
Mn 403.449	2.0	98.0
Cr 425.433	1.9	98.4
Ca 445.478	1.4	98.5
Fe 373.486	1.7	98.9
Cu 324.754	1.1	98.4
Mg 383.829	1.1	99.0

Potential cost savings with the 4200 MP-AES

The example given in Figure 3 is intended to demonstrate the reduction in running costs and thus potential savings of the MP-AES, compared to operating a flame atomic absorption spectrometer.

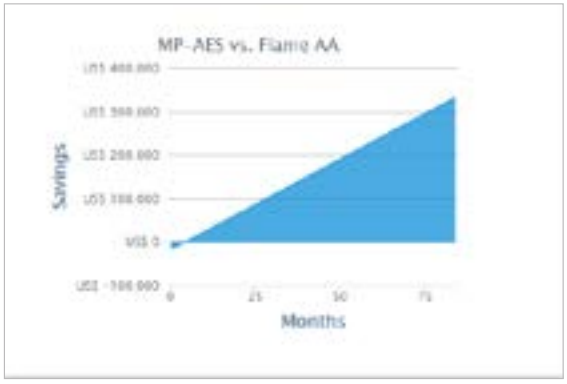

Figure 3. Potential cost savings with MP-AES compared to FAAS over time*

*This example is intended to help you compare the running costs and savings of the MP-AES vs. flame AA. The applied formulas and parameters are correct to the best of our knowledge, but we cannot guarantee the results. Savings may vary depending on factors such as local gas and electricity costs, operator costs, number and types of elements.
For this calculation, operator labor costs were set to USD 25 per hour and electricity costs were set to USD 0.2 per kW.

Operating an MP-AES in place of a FAAS over a 7-year evaluation period could lead to savings of more than USD300K as shown in Figure 3. The cost-comparison was based on the following criteria:

- An FAAS fitted with an air compressor, autosampler, and 1 year of consumables,
- An MP-AES fitted with an air compressor, SPS 4 autosampler and 1 year of consumables
- Seven elements measured under method conditions
- Based on the analysis of 300 samples per week

Conclusions

The Agilent 4200 MP-AES is ideally suited to the analysis of major and trace elements in domestic sludge following a simple microwave digestion sample preparation procedure. Excellent recoveries of the standard reference material were achieved, with good precision. Instrument robustness was demonstrated with exceptional stability over 12 hours—without the need to recalibrate.

The 4200 MP-AES offers multiple benefits over FAAS including:

- Higher performance with fast sequential operation, lower detection limits and wider dynamic range, meaning higher sample throughput and fewer manual dilutions.
- Improved safety and reduced running costs with the use of nitrogen to generate the plasma.
- Simplified workflow with no need to change and optimize lamps, and no need for complicated element specific sample preparation with addition of modifiers or buffers.

In addition to analytical performance advantages, MP-AES is considerably more cost-effective over the long term than FAAS - an important consideration for any lab looking to invest in new or replacement instrumentation.

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Determination of metals in industrial wastewaters by microwave plasma-atomic emission spectrometry

Application note

Environmental

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Introduction

Elevated levels of metal and metalloid contaminants in the environment pose a risk to human health and are a source of considerable concern to agricultural, livestock and aquatic industries. Industrial wastewaters are the main source of these contaminants, which can persist indefinitely in the environment as they do not degrade with time, and have the potential to pollute not only farm and urban land but also surface and ground waters used for agriculture and drinking. Consequently, the determination of metals in wastewaters is an important aspect of environmental monitoring.

This application note describes a new, simple, and relatively inexpensive analytical spectrometric method for the analysis of wastewater using microwave plasma-atomic emission spectrometry (MP-AES). This is a novel atomic emission spectroscopy method is based on magnetically coupling microwave energy to generate a self-sustained atmospheric pressure nitrogen plasma. The Agilent 4100 MP-AES allows easy entrainment of

sample aerosol, both aqueous and organic, produced by a conventional nebulizer and spray chamber system. The system provides good tolerance to aqueous and organic solvent loading. Refer to Reference [1] for more details about the operational characteristics of the MP-AES.

Experimental

Sample preparation

A series of unfiltered mine site wastewater samples were acidified at the time of collection. The samples were acid digested for the total metal determination using the following procedure: 0.5 mL of concentrated HCl and 0.2 mL of concentrated HNO_3 were added to 10 mL sample aliquots in 16 x 125 mm polypropylene tubes and digested at 90–100 °C in a sand bath on a hotplate until the final digested volume was 10 mL. If the sample volume was less than 10 mL, Milli-Q water was added to make up the sample volume to the 10 mL volume mark. All water and QC samples were digested, when applicable, accordingly. Results obtained by the 4100 MP-AES were compared with results provided by a commercial service provider.

Instrumentation

An Agilent 4100 MP-AES was used for the total metal determination of Al, B, Co, Cu, Mg, Mn, Ni and Zn in wastewaters. The viewing position and nebulizer pressures were optimized automatically using the Agilent MP Expert software. Table 1 lists the instrumental parameters used for sample analysis. Manual sample introduction mode was used.

Table 1. Agilent 4100 MP-AES operating conditions

Analyte	Wavelength (nm)	Read time (s)	Nebulizer	Background correction
Al	396.152	3	240	Auto
B	249.773	3	160	FLIC
Co	340.511	3	220	Auto
Cu	223.009	3	220	Auto
Fe	373.486	3	220	Auto
Mg	383.829	3	240	Auto
Mn	259.372	3	160	Auto
Ni	341.476	3	240	Auto
Zn	472.215	3	160	Auto

Analytical calibration

Table 2 lists wavelengths, calibration fit types and maximum applicable analyte concentration. The criterion for wavelength selection was to (a) provide wide dynamic range and (b) avoid spectral interferences. Therefore, most of the analyte lines used for the final analyses were not the most sensitive line listed in the MP Expert software. The auto-background correction feature in MP Expert was used as the background correction method. Where there is a potential spectral interference on the analyte line, Fast Linear Interference Correction (FLIC), an Agilent proprietary spectral interference correction method, can be applied to allow effective removal of the spectral interference. For example, Fe interferences can occur due to the high level of Fe in the samples when determining B using the 249.773 nm primary wavelength. This type of spectral overlap can easily be corrected using FLIC.

Rational calibration fit is a non-linear curve fit of the type $y = (a + bx)/(1 + cx)$. This non-linear curve fitting allows an extended dynamic range so that sample analysis can be carried out using a single wavelength for a given analyte without time-consuming sample dilutions. Samples with analyte concentrations that exceed the maximum concentration given in Table 2 were diluted accordingly and re-analyzed. The acceptance criterion for calibration curve correlation coefficient is 0.999. At least four calibration standards, excluding the calibration blank, were used for calibration. Typical calibration curves for linear and non-linear calibration curves are given in Figures 1 and 2.

Table 2. Calibration parameters used for the sample analysis

Analyte	Wavelength (nm)	Calibration fit	Weighted fit	Through blank
Al	396.152	Rational	On	On
B	249.773	Linear	On	On
Co	340.511	Linear	On	On
Cu	223.009	Rational	On	On
Fe	373.486	Linear	On	On
Mg	383.829	Rational	On	On
Mn	259.372	Linear	On	On
Ni	341.476	Linear	On	On
Zn	472.215	Rational	On	On

Figure 1. Typical linear calibration curve for Co at the 340.511 nm wavelength

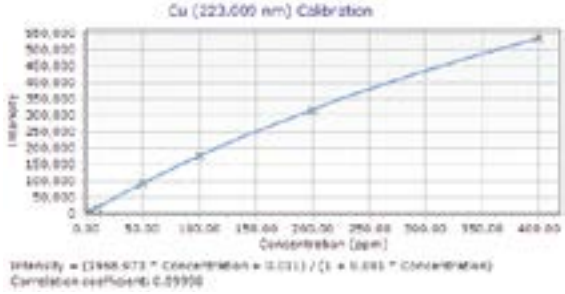

Figure 2. Typical non-linear calibration curve for Cu at the 223.009 nm wavelength. Note the extended range

Quality control

General QC criteria used by routine analytical laboratories were used. This includes the analysis of an initial calibration verification (ICV) solution, a method blank (MB), a laboratory control sample (LCS), duplicate samples (DUPs), matrix spikes (MSs), and a continuing calibration verification solution (CCV). For every 20-sample QC batch, one MB and LCS, and at least two sets of DUPs, one set of MS, and one CCV were analyzed. An ICV solution prepared using a different source was used to verify the integrity of the analytical calibration. The CCV solution measures instrument drift during the sample analysis. These QC samples, when applicable, were digested according to the digestion procedure given in the 'Sample preparation' section. Instrumental detection limits (IDL) were determined by analyzing seven blank solutions and applying a factor of 3.14 times the standard deviation of those results. Limit of reporting (LOR) was set at 10 times the IDL.

Results and discussion

The acceptance criterion for QC standards (ICV and CCV) is ±10% unless otherwise stated. For QC samples, acceptance criteria vary. The acceptable limit for LCS is ±10%, and that for MS recovery is ±25%. The spike concentration for the determination of MS recovery is 10 ppm, and if a sample contains an analyte concentration greater than four times the spike concentration, MS recovery is not determined (ND). Matrix spike recovery is determined only for key analytes; for example, MS recovery for Mg is not determined because Mg is considered to be a part of the matrix. The acceptance criteria for duplicate analyses are as follows:

No %RPD criteria for results < 10xLOR,

%RPD <50% for 10xLOR < result < 20xLOR,

%RPD < 20% for 20xLOR < result,

where %RPD is the Relative Percent Difference. The method blank value should be less than the LOR.

The results presented in Tables 3 to 5 indicate that all QC analyses were within the acceptable limits, except in a few instances. While the recovery of the Zn ICV was about 78%, the recovery of the CCV standard is within ±10%, and there is also very good agreement between results measured using the 4100 MP-AES and the nominal values. For MS recoveries, only the Zn MS recovery for spiked Sample-3 is outside the acceptable limit. However, it is not uncommon to have low MS recoveries for highly-impacted samples. In this particular sample, the sulfate concentration is about 1500 ppm. It should also be noted that the final CCV was measured four and half hours after the first measurement (calibration blank), and the final CCV recovery is still within the ±5% acceptance criteria. This indicates the capability of the instrument hardware and demonstrates that the 4100 MP-AES remains stable during long analytical runs without requiring time-consuming recalibrations.

Figures 3a to 3g are correlation plots of the results obtained using the 4100 MP-AES compared to nominal values. It is clear from these plots that there is good agreement between both sets of results. The results for Boron were not plotted because they were lower than the LOR for B. It is therefore likely that any noticeable differences in the two sets of results are due to sample heterogeneity prior to digestion as these unfiltered samples contained sediments.

