QuikChem® Method 12-107-06-5-A

DETERMINATION OF AMMONIA IN 2 M KCl SOIL EXTRACTS BY FLOW INJECTION ANALYSIS

(Gas Diffusion Method)

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QuikChem® Method 12-107-06-5-A

Ammonia in 2 M KCl Soil Extracts

(Gas Diffusion)

0.1 to 20.0 mg N/L as NH_3

– Principle –

The sample containing ammonium is injected into a continuous carrier stream by means of an injection valve, and is mixed with a continuously flowing stream of an alkaline solution. The ammonia is separated from the matrix in a diffusion cell over a hydrophobic semipermeable membrane and taken up by a flowing recipient stream containing a pH indicator. Due to the resulting pH shift, the indicator solution changes color, which is measured continuously at 590 nm in the flow photometer. The sample loop size is required to be changed to measure NH_3 in the two different concentration ranges.

– Interferences –

1. Volatile amines will diffuse through the membrane and lead to a pH shift. If the concentration of volatile amines (e.g. methylamine or ethylamine) are equal to those of the ammonium, erroneously high results may be expected. In significant cases, prior to analysis an online distillation of the sample, adjusted to a pH of 5.8 may be necessary.
2. Interferences may occur in exceptional cases when the sample does not reach a pH of at least 12 after the addition of the alkaline reagent solution, since then ammonium will not quantitatively be converted into ammonia. In particular, this may occur with strongly acidic or highly buffered samples. In those cases, the pH of the sample should be adjusted to 3 to 5 by the addition of a sodium hydroxide solution.
3. High concentration of metal ions may precipitate as hydroxides. This is eliminated with the addition of EDTA to the alkaline solution.

– Special Apparatus –

Please see Parts and Price list for Ordering Information

1. Diffusion cell (Lachat Part No. 50332) with Teflon tape 1 ½" (Lachat Part No. 50331).

CONTENTS

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DETERMINATION OF AMMONIA IN 2 M KCl SOIL EXTRACTS BY FLOW INJECTION ANALYSIS

1. SCOPE AND APPLICATION

1.1. This method covers the determination of ammonia in 2 M KCl soil extract solutions.

1.2. The method is based on the diffusion of ammonia through a hydrophobic semipermeable membrane.

1.3. The analytical range is 0.1 to 20 mg N/L. The statistically calculated method detection limit is 0.02 mg N/L. The method throughput is 30 injections per hour.

2. INTERFERENCES

2.1. Volatile amines will diffuse through the membrane and lead to a pH shift, causing a positive interference.

2.2. Interferences may occur in exceptional cases when the sample does not reach a pH of at least 12 after the addition of the alkaline reagent solution, since then ammonium will not quantitatively be converted into ammonia. In particular, this may occur with strongly acidic or highly buffered samples. In those cases, the pH of the sample should be adjusted to 3 to 5 by the addition of a sodium hydroxide solution.

2.3. High concentration of metal ions may precipitate as hydroxides. This is prevented by the addition of EDTA to the alkaline solution.

3. SAFETY

3.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

3.2. Each laboratory is responsible for maintaining a current awareness file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

3.3. The following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

  3.3.1. Hydrochloric Acid

  3.3.2. Sodium Hydroxide

4. EQUIPMENT AND SUPPLIES

4.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

4.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

4.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

4.3.1. Sampler

4.3.2. Multichannel proportioning pump

4.3.3. Reaction unit or manifold

4.3.4. Colorimetric detector

4.3.5. Data system

4.4. Special Apparatus

4.4.1. Diffusion cell (Lachat Part No. 50330) with Teflon tape 1 ½” (Lachat Part No. 50331)

5. REAGENTS AND STANDARDS

5.1. PREPARATION OF REAGENTS

Use deionized water (10 megohm) for all solutions.