Table 3. Limit of Reporting for determined analytes and results for method blank (MB), initial calibration verification (ICV) and continuous calibration verification (CCV) solution

Analyte	Wavelength (nm)	LOR (ppm)	MB (ppm)	ICV recovery (%)	CCV-1 recovery (%)	CCV-2 recovery (%)	CCV-3 recovery %
Al	396.152	0.02	<LOR	102.48	103.58	104.85	-
B	249.773	0.02	<LOR	ND	ND	ND	98.48
Co	340.511	0.06	<LOR	95.55	99.15	101.84	-
Cu	223.009	0.25	<LOR	97.11	99.72	101.73	-
Fe	373.486	0.10	<LOR	ND	100.06	102.61	-
Mg	383.829	0.10	<LOR	ND	ND	ND	93.52
Mn	259.372	0.02	<LOR	103.02	100.98	101.28	-
Ni	341.476	0.02	<LOR	97.96	105.71	105.65	-
Zn	472.215	0.20	<LOR	77.96	99.79	101.15	-

Table 4. Results for LCS recoveries and %RDP for duplicate analysis

Analyte	Wavelength (nm)	LCS-1 recovery (%)	LCS-2 recovery (%)	Sample-1 (ppm)	%RPD	Sample-2 (ppm)	%RPD	Sample-3 (ppm)	%RPD
Al	396.152	94.99	100.26	28.18	4.17	117.76	2.03	68.01	2.07
B	249.773	ND	ND	0.02	66.67	0.06	18.18	0.02	22.22
Co	340.511	93.54	89.94	3.57	0.28	1.63	1.22	1.04	0.19
Cu	223.009	96.15	96.76	1520.84	3.82	63.03	0.02	83.72	1.56
Fe	373.486	96.99	95.64	40.99	3.40	100.72	1.77	291.20	5.13
Mg	383.829	ND	ND	64.58	0.23	266.85	0.75	47.88	1.29
Mn	259.372	99.15	92.75	56.40	1.02	88.63	0.19	24.39	0.40
Ni	341.476	97.68	98.77	0.26	12.24	0.21	4.65	0.18	0.55
Zn	472.215	96.75	94.92	2784.74	0.69	28.16	1.02	15.62	0.92

Table 5. Results for matrix spike recoveries

Analyte	Wavelength (nm)	Sample-1 (ppm)	Spike recovery (%)	Sample-2 (ppm)	Spike recovery (%)	Sample-3* (ppm)	Spike recovery (%)
Al	396.152	7.91	107.74	245.6	ND	†	ND
B	249.773	0.01	ND	0.14	ND	0.788	ND
Co	340.511	-0.03	92.06	4.04	97.20	14.865	113.19
Cu	223.009	6.076	85.41	145.22	100.20	26.855	76.27
Fe	373.486	90.90	ND	54.46	97.60	†	ND
Mg	383.829	1.23	ND	476.32	ND	165.378 †	ND
Mn	259.372	0.18	97.7	164.72	119.60	15.205	76.89
Ni	341.476	0.00	95.99	0.6	107.60	2.416	109.1
Zn	472.215	2.81	88.93	88.1	123.20	32.806	67.28

* Sample-3 was subsequently diluted for analysis due to high concentration of Al and Fe.
† Overrange result

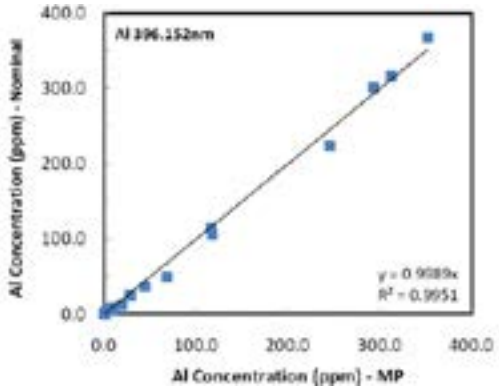

Figure 3a. Correlation between MP-AES results and nominal values for determination of Al

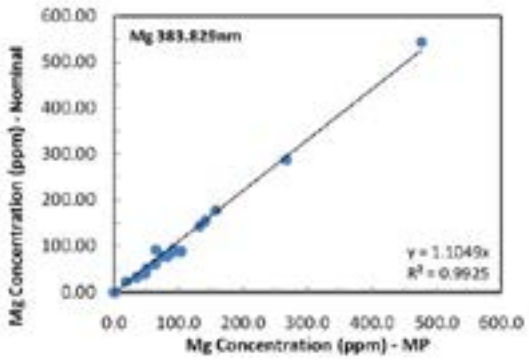

Figure 3c. Correlation between MP-AES results and nominal values for determination of Mg

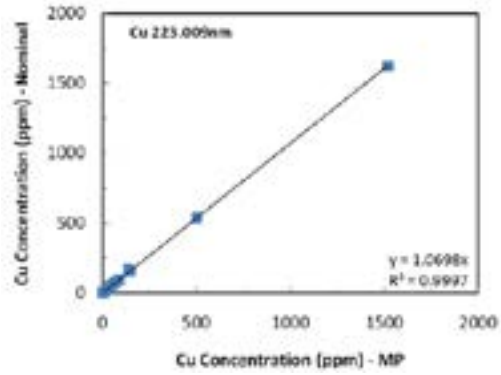

Figure 3b. Correlation between MP-AES results and nominal values for determination of Cu

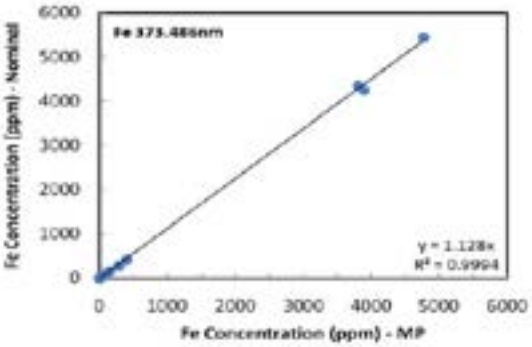

Figure 3d. Correlation between MP-AES results and nominal values for determination of Fe

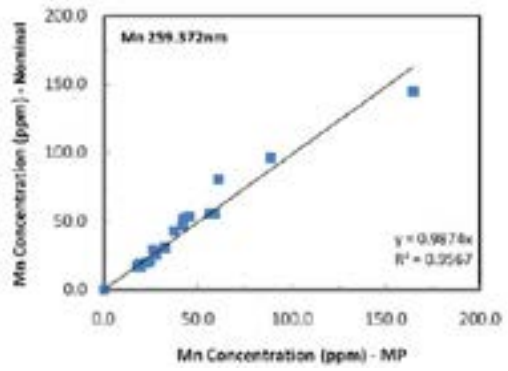

Figure 3e. Correlation between MP-AES results and nominal values for determination of Mn

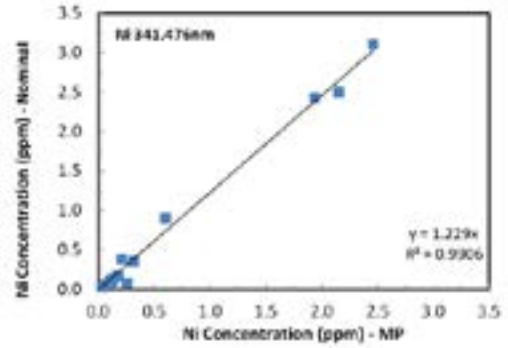

Figure 3f. Correlation between MP-AES results and nominal values for determination of Ni

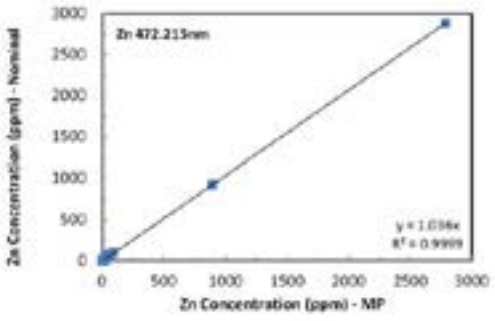

Figure 3g. Correlation between MP-AES results and nominal values for determination of Zn

Conclusions

Results obtained using the Agilent 4100 MP-AES for the analysis of highly-impacted wastewater samples including QC standards (ICV and CCV) and QC samples (MB, LCS, DUPs and MS) clearly indicate that MP-AES is a suitable atomic emission spectrometry technique for the determination of metal contaminants in waters. Method development, instrument optimization and sample analysis can be easily carried out using the intuitive MP Expert software. The analytical range can easily be extended using non-linear rational curve fitting for a single wavelength, therefore eliminating the usual practice of measuring multiple wavelengths or sample dilutions. Spectral interferences can be easily corrected using an Agilent propriety correction method (FLIC). Matrix spike recovery is within the accepted data quality objectives and therefore indicates that microwave plasma is capable of minimizing the potential sample matrix effects. The CCV results indicate no significant instrumental drift after 5 hours of continuous operation. The highly stable, self-sustained atmospheric pressure nitrogen plasma ensures the running costs of MP-AES are low — a key advantage for busy commercial laboratories. The simplicity of the instrument and easy-to-use MP Expert software is even suitable for novice analysts, with minimal training required for routine sample analysis.

Acknowledgement

The author would like to thank Steven McGrath at ALS Environmental Lab, Melbourne for supply of the industrial wastewaters.

Reference

1. M. R. Hammer, A magnetically excited microwave plasma source for atomic emission spectroscopy with performance approaching that of the inductively coupled plasma, Spectrochimica Acta, 456-464, 63B, 2008.

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Chemical/Petrochemical applications

Production demands and efficiency improvements impose increasingly tough demands on your business. Use rugged and reliable MP-AES to provide fast, accurate results for difficult samples.

With the lowest cost of ownership and improved ease of use, the reliable MP-AES instruments are ideal for challenging samples — from volatile organic solvents to used engine oils.

- Vertically oriented torch minimizes blockages, improving long term stability and reducing downtime
- Set up is easy — just plug in the External Gas Control Module (EGCM). No special torch or plasma settings are required
- EGCM injects air into the plasma, preventing carbon build up and reducing background
- Air injection rate is software controlled, and can be changed as you switch between different elements in the sample
- Rapid method development — auto-optimization enables you to select the optimum settings for each wavelength
- Perform sulfur determinations using a nitrogen purge of the optics
- The optional IsoMist programmable temperature controlled spray chamber accurately controls the temperature of the sample introduction system for improved stability with volatile organic solvents and viscous oils samples.

Direct multi-elemental analysis of crude oils using the Agilent 4200/4210 Microwave Plasma-Atomic Emission Spectrometer

Application note

Petrochemical, energy and fuels

Authors

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Introduction

Knowing the metal concentration of crude oil is vitally important to the petroleum industry at all stages of the product cycle. Metals are used to monitor crude migration within an oil reservoir; inform business opportunities; affect the efficiency of catalysts or render them inactive; as well as being integral to the final product quality and specification. Metals are also closely monitored to avoid environmental issues such as soil contamination from the decommissioning of petrochemical facilities and land reclamation.

Agilent Technologies

Typically, techniques such as inductively coupled plasma-optical emission spectroscopy (ICP-OES), ICP-mass spectrometry (ICP-MS), flame atomic absorption (FAAS), X-ray fluorescence (XRF), and neutron activation analysis (NAA) are used in petroleum labs for the identification and quantification of elements in aqueous or organic samples. However, Microwave Plasma-Atomic Emission Spectroscopy (MP-AES) technology is a suitable alternative for this industry, and is increasingly used for the multi-element analysis of a wide range of sample types, including complex organic matrices. In addition, elemental analysis is often required in the field or remote areas where the petroleum industry operates, which can be challenging depending on the location. Agilent's 4200 MP-AES uses magnetically coupled microwave energy to generate a robust and stable plasma using nitrogen gas. The nitrogen needed for the plasma is extracted straight from air using the Agilent 4107 nitrogen generator or from a nitrogen Dewar. Compared to conventional flame AA and ICP techniques, MP-AES eliminates the need for expensive and flammable gases like acetylene and argon gas to sustain the atomization/ionization source, resulting in lower running costs and safe unattended operation.

There are several ASTM methods for the determination of elements in crude oil analysis. For example, ASTM D7691 specifies ICP-OES for the analysis of S, V, Fe and Ni in crude oil after dilution with an organic solvent. Both ASTM D5708 and D5863 specify acid digestion or direct dilution with an organic solvent for the determination of Ni, V and Fe by ICP-OES and Ni, V, Fe and Na by FAAS respectively.

This application note describes the analysis of V, Ca, Fe, Ni, and Na in 20 crude oil samples using the Agilent 4200 MP-AES following a simple 1:10 dilution in *o*-xylene. Results obtained using a combination of ICP-OES and ICP-MS are given for comparison purposes. This application is also applicable for Agilent's 4210 MP-AES instrument.

Experimental

Instrumentation

All measurements were performed using an Agilent 4200 MP-AES, with nitrogen supplied from an Agilent 4107 Nitrogen Generator. The sample introduction system consisted of a MicroMist nebulizer, double pass glass cyclonic spray chamber and solvent resistant sample tubing. An External Gas Control Module (EGCM) accessory was used to inject a flow of air into the plasma to prevent carbon deposits from building up in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and to reduce background emissions caused by carbon species in the plasma.

The instrument is controlled by the intuitive MP Expert software. The MP-AES features continuous wavelength coverage and MP Expert software automatically adds the recommended wavelength, nebulizer flow rate, and EGCM setting when elements are selected for simplified method development. The powerful Auto background correction mode easily handles any background emission arising from the organic matrix, making accurate corrections without any user intervention.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b.

Table 1a. Agilent 4200 MP-AES operating conditions.

Parameter	Value
EGCM setting	Low
Pump rate (RPM)	5
Sample tubing	Viton Organic black/black
Waste tubing	Viton Organic blue/blue
Read time (s)	3
Number of replicates	3
Sample uptake delay (s)	55
Stabilization delay (s)	10
Fast pump during uptake	Yes
Background correction	Auto

Table 1b. List of analytes with wavelength and nebulizer flow.

Element	Wavelength (nm)	Nebulizer Flow (L/min)
Ca	396.847	0.7
Fe	259.940	0.7
K	769.897	0.7
Na	588.995	0.7
Ni	341.476	0.7
V	311.070	0.7
Sc (internal standard)	335.372	0.7

Standards and samples

Twenty crude oil samples covering a wide range of American Petroleum Institute (API) gravity, nitrogen and sulfur (N&S) content, and density were analyzed in this study.

Each crude oil sample was diluted ~ 1:10 in *o*-xylene (Fisher Scientific) by weight. A matrix modifier of mineral oil (Fisher Scientific), a dispersant (Chevron Oronite) and scandium (Conostan®), as the internal standard were added to all standards, samples and blanks, to give a total oil concentration of 10% (w/w) in each solution. Sample dilution reduces sample preparation time to a minimum compared to acid digestion ensuring that a wide range of samples can be analyzed in a timely manner whilst minimizing analyte loss and contamination.

Calibration standards were prepared for V, Ca, Fe, Ni, Na, and K at the 0, 2, 5 and 10 ppm level by diluting by weight with Conostan® S-21+K standard into pre-prepared *o*-xylene diluent. The *o*-xylene diluent containing a matrix modifier and Scandium internal standard was run as the blank for the calibration.

To test recoveries of Ca, Fe, K, Na, Ni and V, crude oil samples were spiked with 885 ppm of Conostan® S-21+K standard.

Results and discussion

Working calibration range

The calibration curve for Fe is presented in Figure 1, highlighting the working range for the MP-AES. All correlation coefficients were greater than 0.999 (Table 2).

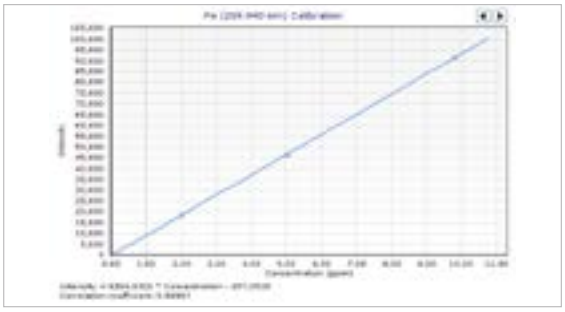

Figure 1. Calibration curve for Fe 259.940 nm.

Table 2. Wavelength and working calibration concentration range.

Element & wavelength (nm)	Concentration range (ppm)	Correlation coefficient	Calibration Fit
Fe 259.940	0-10	0.9999	Linear
V 311.070	0-10	1.0000	Rational
Ni 341.476	0-10	0.9999	Rational
Ca 396.847	0-10	1.0000	Rational
Na 588.995	0-10	1.0000	Rational
K 769.897	0-10	0.9998	Rational

Method Detection Limit

Method detection limits (MDLs) (3σ) were calculated by measuring 10 consecutive blank readings. The MDLs (Table 3) demonstrate the ability of the Agilent 4200 MP-AES to provide excellent detection limits.

Table 3. Method detection limits (ppm) for Fe, V, Ni, Ca, Na and K.

Element & wavelength (nm)	MDL (ppm)
Fe 259.940	0.016
V 311.070	0.009
Ni 341.476	0.008
Ca 396.847	0.015
Na 588.995	0.022
K 769.897	0.190

QC spike recovery tests

To check the validity of the method, three separate Quality Control (QC) spike recovery tests were carried out. First, a Continuing Calibration Verification (CCV) sample at the midpoint concentration of the calibration (5 ppm) was analyzed 7 times, with a recovery within ±10% of the target values.

Secondly, a crude oil sample was spiked with S21+K at 885 ppm to validate the method at a high concentration level, with all recoveries within ±10%. Finally, a certified reference sample, NIST 1634c Trace Elements in Fuel Oil (NIST, Gaithersburg MD) was analyzed 7 times for vanadium (certified at 28.19 ppm) and nickel (certified value of 17.54 ppm) only, with recoveries within ±10%. A summary of the data is given in Table 4.

Table 4. QC spike recovery results of a CCV sample, S21 + K spiked crude oil sample and NIST 1634c Trace Elements in Fuel Oil CRM.

	Element and wavelength (nm)					
	Fe 259.940	**V 311.070**	**Ni 341.476**	**Ca 396.847**	**Na 588.995**	**K 769.897**
5 ppm CCV sample (mean, n=7)	4.83	4.94	4.96	5.03	4.94	5.04
% Recovery	**97**	**99**	**99**	**101**	**99**	**101**
885 ppm S-21+K spiked sample (mean, n=7)	862.9	894.4	876.5	853.0	834.9	940.9
Certified value (ppm)	885.0	885.0	885.0	885.0	885.0	885.0
% Recovery	**98**	**101**	**99**	**96**	**94**	**106**
NIST 1634c CRM (mean, n=7)	-	30.95	18.03	-	-	-
Certified value (ppm)	-	28.19	17.54	-	-	-
% Recovery	-	**110**	**103**	-	-	-

Spike recoveries of a crude oil sample

Accuracy of the method was checked by spiking a crude oil sample in triplicate with S21 +K at 79.89 ppm for all analytes. The spike recovery results are shown in Table 5. For all analytes, recoveries were within the ±10% range of the target values. The results demonstrate the ability of the 4200 MP-AES to analyze Fe, V, Ni, Ca, and K spikes accurately.

Table 5. Results of 79.89 ppm concentration spike recovery test in a crude oil sample.

	Element and wavelength (nm)					
	Fe 259.940	**V 311.070**	**Ni 341.476**	**Ca 396.847**	**Na 588.995**	**K 769.897**
Average (ppm)	74.24	78.23	75.82	76.45	72.43	75.60
Spiked conc. (ppm)	76.89	76.89	76.89	76.89	76.89	76.89
% Recovery	**97**	**102**	**99**	**99**	**94**	**98**

Analysis of crude oil samples

The developed method for MP-AES was applied to the determination of Fe, V, Ni, Ca and Na in 20 crude oil samples. Displayed, in Tables 6a and 6b, are the results for three of the crude oil samples; S1, S10 and S20. The results presented show that the concentration level of each element varies between the different oil samples. Sample "S20" was analyzed in duplicate, with good agreement between the 2 sets of results.

Table 6a. Measured concentrations of metallic impurities in crude oil samples S1, S10 and S20 (ppm).

Sample	Fe 259.940 (nm)	SD	V 311.070 (nm)	SD	Ni 341.476 (nm)	SD
S1	0.46	0.13	13.86	0.03	9.51	0.05
S10	9.65	0.57	0.13	0.03	0.87	0.03
S20	130.99	1.05	87.48	0.21	68.08	0.18
*S20b	130.81	0.86	87.08	0.32	68.15	0.06

Table 6b. Measured concentrations of metallic impurities in crude oil samples S1, S10 and S20 (ppm).

Sample	Ca 396.847 nm	SD	Na 588.995 nm	SD
S1	<LOD	-	<LOD	-
S10	5.05	0.33	5.99	0.39
S20	58.29	0.27	26.59	0.41
*S20b	59.43	0.62	25.89	0.22

* Duplicate sample of S20

<LOD indicates the result was below the limit of detection

Comparative results with ICP-MS/ICP-OES

Quantitative measurements of Ni, V, Fe and Ca in the 20 crude oil samples by MP-AES were in good agreement with the data obtained using a combination of ICP-OES and ICP-MS, showing good correlation between techniques (Figure 2).

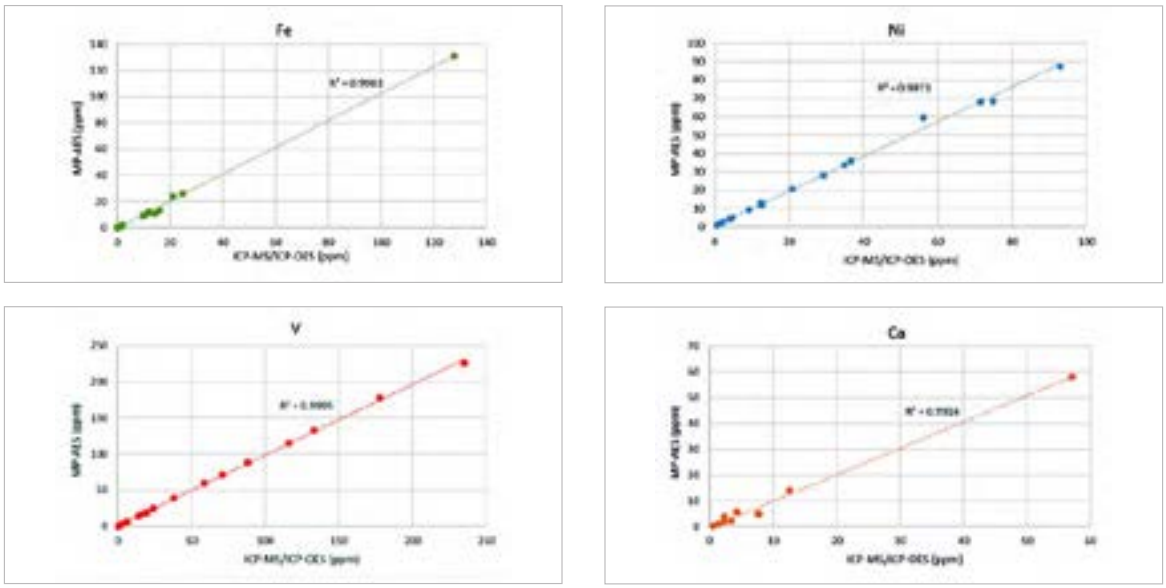

Figure 2. Comparison of measured values for Ni, V, Fe and Ca in crude oil samples obtained using a combination of ICP-MS & ICP-OES and MP-AES, including correlation coefficients.

Conclusions

The Agilent 4200 MP-AES fitted with the EGCM accessory was used successfully for the analysis of 20 crude oil samples following a simple 10x dilution in *o*-xylene, comparatively to preparation methods and procedures as defined in ASTM D7691.

Excellent detection limits and spike recoveries were achieved for Ni, V, Fe, Ca, Na and K in this difficult matrix.

The recoveries obtained from the analysis of the three QC test materials were within ±10% of the actual/certified values. A wide-API range of crude oil samples was evaluated and the MP-AES results compared well with measured values obtained by ICP-OES or ICP-MS.

The 4200's use of a nitrogen-based plasma eliminates the need for hazardous gases such as acetylene, ensuring a significant reduction in running costs associated with ongoing gas supply and greatly improving laboratory safety for unattended operation.

Productivity is further improved with the new generation of MP Expert software that facilitates simultaneous auto background correction and a series of ease-of-use features, including application-specific software applets plus plug-and-play hardware, that simplify method development and torch alignment, with minimal training.

Reference

J. Nelson, G. Gilleland, L. Poirier, D. Leong, P. Hajdu,and F. Lopez-Linares, Elemental Analysis of Crude Oils Using Microwave Plasma Atomic Emission Spectroscopy, *Energy & Fuels,* 2015, 29 (9), 5587–5594.

www.agilent.com/chem/4210mp-aes

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Determination of trace elements in isopropyl alcohol using an Agilent 4200 MP-AES with External Gas Control Module

Application note

Semiconductor and petrochemical

Authors

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Introduction

Isopropyl alcohol (IPA) is one of the most commonly used organic solvents in the semiconductor industry. Silicon wafers are dried after surface cleaning in the manufacturing process and IPA is frequently used during the drying step. The purity of IPA used is critical since these materials come in direct contact with the silicon wafers and any contaminants present at this stage could be detrimental to the overall performance of the final product.

Plasma-based instrumentation is widely used in the semiconductor industry due to its multielement capability and sensitivity compared to techniques such as Flame Atomic Absorption Spectroscopy (FAAS). However a robust plasma is required for the analysis of organic matrices. Microwave Plasma Atomic Emission Spectroscopy (MP-AES) uses magnetically-coupled microwave energy to generate a stable plasma that is highly suited to the analysis of organic solvents. The Agilent 4200 MP-AES features an advanced microwave cavity and a torch designed to handle a wide range of samples, with better detection limits and an increased working range, compared to FAAS. Major elements (Ca, K, Na and Mg) in IPA can be easily determined using MP-AES with little sample preparation.

The nitrogen used to generate the 4200's plasma can be generated from air using a nitrogen generator. This eliminates the need for the hazardous or expensive gases required by other techniques, reduces running costs and greatly improves laboratory safety. The instrument is relatively simple to use, even for inexperienced users. It has a plug-and-play torch and intuitive MP Expert software that facilitates instrument setup and method development with minimal training.

This application describes the direct determination of trace elements in undiluted, high purity IPA using the Agilent 4200 MP-AES fitted with an External Gas Control Module (EGCM).

Experimental

Instrumentation

Figure 1. External Gas Control Module (EGCM) accessory for the Agilent 4200 MP-AES

All measurements were performed using an Agilent 4200 MP-AES. In order to analyze Na, K, Mg, and Ca in IPA directly, without dilution, the instrument was fitted with an Agilent Organics Kit comprising the EGCM, inert OneNeb nebulizer, solvent resistant tubing, and a double pass spray chamber.

The EGCM (shown in Figure 1) injects air into the plasma. This prevents carbon deposition in the torch, overcomes any plasma instability that may arise from the analysis of organic samples, and reduces carbon based background emissions. The EGCM setting is selected automatically for each wavelength by the MP Expert software, but can be fine-tuned if required.

The OneNeb inert nebulizer is ideally suited to the analysis of organic solvents such as IPA. It offers increased nebulization efficiency and a narrow distribution of small droplets compared to other nebulizers.

The 4200 MP-AES operates in fast sequential mode and has a peltier cooled charge coupled device (CCD) detector which allows background and spectral interferences to be simultaneously corrected easily and accurately using the MP Expert software. Auto background correction mode was used to correct for any emission background arising from the organic matrix.

Instrument operating parameters and method conditions are listed in Tables 1 and 2.

Table 1. Agilent 4200 MP-AES operating conditions

Parameter	Value
Sample tubing	Orange/green solvent resistant
Waste tubing	Blue/blue solvent resistant
Read time (s)	3
Number of replicates	3
Sample uptake delay (s)	10
Stabilization delay (s)	10
Rinse time (s)	10 (fast pump: On)
Pump speed (rpm)	7

Table 2. MP-AES method conditions: list of analytes with wavelength, background correction, nebulizer flow and automatically-set EGCM settings.

Element	Wavelength (nm)	Background Correction	Nebulizer Flow (L/min)	EGCM Setting
Na	588.995	Auto	0.6	High
K	766.491	Auto	0.6	High
Mg	285.213	Auto	0.6	Low
Ca	393.366	Auto	0.6	Medium

Samples and sample preparation
Electronic grade IPA (99.9% purity) purchased from Dongwoo Fine-Chem Co., Ltd., South Korea was analyzed directly, without any sample preparation. IPA was spiked with a multi-element standard at 106.5 ppb to test the stability of the method.

Results and discussion

Linear Dynamic Range
The linear dynamic range (LDR) for Na, K, Mg, and Ca was determined by calibrating against a set of standards at 10 ppb, 50 ppb, 100 ppb and 200 ppb. All elements showed excellent linearity over the calibrated range with a correlation coefficient of >0.999 in all cases. The calibration curves for Na, K, Mg, and Ca are shown in Figure 2

Methods Detection Limits
Method Detection Limits (MDLs) were determined by analyzing 7 samples at a concentration of 106.5 ppb. For seven samples (with six degrees of freedom), the t value for a 99% confidence interval is 3.14. The MDLs were found to be under 5 ppb for all elements. Results are shown in Table 3.

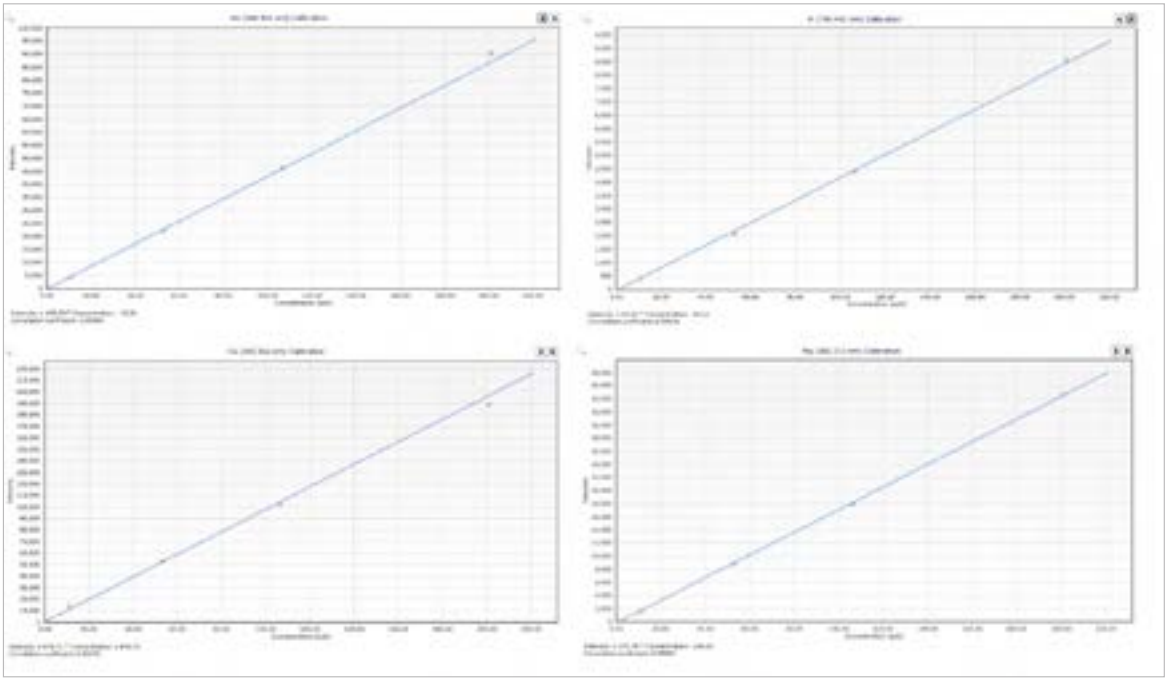

Figure 2. Calibration curves for Na 588.995, K 766.491, Ca 393.366 andMg 285.213

Spike recoveries

To test the method, a spike of 106.5 ppb was analyzed repeatedly over more than 3 hours. The average spike recovery for each element over the duration of the experiment was found to be within 97% to 102%. Spike recoveries are shown in Table 3.

Table 3. MDL, recovery of 106.5 ppb spike, and long term stability for Na, K, Mg, and Ca in IPA.

Element (ppb)	Wavelength (nm)	MDL (ppb)	Spike Recovery (%)	Long Term Stability (% RSD)
Na	588.995	2.5	100	1.4
K	766.491	3.0	97	1.4
Mg	285.213	2.8	102	1.6
Ca	393.366	3.8	97	0.9

Long term stability

The long term stability was measured for Na, K, Mg, and Ca spiked at 106.5 ppb in IPA. The stability plot is shown in Figure 3 and the %RSD for each element is given in Table 3. Excellent stability was achieved with %RSD of less than 2% over more than 3 hours.

Figure 3. Long term stability plot for Na, K, Mg, and Ca in IPA.

Conclusions

The Agilent 4200 MP-AES fitted with the EGCM accessory was successfully used to determine ppb levels of Na, K, Mg, and Ca in undiluted isopropyl alcohol. With method detection limits of less than 5 ppb for all elements, excellent spike recoveries within the range 97% to 102%, and long term stability of less than 2% RSD, the method is highly suited to the routine analysis of these 4 key elements in IPA.

The 4200 MP-AES offers:

- Improved performance and sample throughput compared to FAAS
- Ease-of-use through the MP Expert software and plug-and-play hardware that simplify method development and torch alignment, with minimal operator training
- Improved safety by eliminating hazardous or expensive gases, such as acetylene or argon
- Productivity gains with safe, unattended operation.

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Agilent Technologies

Measurement of additives in lubricating oils using the Agilent 4100 MP-AES

Application note

Energy and fuels

Authors

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Introduction

The regular tracking of the additives present in oils used to lubricate machinery is a vital preventive maintenance task used to gauge the condition of the lubricant and machine over time. Several compounds such as Zn, P, Ca, Ba and Mg are typically added to lubricating oils. These metal-containing additives act as detergents, oxidation and corrosion inhibitors, dispersants, anti-wear agents, viscosity index improvers, emulsifiers and anti-foaming agents etc.

With engines and machinery being central to most transport and manufacturing industries, many laboratories are required to analyze a high volume and variety of oil samples per day, for multiple elements. While flame atomic absorption spectrometry (FAAS) has been used extensively to study additives used in oils, the sheer number of samples has forced

many laboratories to consider a faster, multi-element technique that is capable of high sample throughput.

This can now be effectively achieved using fast sequential atomic emission spectroscopy in the form of the Agilent 4100 Microwave Plasma Atomic Emission Spectrometer (MP-AES). The 4100 uses magnetically coupled microwave energy to generate a robust and stable plasma using nitrogen gas. Both aqueous and organic samples can be introduced into the MP-AES with a good tolerance to organic solvent load.

Experimental

Instrumentation

An Agilent 4100 MP-AES was used with an External Gas Control Module (EGCM) for air injection into the plasma to prevent carbon deposition in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and to reduce background emissions. The instrument was set up with the Organics kit comprising the EGCM, the inert OneNeb nebulizer [1] and solvent resistant tubing, along with a double pass spray chamber. The OneNeb nebulizer offers superior performance for this application over other comparable nebulizers as it offers increased nebulization efficiency and a narrow distribution of small droplets. This allows the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, while maintaining excellent sensitivity. An Agilent SPS 3 Sample Preparation System was used for automatic sample delivery.

The instrument is controlled using Agilent's unique worksheet-based MP Expert software, which runs on the Microsoft® Windows® 7 operating system, and features automated optimization tools to accelerate method development by novice operators. For example, the software automatically adds the recommended wavelength, nebulizer pressure, and EGCM setting when elements are selected.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b. Viewing position and nebulizer pressure settings were optimized using the auto-optimization routines in MP Expert.

Samples and sample preparation

Standards were prepared at concentrations of 5 ppm, 10 ppm, 25 ppm and 50 ppm from a 500 ppm oil-based metal calibration standard S21+K (Conostan). Shellsol 2046 (Shell) was used as the diluent. All standards were matrix matched with 10% Blank Oil (Conostan).

NIST SRM 1085b Wear Metals in Lubricating Oil was prepared by performing a 1:10 dilution in Shellsol.

A sample of mixed gear oils were diluted 1:100 with Shellsol and a spiked with S21+K giving a final spike concentration of 10.1 mg/kg.

Table 1a. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	Inert OneNeb
Spray chamber	Double-pass glass cyclonic
Sample tubing	Orange/green solvent-resistant
Waste tubing	Blue/blue solvent-resistant
Read time	3 s
Number of replicates	3
Stabilization time	15 s
Rinse time	45 s
Fast pump during sample uptake	On
Background correction	Auto
Pump speed	5 rpm

Table 1b. Analyte nebulizer pressures and EGCM settings

Element & wavelength (nm)	Nebulizer pressure (kPa)	EGCM setting
Mg 285.213	180	High
Ca 422.673	240	High
Zn 481.053	120	High
Ba 614.171	240	High
P 213.618	120	Medium

Calibration parameters

The calibration fit and correlation coefficients for the elements analyzed are shown in Table 2. Rational fit is a non-linear curve fit and allows an extended working range so that sample analysis can be carried out using a single wavelength without further dilutions being required. The excellent correlation coefficients demonstrate the capability of the MP-AES to cover the

range of concentrations expected in this analysis. The calibration curve for Zn is shown in Figure 1.

Table 2. Analyte calibration fits and correlation coefficients

Element & wavelength (nm)	Calibration fit	Correlation coefficient
Ba 614.171	Rational	0.99908
Ca 422.673	Linear	0.99958
Mg 285.213	Rational	0.99933
Zn 481.053	Linear	0.99999
P 213.618	Rational	0.99998

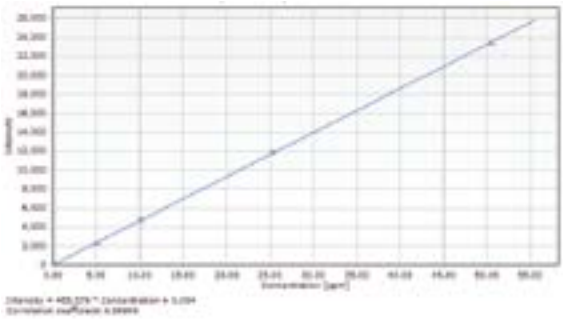

Figure 1. Calibration curve for Zn 481.0.53 nm showing excellent linearity up to 50 ppm with a correlation coefficient of 0.99999

Results and discussion

Analysis of standard reference materials

To test the validity of the method, NIST SRM 1085b was analyzed. The results given in Table 3 show excellent agreement (accuracy) between the MP-AES measured results and the certified values.

Table 3. Measured results versus certified values

Element & wavelength (nm)	Measured concentration (mg/kg)	Certified (mg/kg)	Recovery (%)
P 213.618	301.5 ± 0.1	299.9 ± 7.2	101
Zn 481.053	314.9 ± 0.3	296.8 ± 6.8	106
Mg 285.213	300.6 ± 0.2	297.3 ± 4.1	101
Ca 422.673	279.6 ± 0.1	(298)	94
Ba 614.171	281.2 ± 0.1	300.1 ± 2.4	94

Spike recoveries

The recoveries obtained for the spiked mixed gear oil sample are given in Table 4. Excellent recoveries were obtained for all elements analyzed, demonstrating the validity of the analytical method. The spectrum for Zn is shown in Figure 2.

Table 4. Accurate recovery for all analytes of 10 ppm spikes in a mixed gear oils sample

Element & wavelength (nm)	Unspiked gear oil (ppm)	Spiked gear oil (ppm)	Spike recovery (%)
P 213.618	17.16	26.71	95
Zn 481.053	6.99	17.17	101
Mg 285.213	1.53	11.32	97
Ca 422.673	8.89	19.69	107
Ba 614.171	0.00	9.16	91

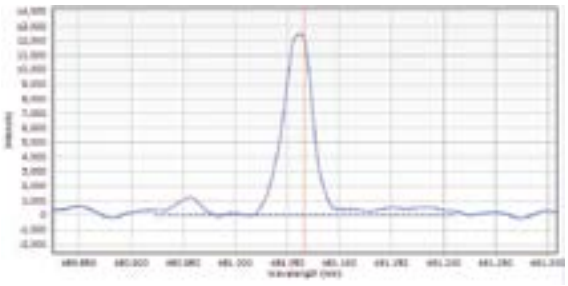

Figure 2. The spectrum for Zn 481.053 nm corrected with Auto background correction

Conclusions

The new Agilent 4100 MP-AES equipped with a OneNeb [1] nebulizer and fitted with the EGCM is an ideal solution for the routine multi-element analysis of additives in oils. The nitrogen-based plasma excitation source exhibits a high tolerance to organic solvent load. Furthermore, the Agilent 4100 MP-AES has the lowest operating costs of comparable techniques such as flame AA, and by using non-flammable gases, removes safety concerns associated with acetylene and nitrous oxide. By injecting a controlled flow of air into the plasma via the EGCM to prevent carbon buildup in the injector, excellent recoveries were achieved on SRM samples and on spike solutions at the 10 ppm level.

Reference

1. J. Moffett and G. Russell, "Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer", Agilent Application Note 5990-8340EN

www.agilent.com

Published October 12, 2012
Publication number: 5990-8925EN

Agilent Technologies

Analysis of wear metals and contaminants in engine oils using the 4100 MP-AES

Application note

Energy and fuels

Authors

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Introduction

The regular tracking of the metals present in oils used to lubricate machinery is a vital preventive maintenance task used to gauge the condition of the lubricant and machine over time. Analysts are particularly interested in the elements found in engines, such as Cu, Fe and Al, which are present in the oil as a result of wear and tear, and elements like Na and Si, which are present as a result of contamination from water or road dust. The trend analysis of these metals is performed on the oils so that any action required to keep the engine in service can be taken and costly repairs and downtime can be avoided.

With engines and machinery being central to most transport and manufacturing industries, many laboratories are required to analyze a high volume and variety of oil samples a day, for multiple elements. While flame atomic absorption spectrometry (FAAS) has been used extensively to study trace wear metals in used oils, the sheer number of samples has forced many laboratories to consider a faster, multi-element technique that is capable of high sample throughput.

This can now be effectively achieved using fast sequential atomic emission spectroscopy in the form of the Agilent 4100 Microwave Plasma Atomic Emission Spectrometer (MP-AES). The 4100 MP-AES uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. Both aqueous and organic samples can be introduced into the MP-AES, which has good tolerance to the organic solvent load.

Experimental

Instrumentation

An Agilent 4100 MP-AES was used with an External Gas Control Module (EGCM) allowing air injection into the plasma to prevent carbon deposition in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and to reduce background emissions. The instrument was set up with the Organics kit comprising the EGCM, the inert OneNeb nebulizer [1] and solvent resistant tubing, along with a double pass spray chamber. The OneNeb nebulizer offers superior performance for this application over other comparable nebulizers as it offers increased nebulization efficiency and a narrow distribution of small droplets. This allows the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, while maintaining excellent sensitivity. An Agilent SPS 3 Sample Preparation System was used for automatic sample delivery.

The instrument is controlled using Agilent's unique worksheet-based MP Expert software, which runs on the Microsoft® Windows® 7 operating system, and features automated optimization tools to accelerate method development by novice operators. For example, the software automatically adds the recommended wavelength, nebulizer pressure, and EGCM setting when elements are selected.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b. Viewing position and nebulizer pressure settings were optimized using the auto-optimization routines in MP Expert. Rational fit is a non-linear curve fit and allows an extended working range so that sample analysis can be carried out using a single wavelength without further dilutions being required.

Samples and sample preparation

Standards were prepared at concentrations of 5 ppm, 10 ppm, 25 ppm and 50 ppm from a 500 ppm oil-based metal calibration standard S21+K (Conostan). Shellsol 2046 (Shell) was used as the diluent. All standards were matrix-matched with 10% Blank Oil (Conostan).

NIST SRM 1085b Wear Metals in Lubricating Oil was prepared by performing a 1:10 dilution in Shellsol.

A sample consisting of a mix of used gear oils was diluted 1:10 with Shellsol and spiked with S21+K, giving a final spike concentration of 10.2 ppm.

Table 1a. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	Inert OneNeb
Spray chamber	Double-pass glass cyclonic
Sample tubing	Orange/green solvent-resistant
Waste tubing	Blue/blue solvent-resistant
Read time	3 s
Number of replicates	3
Stabilization time	15 s
Rinse time	45 s
Fast pump (80 rpm) during sample uptake	On
Background correction	Auto
Pump speed	5 rpm

Table 1b. Analyte nebulizer pressures and calibration cuves

Element & wavelength (nm)	Nebulizer pressure (kPa)	Calibration curve
Cd 228.802	140	Rational
Mn 259.372	120	Rational
Fe 259.940	100	Rational
Cr 276.653	140	Rational
Pb 283.305	220	Rational
Sn 303.411	240	Rational
Ni 305.081	180	Linear
V 310.229	220	Rational
Mo 319.398	240	Rational
Ti 323.452	220	Rational
Cu 327.395	200	Linear
Ag 328.068	200	Linear
Al 396.152	240	Rational
Na 589.592	240	Linear
Si 251.611	140	Linear

Results and discussion

Analysis of standard reference materials

To test the validity of the method, NIST SRM 1085b was analyzed. The results presented in Table 2 show excellent agreement (accuracy) between the MP-AES measured results and the certified values.

Table 2. Measured results versus certified values

Element & wavelength (nm)	Measured (mg/kg)	Certified (mg/kg)	Recovery (%)
Fe 259.940	314.7 ± 0.3	301.2 ± 5.0	104
Mn 259.372	289.9 ± 0.2	300.7 ± 2.0	96
Cd 226.502	290.9 ± 2.9	302.9 ± 5.1	96
Cr 276.653	305.2 ± 0.1	302.9 ± 3.9	101
Si 251.611	295.7 ± 1.9	300.2 ± 5.0	99
Ni 305.081	291.6 ± 0.1	295.9 ± 7.4	99
Cu 327.395	300.9 ± 0.1	295.6 ± 8.5	102
Ag 328.068	308 ± 0.2	304.6 ± 8.9	101
Pb 283.305	296.1 ± 0.1	297.7 ± 6.8	99
V 310.229	287.6 ± 0.1	297.8 ± 4.6	97
Ti 323.452	293.9 ± 0.1	301.1 ± 2.9	98
Sn 303.411	295.3 ± 0.3	299.4 ± 4.8	99
Mo 319.398	296.9 ± 0.1	300.6 ± 3.2	99
Al 396.152	291.7 ± 0.2	300.4 ± 9.3	97
Na 589.592	297.4 ± 0.1	305.2 ± 7.0	97

Spike recoveries

The recoveries obtained for the spiked mixed gear oil sample are presented in Table 3. Excellent recoveries were obtained for all elements analyzed, demonstrating the validity of the analytical method. The signal graph and calibration curve for Cu are shown in Figures 1 and 2 respectively.

Table 3. Accurate recovery for all analytes of 10 ppm spikes in a mixed gear oils sample

Element	Wavelength (nm)	Unspiked gear oil (ppm)	Spiked gear oil (ppm)	Spike recovery (%)
Ag	328.068 nm	0.27	11.01	105
Al	396.152 nm	0.32	10.31	98
Cd	228.802 nm	0.14	9.85	95
Cr	276.653 nm	0.25	9.92	95
Cu	327.395 nm	2.68	13.14	103
Fe	259.940 nm	10.41	20.09	95
Mn	259.372 nm	0.80	11.54	105
Mo	319.398 nm	9.02	19.34	101
Na	589.592 nm	0.46	10.70	100
Ni	305.081 nm	0.07	10.13	99
Pb	283.305 nm	0.25	11.36	109
Si	251.611 nm	2.23	11.60	92
Sn	303.411 nm	0.16	10.62	103
Ti	323.452 nm	0.01	10.87	106
V	310.229 nm	0.15	10.71	104

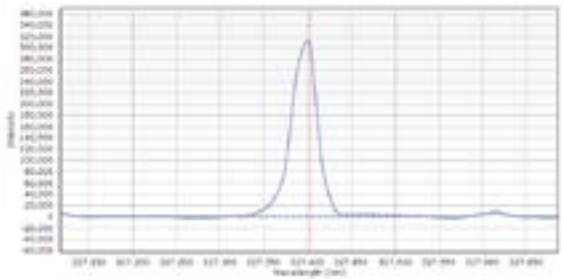

Figure 1. The signal from Cu 327.395 nm at 5 ppm shows the excellent sensitivity of the Agilent 4100 MP-AES

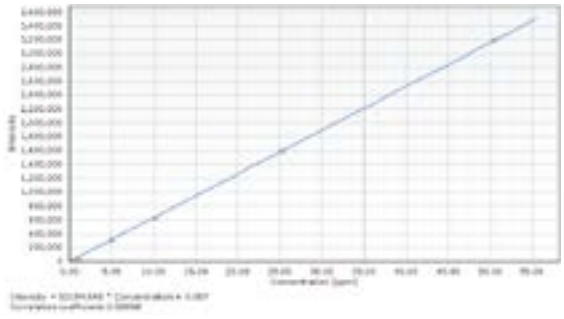

Figure 2. The calibration curve for Cu 327.395 nm up to 50 ppm shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99998

Using the Agilent SPS 3 Sample Preparation System, the sample throughput time for the analysis was under 5 minutes per sample, or about 13 samples per hour. With the ability to run unattended, the 4100 MP-AES is capable of greater sample throughput than FAAS.

Long-term stability

Long-term stability of the MP-AES was investigated by continuously aspirating a 10 ppm S21+K solution over an 8 hour period. The resulting stability plot is shown in Figure 3, and the %RSDs for each element are listed in Table 4.

The sample handling capability of the vertically-oriented plasma in the 4100 MP-AES, combined with the air injection from the EGCM and the solids handling of the inert OneNeb nebulizer [1] means that excellent long-term stability (< 1% RSD) can be achieved, even when analyzing challenging organic samples.

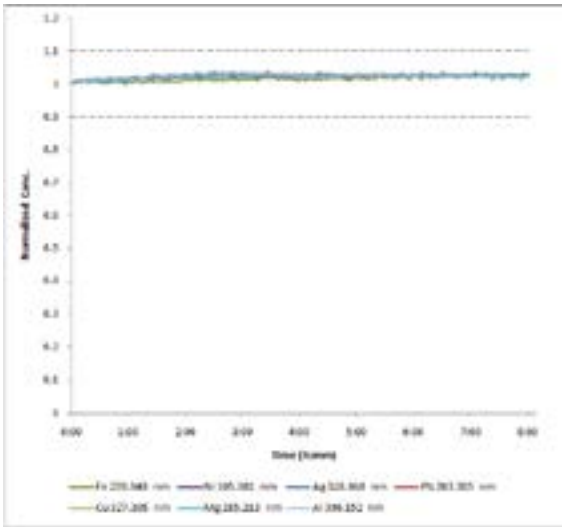

Figure 3. Normalized stability plot for 10 ppm S21+K solution run repeatedly over an 8 hour period

Table 4. %RSDs for each element spiked at 10 ppm level over an 8 hour sampling period

Element	Wavelength (nm)	%RSD
Fe	259.940	0.7
Ni	305.081	0.5
Ag	328.068	0.5
Pb	283.305	0.6
Cu	327.395	0.6
Al	396.152	0.6

Conclusions

The Agilent 4100 MP-AES equipped with a OneNeb nebulizer and fitted with the EGCM is an ideal solution for the routine multi-element analysis of wear metals in oils. Furthermore, the Agilent 4100 MP-AES has the lowest operating costs of comparable techniques such as flame AA, and by using non-flammable gases, removes safety concerns associated with acetylene and nitrous oxide. By injecting a controlled flow of air into the plasma via the EGCM to prevent carbon buildup in the injector, excellent recoveries were achieved for SRM samples and on spiked solutions at the 10 ppm level. Excellent long-term stability was also achieved.

Reference

1. J. Moffett and G. Russell, “Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer”, Agilent Application Note 5990-8340EN

www.agilent.com/chem/4210mp-aes

Published September 1, 2011
Publication number: 5990-8753EN

Analysis of diesel using the 4100 MP-AES

Application note

Energy and fuels

Authors

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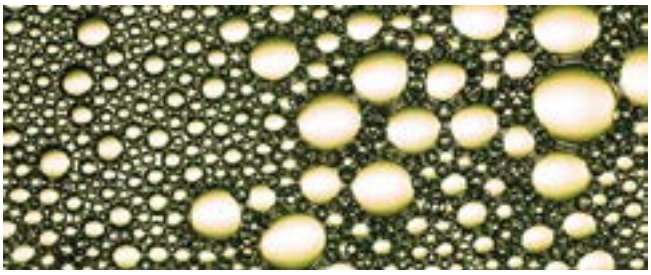

Introduction

The presence of certain trace elements in petro-diesel and biodiesel fuels can cause corrosion and deposition on engine or turbine components, especially at elevated temperatures. Some diesel fuels therefore specify the maximum levels of these elements to guard against the occurrence of engine deposits. For instance ASTM method D6751 specifies a limit of 5 ppm for the combined concentration of Ca and Mg, and 5 ppm for the combined concentration of Na and K [1]. Trace elemental analysis is used to determine the level of contamination of diesel fuels.

The Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES) uses magnetically-coupled microwave energy to generate a robust and stable plasma using nitrogen gas. This stable plasma is capable of analyzing not only aqueous solutions, but also challenging organic matrices. When compared to conventional flame AA, the 4100 MP-AES eliminates expensive and dangerous gases such as acetylene, resulting in lower running costs, unattended operation, and improved productivity.

This application note describes the determination of trace elements in diesel fuels using the Agilent 4100 MP-AES.

Experimental

Instrumentation

The Agilent 4100 MP-AES was fitted with an External Gas Control Module (EGCM) allowing air injection into the plasma to prevent carbon deposition in the torch, overcome any plasma instability that may arise from the analysis of organic samples, and reduce background emissions. The instrument was set up with the Organics kit comprising of the EGCM, the inert OneNeb nebulizer [2] and solvent resistant tubing, along with a double pass spray chamber. The OneNeb nebulizer offers increased nebulization efficiency and a narrow distribution of small droplets. This allows the analysis to be performed at lower flow rates, reducing the solvent loading on the plasma, whilst maintaining excellent sensitivity.

The instrument was controlled using Agilent's unique worksheet-based MP Expert software, which runs on the Microsoft® Windows® 7 operating system, and features automated optimization tools to accelerate method development by novice operators. For example, the software automatically adds the recommended wavelength, nebulizer pressure, and EGCM setting when elements are selected. Also, the powerful Auto background correction mode easily and accurately corrects for the emission background arising from the organic matrix.

Instrument operating conditions and analyte settings are listed in Tables 1a and 1b.

Table 1a. Agilent 4100 MP-AES operating conditions

Instrument parameter	Setting
Nebulizer	Inert OneNeb
Spray chamber	Double-pass glass cyclonic
Sample tubing	Orange/green solvent-resistant
Waste tubing	Blue/blue solvent-resistant
Read time	3 s
Number of replicates	3
Sample uptake delay	15 s
Stabilization time	30 s
Fast pump during sample uptake	On
Background correction	Auto
Pump speed	5 rpm

Table 1b. Analyte viewing positions, nebulizer pressures and EGCM settings

Element & wavelength (nm)	Nebulizer pressure (kPa)	EGCM setting
Mg 285.213	240	High
Ca 422.673	240	High
Na 588.995	240	High
K 766.491	240	High

Samples and sample preparation

Method EN 14538 [3] was followed for the analysis of the diesel samples. Calibration standards were prepared at concentrations of 0.5 ppm, 1 ppm, 5 ppm and 10 ppm by diluting a 500 ppm S21+K solution (Conostan) with Shellsol (Shell). All standards were matrix matched with Blank Oil 75 (Conostan).

A commercial diesel sample was spiked with S21+K at the 0.5 ppm level and the spikes were measured to validate the method.

Results and discussion

Detection limits

Method detection limits were calculated as the concentration equivalent to 3 standard deviations of 10 blank diesel measurements. The detection limits reported in Table 2 are in solution, and are sufficiently low for the requirements of the analysis. These detection limits demonstrate the ability of the 4100 MP-AES to handle tough organic samples, provide excellent detection limits at low sample flow rates, and handle the challenging background from carbon emissions using the power and simplicity of auto background correction.

Table 2. Method detection limits (ppb) for Mg, Ca, K, and Na

Element	Wavelength (nm)	MDL (ppb)
Mg	285.213	2.7
Ca	422.673	8.2
Na	588.995	18.7
K	766.491	2.7

Spike recoveries

The spike recoveries in diesel fuel are shown in Table 3. The spike concentration was 0.55 ppm and all recoveries were within ±10% of the target value. The excellent recoveries demonstrate the ability of the 4100 MP-AES to accurately determine Mg, Ca, Na and K at the levels required in the diesel fuel samples. A typical spectrum and calibration graph for K are shown in Figures 1 and 2 respectively.

Table 3. Results of spike recovery test

Element and wavelength (nm)	Sample (ppm)	Spike (ppm)	Recovery (%)
Mg 285.213	< MDL	0.53	97
Ca 422.673	< MDL	0.51	93
Na 588.995	< MDL	0.51	93
K 766.491	< MDL	0.51	93

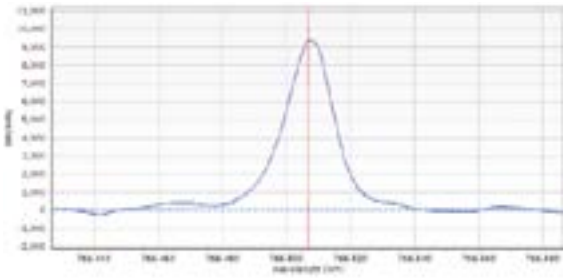

Figure 1. Signal for K 766.491 at 0.5 ppm showing the excellent sensitivity of the 4100 MP-AES when analyzing fuel samples

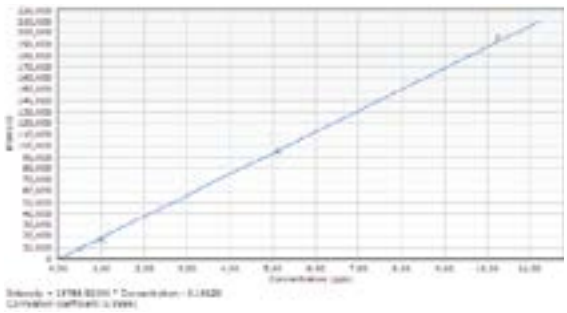

Figure 2. Calibration curve for K 766.491 showing excellent linearity across the calibrated range and a correlation coefficient of 0.99991

Conclusions

The Agilent 4100 MP-AES equipped with the OneNeb nebulizer and the EGCM provides an ideal solution for the routine analysis of semi-volatile organic samples such as diesel. The nitrogen-based plasma excitation source exhibits a high tolerance to the organic solvent load and the easy-to-use yet powerful features of the MP Expert software, such as the auto background correction mode, ensure excellent detection limits. By injecting a controlled flow of air into the plasma via the EGCM to prevent carbon buildup in the injector, excellent calibrations, detection limits, and recoveries were achieved in spiked diesel fuel samples at levels likely to be encountered in this analysis (low ppm).

Furthermore, the Agilent 4100 MP-AES has the lowest operating costs of comparable techniques such as flame AA, and by using non-flammable gases, removes safety concerns associated with acetylene and nitrous oxide. The 4100 MP-AES also improves sample throughput and removes the need for consumables like hollow cathode lamps.

Reference

1. ASTM D6751 – 11b, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, www.astm.org

2. J. Moffett and G. Russell, "Evaluation of a novel nebulizer using an inductively coupled plasma optical emission spectrometer", Agilent Application Note 5990-8340EN

3. EN 14538:2006, Fat and oil derivatives – Fatty acid methyl ester (FAME) – Determination of Ca, K, Mg and Na content by optical emission spectral analysis with inductively coupled plasma (ICP OES), European Committee for Standardization, www.cen.eu

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Direct analysis of Cr, Ni, Pb and V in ethanol fuel by Microwave Plasma-Atomic Emission Spectrometry

Application note

Energy and fuels

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Abstract

A simple dilute-and-shoot procedure for determination of Cr, Ni, Pb and V in ethanol fuel by Microwave Plasma-Atomic Emission Spectrometry (MP-AES) is proposed. Samples were easily prepared and neither special nor expensive gases were needed for performing analyses. All limits of detection from 0.3–40 µg/L were compatible with the requirements taken into account when considering fuel impacts on environment and engine performance.

Chemical/Petrochemical Applications

Introduction

Ethanol fuel has been commonly used in automobiles since the first petroleum crisis in the middle of the 1970s. More recently, the large number of flexfuel engines available, combined with the environmental advantages of using this renewable source of energy, have boosted the production and consumption of ethanol around the world. In Brazil, this fuel is produced from sugar cane, which provides high yields and is an example of a sustainable source of energy [1].

The presence of metals in fuels may reduce engine performance and/or deteriorate the quality of the fuel by oxidative decomposition reactions [2]. In addition, some potentially toxic elements can be naturally present in ethanol as a result of the soil composition where the sugar cane has grown. Alternatively, these elements can be introduced into the fuel during its production, storage and/or transport. Thus, after fuel combustion, these elements can significantly increase air pollution [3].

In this application note, we present the direct analysis of ethanol fuel for determination of Cr, Ni, Pb and V using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). This instrument is based on a nitrogen plasma, which is generated by magnetically-coupled microwave energy. One of its main advantages is the reduced costs of operation and maintenance. No separate gas source is required, since a nitrogen gas generator and a simple air compressor are sufficient to run the plasma. In this work, accurate results were obtained simply by diluting ethanol samples with 1% v/v HNO_3 aqueous solutions.

Experimental

Instrumentation

All measurements were carried out with the Agilent 4100 MP-AES. The sample introduction system was composed of solvent-resistant tubing, a double-pass cyclonic spray chamber and the inert OneNeb nebulizer. Because fuel samples were directly introduced with no previous treatment but dilution in aqueous solution, air was injected into the nitrogen plasma by an external gas control module (EGCM) to avoid carbon deposition on the torch or the pre-optics window. The injection of air also contributed to maintaining the plasma stability and reducing background emission.

Background correction was performed automatically using the Auto Background Correction in the Agilent MP Expert software, which records, stores and subtracts the background spectrum for each element. The background spectrum is obtained from a blank solution. This spectrum is then subtracted from all reference and sample solutions. In addition, parameters such as nebulizer pressure and viewing position for each monitored wavelength can be automatically optimized. Tables 1 and 2 show the instrumental operating conditions and settings to determine Cr, Ni, Pb and V in ethanol fuel samples.

Table 1. Agilent 4100 MP-AES operating conditions for the direct analysis of ethanol fuel samples

Instrument parameter	Operating condition
Nebulizer	Inert OneNeb
Spray chamber	Cyclonic double-pass
Read time (s)	5
Number of replicates	3
Stabilization time (s)	15
Background correction	Auto

Table 2. Nebulizer pressures and EGCM settings for Cr, Ni, Pb and V measurements

Element	Wavelength (nm)	Nebulizer pressure (kPa)	EGCM*
Cr	425.433	240	High
Ni	352.454	180	High
Pb	405.781	100	High
V	437.923	240	High

Reagents and standard solutions

Nitric acid (Merck, Darmstadt, Germany) previously purified by a sub-boiling distillation system (Milestone, Sorisole, Italy) was used to prepare all solutions. Stock mono-element solutions containing 1000 mg/L of Cr, Ni, Pb or V (Tec-Lab, Hexis, São Paulo, SP, Brazil) were used to prepare standard reference solutions and to carry out spike experiments. Analytical grade ethanol (J. T. Baker, Hexis, São Paulo, SP, Brazil) was used to matrix-match the standard reference solutions used to build the analytical calibration curves.

Samples and sample preparation

Ethanol fuel samples (hydrated ethanol) were obtained in local gas stations in São Carlos, SP, Brazil. According to the Brazilian legislation, the maximum allowable amount of water in hydrated ethanol fuel is 4.9% v/v [4]. Samples were diluted 10-fold in HNO_3 1% v/v. Standard reference solutions used in the external calibration method were prepared by diluting adequate volumes of inorganic standard solutions of Cr, Ni, Pb or V in 1% v/v HNO_3. Ethanol was also added to each standard reference solution to a final concentration of 10% v/v.

Results and discussion

Figures of merit

The analytical performance for each analyte was evaluated before the sample analysis. Limits of detection (LOD) and quantification (LOQ) were calculated by using the background equivalent concentrations (BEC), the signal-to-background ratios (SBR) and the relative standard deviations for 10 consecutive blank measurements in each case. Table 3 presents the LOD and LOQ values obtained. From these data one can notice the superior detection power of the 4100 MP-AES when compared to flame atomic absorption spectrometry (FAAS), for example. The microwave plasma is especially advantageous for refractory elements such as Cr and V. In this case, the higher temperatures reached in the plasma allow for lower LODs, with no addition of special gases as would be the case in FAAS determinations with nitrous oxide-acetylene flames [5].

To evaluate accuracy in direct analyses of ethanol fuel samples, spike experiments were performed with at least two different concentrations of each analyte added to the sample solution. Results are presented in Table 4. For all analytes evaluated, recoveries varied from 92 to 108% indicating low intensity of matrix effects commonly caused by organic compounds and concomitant elements such as Cu, Na, and Fe.

Table 3. Figures of merit for Cr, Ni, Pb and V determinations in ethanol fuel by MP-AES.
* Instrumental limits of detection and quantification.
† Limit of detection considering sample dilution (1:9 v/v ethanol fuel in HNO_3 1% v/v).

Element	LOD* (µg/L)	LOQ* (µg/L)	LOD in the sample† (µg/kg)
Cr	0.7	2.2	9
Ni	16	52	200
Pb	40	130	490
V	0.3	0.9	4

Table 4. Spike experiments for Cr, Ni, Pb and V determination in ethanol fuel samples

Element	Added (µg/L)	Found (µg/L)	Recovery (%)
Cr	20	21.2 ± 1.2	106
	100	95.1 ± 1.2	95
	500	460 ± 30	92
Ni	100	95.3 ± 0.8	95
Pb	400	430 ± 10	108
	1000	990 ± 10	99
V	20	19.8 ± 1.6	99
	100	98.4 ± 1.4	98
	500	460 ± 20	92

Conclusions

The direct analysis of ethanol fuel samples using the Agilent 4100 MP-AES is a simple and effective method that can easily be implemented in routine analysis. Four samples were analyzed and none were contaminated. A simple dilute-and-shoot procedure, with solutions in 1% v/v HNO_3, was adequate for accurate and precise determinations of Cr, Ni, Pb and V in ethanol. The EGCM prevented carbon deposition on the torch or on the pre-optical components and contributed to reduce the background signals and improve accuracy.

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References

1. Silva, J. E., Silva, F. A., Pimentel, M. F., Honorato, R. S., Silva, V. L., Montenegro, M. C. B. S. M. & Araújo, A. N. (2006). A flow-batch internal standard procedure for iron determination in hydrated ethanol fuel by flame atomic absorption spectrometry. *Talanta, 70*, 522–526.

2. Oliveira, M. F., Saczk, A. A., Okumura, L. L., Fernandes, A. P., Moraes, M. & Stradiotto, N. R. (2004). Simultaneous determination of zinc, copper, lead, and cadmium in fuel ethanol by anodic stripping voltammetry using a glassy carbon-mercury film electrode. *Anal. Bioanal. Chem., 380*, 135–140.

3. Saint'Pierre, T. D., Maranhão, T. A., Frescura, V. L. A. & Curtius, A. J. (2005). The development of a method for the determination of trace elements in fuel alcohol by electrothermal vaporization - inductively coupled plasma mass spectrometry using external calibration. *Spectrochim. Acta Part B, 60*, 605–613.

4. Brazilian National Agency of Petroleum, Natural Gas and Biofuels. Resolution ANP 7, D.O.U. 10.2.2011.

5. Amorim, F. A. C., Welz, B., Costa, A. C. S., Lepri, F. G., Vale, M. G. R. & Ferreira, S. L. C. F. (2007). Determination of vanadium in petroleum and petroleum products using atomic spectrometric techniques. *Talanta, 72*, 349–359.

www.agilent.com/chem

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Agilent Technologies

Determination of silicon in diesel and biodiesel by Microwave Plasma-Atomic Emission Spectrometry

Application note

Energy and fuels

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Introduction

The presence of metals and metalloids in petrochemical products can influence the performance of engines, and contribute to shortening the lifetime of the machinery. In addition, some elements act as catalyst poison, contributing to increases in the amount of toxic gases and particulate matter emitted by vehicles. Silicon compounds such as siloxanes, for example, are added to diesel as anti-foaming agents. During combustion, these compounds decompose to form silicon oxide, which can form a coating layer on the catalyst element of the exhaust system and significantly increase air pollution [1]. Thus, regulation in this field of analysis is increasingly common and recent legislation in Brazil has established the maximum concentration of Si plus Al in diesel as 80 mg kg^{-1} [2].

This application note describes the determination of Si in diesel and biodiesel samples using the Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). This instrument produces a robust and stable plasma using magnetically-coupled microwave energy. A nitrogen gas generator feeds the microwave plasma and no additional gas source is required to run the instrument, which significantly reduces operating costs.

Different sample preparation procedures were evaluated and the instrument robustness was demonstrated by analyzing samples diluted in 90% ethanol. In this case, adequate recoveries were achieved even by applying a simple non-matrix-matched external calibration method with aqueous standard solutions.

Experimental

Instrumentation

The Agilent 4100 MP-AES was used in all determinations. The sample introduction system was composed of solvent-resistant tubing, a double-pass cyclonic chamber and the inert OneNeb nebulizer. This nebulizer provides a more homogeneous aerosol, with smaller and narrow-distributed particles, which increases nebulization efficiency and improves sensitivity [3].

An external gas control module (EGCM) was used to inject air into the plasma and prevent carbon deposition on the torch and the optical components. This device also contributes to plasma stability and background emission reduction in organic sample analyses.

The Agilent MP Expert software allows automatic background correction (Auto), improving precision and accuracy. The Auto background correction consists of recording, storing and automatically subtracting a background spectrum from each standard and sample solution analyzed. The MP Expert software also performs the optimization of nebulizer pressure and viewing position for each wavelength used. In this work, a standard reference solution used to obtain the analytical calibration curve was also used to very quickly and easily optimize such parameters. The instrumental operating conditions and settings to determine Si are presented in Tables 1 and 2.

Table 1. Agilent 4100 MP-AES operating conditions for Si determination in diesel and biodiesel samples

Instrument parameter	Operating condition
Nebulizer	Inert OneNeb
Spray chamber	Cyclonic double-pass
Read time (s)	10
Number of replicates	3
Stabilization time (s)	15
Background correction	Auto

Table 2. Silicon viewing positions, nebulizer pressures and External Gas Control module (EGCM) settings

Sample medium	Wavelength (nm)	Nebulizer pressure (kPa)	EGCM
Micro-emulsion	251.611	100	Medium
	288.158	120	Medium
Aqueous	251.611	120	Medium
	288.158	160	Medium

A closed-vessel microwave oven (Ethos 1600, Milestone, Sorisole, Italy) equipped with 45 mL PFA vessels was employed for the digestion of diesel and biodiesel samples.

Reagents and standard solutions

Nitric acid (Merck, Darmstadt, Germany) previously purified by a sub-boiling distillation system (Milestone), and hydrogen peroxide 30% m/m (Synth, São Paulo, SP, Brazil) were employed to digest the samples. Polyoxylene(10)octylphenil ether (Triton X-100, Acros Organics, Geel, Belgium), n-propanol and light mineral oil (Tedia, Rio de Janeiro, RJ, Brazil), without any additional purification, were used for the preparation of micro-emulsions. A 1000 mg/L Si stock solution (Tec-Lab, Hexis, São Paulo, SP, Brazil) was adequately diluted to prepare aqueous and micro-emulsion standard reference solutions and to carry out spiking studies in digested samples and micro-emulsions. Analytical grade ethanol (J. T. Baker, Hexis, São Paulo, SP, Brazil) was used for direct sample dilution. A Si 1000 mg/L stock solution in organic medium (Conostan, Quimlab, Jacareí, SP, Brazil) was used in spike studies of ethanol-diluted diesel and biodiesel samples. External calibration with aqueous standard reference solutions in HNO_3 1% v/v was performed for Si determination in both the digested samples and those simply diluted in 90% v/v ethanol.

Samples and sample preparation

Biodiesel samples were provided by the Center of Characterization and Development of Materials (CCDM, Federal University of São Carlos, São Carlos, SP, Brazil). Diesel fuel samples containing 5% v/v of biodiesel (B5), in accordance to the Brazilian legislation [4], were obtained in local gas stations of São Carlos, SP, Brazil.

Three sample preparation procedures were evaluated: microwave-assisted digestion, micro-emulsion preparation in n-propanol, and dilution in ethanol. The sample digestions were performed by using 50% v/v HNO_3 (7 mol/L) and 3.0 mL of H_2O_2 30% m/m. Table 3 presents the heating program employed.

Table 3. Heating program for the microwave-assisted acid digestion of diesel and biodiesel samples

Step	Applied power (W)	Time (min)	Temperature (°C)
1	250	2	80
2	0	3	80
3	550	4	120
4	650	5	200
5	750	5	200

Micro-emulsions were prepared by adding 0.5 mL of Triton X-100 and 0.5 mL of a 20% v/v HNO_3 aqueous solution to 1.0 mL of diesel or biodiesel. The volume was then made up to 10 mL with n-propanol and the mixture was homogenized for 2 min with a vortex mixer [5]. During the preparation of the micro-emulsion standard reference solutions, the sample was replaced by 0.2 mL of mineral oil, which simulates the sample matrix viscosity. The direct dilution of samples in ethanol was carried out by adding 9 mL of the solvent to 1 mL of sample.

Results and discussion

Instrumental limits of detection in different media

Limits of detection (LOD) and quantification (LOQ) for both 1% v/v HNO_3 and micro-emulsion media were calculated by using the background equivalent concentrations (BEC) and the signal-to-background ratios (SBR) obtained with a Si 1.0 mg/L standard reference solution and 10 consecutive blank measurements in each case. The LOD and LOQ values are presented in Table 4.

Table 4. Figures of merit for silicon determination by MP-AES.
a = Linear dynamic range starting at the limit of detection.
b = Repeatability presented as the relative standard deviation for a 2 mg/L Si solution (n = 10).

	HNO_3 1% v/v			Micro-emulsion		
	LOD (µg/L)	LDR[a] (Decades)	RSD[b] (%)	LOD (µg/L)	LDR[a] (Decades)	RSD[b] (%)
Si (251.611 nm)	20	2.3	1.6	5	2.6	1.6
Si (288.158 nm)	240	0.9	1.3	5	2.5	0.4

Considering the legislation for Si [2], all three procedures developed presented adequate sensitivity for application in quality control. It is important to note that the plasma produced by the 4100 MP-AES is stable and it was not extinguished even by introducing high concentrations of n-propanol or ethanol. Moreover, no carbon deposition was observed either on the torch or on the pre-optic window after several hours of operation.

Accuracy

The accuracy of all three procedures was evaluated using spike studies with both sample matrices. For the digested samples and the micro-emulsions, volumes of 3.0 or 1.0 mg/L of Si in aqueous medium were respectively added either after the digestion or directly to the samples during the micro-emulsion preparation. Two different spike concentrations were evaluated for the ethanol dilution procedure: 0.5 and 1.0 mg/L of Si in organic medium. Results are shown in Table 5 and all recoveries were between 80 and 102%.

The combination of a homogeneous nebulization obtained through using the OneNeb nebulizer, the efficient background reduction from the EGCM and the reliable background correction provided by the Auto feature of the software were all fundamental to obtaining precise and accurate results for the analyses of such high carbon matrices.

Table 5. Spike experiments for Si determination in diesel and biodiesel after sample digestion, dilution in 90% v/v ethanol or micro-emulsion preparation. Concentrations reported in mg/L.
a = Spike solution in aqueous medium. b = Spike solution in organic medium.

Sample	Si emission line (nm)	Digestion[a]		Ethanol[b]		Micro-emulsion[a]	
		Added	Recovered	Added	Recovered	Added	Recovered
Biodiesel	251.611	3.0	3.05 ± 0.07	0.5	0.45 ± 0.03	1.0	0.89 ± 0.05
				1.0	0.99 ± 0.09		
	288.158	3.0	3.05 ± 0.01	0.5	0.40 ± 0.04	1.0	0.89 ± 0.06
				1.0	1.02 ± 0.17		
Diesel	251.611	3.0	3.09 ± 0.10	0.5	0.47 ± 0.01	1.0	0.96 ± 0.03
				1.0	0.91 ± 0.01		
	288.158	3.0	3.07± 0.15	0.5	0.46 ± 0.01	1.0	0.96 ± 0.04
				1.0	0.95 ± 0.01		

Conclusions

Silicon determination is not an easy task, especially for fuel matrices, which present high viscosity and a high carbon load. In this work, accurate Si determinations were successfully carried out simply by diluting the samples in ethanol and using external calibration with aqueous solutions. The sample preparation procedures evaluated are environmentally friendly since less toxic solvents are used. In addition, high sample throughput can easily be achieved in routine, unattended automated analyses. No carbon deposit or reduction of performance was observed while introducing high carbon loads to the Agilent 4100 MP-AES without the use of a cooled spray chamber. Two important advantages of this instrument are its low running costs and laboratory safety, as no expensive or flammable gases are required. Considering cost, performance and multielement capabilities, the Agilent 4100 MP-AES is a suitable and efficient alternative to flame AA for this application and presents better performance for critical elements such as the one investigated here. The simple dilution in ethanol and external calibration with aqueous solutions is recommended for the determination of Si in diesel and biodiesel samples considering its simplicity and sample throughput.

References

[1] Sánchez, R., Todolí, J. L., Lienemann, C. P. & Mermet, J. M. (2009). Effect of the silicon chemical form on the emission intensity in inductively coupled plasma atomic emission spectrometry for xylene matrices. *J. Anal. At. Spectrom. 24*, 391–401.

[2] Brazilian National Agency of Petroleum, Natural Gas and Biofuels. Resolution ANP 52 of December, 2010, DOU 30/12/2010.

[3] Aguirre, M. A., Kovachev, N., Almagro, B., Hidalgo, M. & Canals, A. (2010). Compensation for matrix effects on ICP-OES by on-line calibration methods using a new multi-nebulizer based on Flow Blurring technology. *J. Anal. At. Spectrom., 25*, 1724–1732.

[4] Brazilian National Agency of Petroleum, Natural Gas and Biofuels. Resolution ANP 6 of October, 2009, DOU 26/10/2009.

[5] Amais, R. S., Garcia, E. E., Monteiro, M. R. & Nóbrega, J. A. (2012). Determination of Ca, Mg, and Zn in biodiesel micro-emulsions by FAAS using discrete nebulization. *Fuel, 93*, 167–171.

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Determination of major elements in methanol using the Agilent 4200 MP-AES with External Gas Control Module

Application note

Petrochemical

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Introduction

The conversion of Methanol to Olefins (MTO) is fast gaining momentum as an alternative approach to the production of light olefins (ethylene and propylene) over conventional methods such as naphtha steam and fluid catalytic cracking. Already commercially viable in China, MTO offers low costs of production by utilizing the abundant supply of methanol feedstock produced from natural gas and coal. However, catalysts used during the MTO process are susceptible to deactivation by certain impurities in the methanol feedstock. Major elements such as calcium, potassium, magnesium and sodium present in methanol can interfere with catalytic activity during the MTO process.

Microwave Plasma Atomic Emission Spectrometry (MP-AES) is becoming increasingly popular as a lower cost and safer alternative to Flame Atomic Absorption Spectrometry (FAAS) for multi-elemental analysis of organic samples. For labs handling organic solvents, the presence of the flame of an FAAS is a concern, requiring constant supervision.

The Agilent 4200 MP-AES uses magnetically-coupled microwave energy to generate a robust and stable plasma, capable of the direct measurement of major elements in organic solvents.

Advantages of MP-AES

- Safe technique with low running costs: the microwave plasma is generated using nitrogen gas from a Dewar or a nitrogen generator. This eliminates the need for expensive and/or hazardous gases and allows for unattended operation over long time periods.

- High performance for difficult organic samples: with the use of the External Gas Control Module (EGCM) accessory, air can be added to the plasma to prevent carbon build up and reduce background emissions from carbon species in the plasma.

- Ease of use: intuitive MP Expert software routines and automated hardware features such as the Plug and Play torch simplify instrument set-up and method development.

This application note describes the determination of major elements in methanol using the Agilent 4200 MP-AES fitted with an EGCM accessory.

Experimental

Instrumentation

All measurements were performed using the Agilent 4200 MP-AES fitted with an Agilent Organics Kit comprising the EGCM, OneNeb nebulizer and solvent resistant tubing, in conjunction with the IsoMist programmable temperature controlled spray chamber. By injecting air into the plasma, the EGCM prevents any plasma instability that may arise from the analysis of organic samples by minimizing carbon build up on the torch. It also reduces carbon emissions from the organic solvent leading to increased sensitivity and lower detection limits. As an example, the Instrument Detection Limits (IDLs) in methanol for K 766.491 nm were determined using the 4200 MP-AES with and without the EGCM accessory. The IDLs were found to be 1.23 and 0.24 ppb respectively, showing that lower IDLs are achievable using the EGCM for organic solvents.

The OneNeb inert nebulizer offers high nebulization efficiency of organic solvents and a narrow distribution of small droplets compared to other nebulizers. A cooled spray chamber was used in order to reduce vapor loading on the plasma. Instrument operating parameters and method conditions are listed in Table 1.

Table 1. Agilent 4200 MP-AES operating conditions

Parameter	Value			
Element	Ca	Mg	Na	K
Wavelength (nm)	422.673	285.213	588.995	766.491
Read time (s)	10	5	10	5
Background correction	Off-peak	Auto	Off-peak	Auto
Nebulizer	OneNeb			
Nebulizer flow rate (L/min)	1			
Spray chamber	IsoMist temperature controlled spray chamber			
Spray chamber temp (°C)	0			
Pump rate (rpm)	10			
Sample pump tubing	Orange/Green Organic			
Waste pump tubing	Blue/Blue Organic			
EGCM	On			
Air injection flow rate	High			
Number of replicates	3			
Sample uptake delay (s)	10			
Rinse time (s)	30			
Stabilization time (s)	10			
Gas source	Dewar nitrogen			

Samples and sample preparation

A pre-distillation crude methanol (100% purity) sample obtained from a commercial production process was used for the analysis. The sample was analyzed directly, without any sample preparation.

Multi-elemental calibration standards of Ca, K, Mg and Na were prepared from Agilent 1000 mg/L single element stock solutions at concentrations of 25 ppb, 50 ppb, and 100 ppb. All calibration blanks and standards were prepared using crude methanol as the diluent.

To test for the recovery of Ca, K, Mg and Na in methanol, a sample was spiked with 30 ppb of each elemental standard.

Results and discussion

Working concentration range

All elements showed excellent linearity over the calibrated range with each calibration coefficient being >0.999 (Table 2) and with <10% calibration error for each point for all elements (Table 3). Figure 1 shows the calibration curve for Na 588.995 nm.

Table 2. Wavelength and working calibration concentration range

Element and line (nm)	Concentration Range (ppb)	Concentration coefficient
Ca 422.673	0-100	0.99946
Mg 285.213	0-100	0.99978
Na 588.995	0-100	0.99988
K 766.491	0-100	0.99963

Figure 1. The calibration curve for Na 588.995 nm shows excellent linearity across the calibrated range, with a correlation coefficient of 0.99988.

Table 3. Calibration error (%) for each calibration point for Na 588.995 nm

Standards	Calibration error (%)
Blank	0.00
Standard 1- 25 ppb	4.15
Standard 2- 50 ppb	1.11
Standard 3- 100 ppb	0.01

Methods Detection Limits (MDLs)

The MDLs shown in Table 4 are based on three sigma of ten replicate measurements of the 30 ppb spiked sample carried out during the analytical run. An MDL of less than 3 ppb was achieved for each of the four elements analyzed.

Table 4. Element wavelengths and MDLs

Element	Wavelength (nm)	MDL (ppb)
Ca	422.673	1.57
K	766.491	1.35
Mg	285.213	0.93
Na	588.995	2.75

Spike recoveries

To validate the method, ten replicate measurements of the methanol sample, spiked at 30 ppb, were analyzed. This was performed on two instruments, with three determinations on each, for a total of six runs. The plug and play torch was re-loaded on each occasion, to demonstrate the ability of the MP to achieve reproducible results. The average spike recovery for each element was found to be within 97 to 102%, with good precision. The measured values for Ca, Mg, Na, K in methanol were within ±10% of the assigned value. The results are shown in Table 5.

Table 5. Spike recoveries for Ca, K, Mg and Na at 30 ppb in methanol

Element	Ca 422.673	K 766.491	Mg 285.413	Na 588.995
Measured value (mean, n=6, ppb)	29.17	30.16	30.58	30.11
Assigned value (ppb)	30	30	30	30
% RSD	1.79	1.50	1.02	3.05
% Recovery	97	101	102	100

Long term stability (LTS)

The LTS of the Agilent 4200 MP-AES was measured by continuously analyzing the methanol sample, spiked with Na, K, Mg, and Ca at 30 ppb, over a 2 hour period. The resulting stability plot (Figure 2) demonstrates excellent stability (<4% RSD) for all four elements (Table 6).

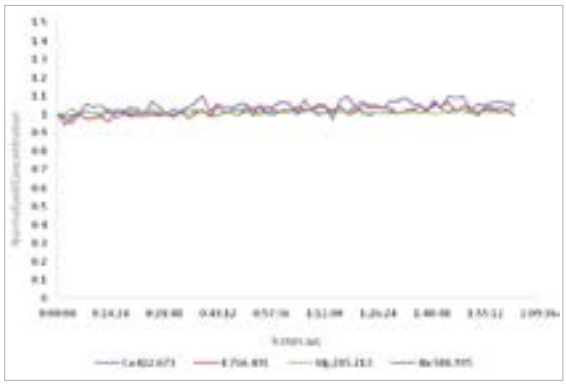

Figure 2. Normalized concentration of Ca, K, Mg and Na in a 30 ppb spiked methanol sample measured over 2 hours.

Table 6. LTS % RSD results for 30 ppb Ca, K, Mg and Na in methanol

Element	Wavelength (nm)	%RSD
Ca	422.673	1.55
K	766.491	2.34
Mg	285.213	1.00
Na	588.995	3.25

Conclusions

The Agilent 4200 MP-AES is highly suited to the analysis of volatile organic solvents. In this study the EGCM accessory and Isomist temperature controlled spray chamber ensured excellent plasma stability, allowing the direct analysis of methanol for Na, K, Ca and Mg at the ppb level. The MP-AES demonstrated:

- High analytical performance with MDLs at single figure ppb level and 30 ppb spike recoveries for all elements within ±10% of the target values.
- Excellent Long Term Stability with %RSD values less than 4% for all four elements.

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