Degassing with helium:

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in^2) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

Reagent 1. Sodium Hydroxide, 5 M

By Volume: In a **1 L** volumetric flask, dissolve **200 g sodium hydroxide** (NaOH) in approximately **600 mL DI water**. Mix with a magnetic stirrer. **Caution:** The flask will become very hot! Cool the flask and dilute to the mark with **DI water**. Mix with a magnetic stirrer.

Reagent 2. Sodium Hydroxide, 0.1 M

By Volume: In a **1 L** volumetric flask, dissolve **0.40 g sodium hydroxide** (NaOH) in approximately **600 mL DI water**. Dilute to the mark with **DI water**. Mix with a magnetic stirrer.

Reagent 3. Hydrochloric Acid, 1 M

By Volume: In a **1 L** volumetric flask add approximately **600 mL DI water**. Cautiously add **82.6 mL concentrated hydrochloric acid** (HCl). Mix with a magnetic stirrer and dilute to the mark with **DI water**.

Reagent 4. Hydrochloric Acid, 0.1 M

By Volume: Pipette **100 mL** of **1 M hydrochloric acid** (Reagent 3) into a **1 L** volumetric flask. Dilute to the mark with **DI water** and mix with a magnetic stirrer.

Reagent 5. Hydrochloric Acid, 0.01 M

By Volume: Pipette **100 mL** of **0.1 M hydrochloric acid** (Reagent 4) into a **1 L** volumetric flask. Dilute to the mark with **DI water** and mix with a magnetic stirrer.

Reagent 6. Stock Mixed Indicator

In a mortar prepare a dry mixture consisting of **10 g bromocresol purple, sodium salt** (Aldrich Chemical Co., Catalog No. 86,089-1), **5 g bromothymol blue, sodium salt** (Aldrich Chemical Co., Catalog No. 11,442-1), **2.5 g cresol red, sodium salt** (Aldrich Chemical Co., Catalog No. 11,448-0) and **45 g potassium chloride**. The given quantities can be reduced (e.g., by one tenth). **1.25 g** of **Stock Mixed Indicator** will make **250 mL** of **Stock Indicator Solution**.

Reagent 7. Stock Indicator Solution

By Volume: In a **250 mL** volumetric flask, dissolve **1.25 g** of the **stock mixed indicator** (Reagent 6) in **62.5 mL 0.01 M sodium hydroxide** (Reagent 2). Add approximately **180 mL DI water**. The solution has a bright orange-red color. If it has a blue color, add **1.0 M hydrochloric acid** (Reagent 3) until the color changes. Dilute to the mark with **DI water**. Filter off any undissolved particles. This solution can be stored at room temperature for three months in a brown glass bottle.

Reagent 8. Ammonia Recipient Solution

By Volume: To a graduated **500 mL** volumetric flask, add **10 mL stock indicator solution** (Reagent 7) and approximately **480 mL DI water**. The absorbance of the solution should be 0.3 to 0.5 at 590 nm (path length 10 mm). An absorbance of 0.3 to 0.5 results in a pH between 5.42 to 5.74 pH units. Otherwise, add dropwise **0.01 M sodium hydroxide** (Reagent 2) until an absorbance value of 0.3 to 0.5 is obtained (pH 5.42 to pH 5.74). Dilute to the mark with **DI water**.

Degas solution with helium and let it stand for two hours before using.

Immediately before starting the analysis, check the **absorbance** and adjust, if necessary, to the absorbance specified above by adding **0.01 M sodium hydroxide** (Reagent 2) or **0.01 M hydrochloric acid** (Reagent 5). This solution can be stored at room temperature for two weeks in a glass bottle, but the absorbance must be checked prior to use.

Reagent 9. Alkaline Donor Solution

By Volume: To a **1 L** volumetric flask add approximately **800 mL DI water** and **30.0 g ethylenediamine tetraacetic acid, disodium salt** (Aldrich Chemical Co., Catalog No. 25,235-2). Mix with a magnetic stirrer. Add **12.4 g boric acid** (Aldrich Chemical Co., Catalog No. 18,509-4). While mixing add dropwise to the suspension **100 mL** of **5 M sodium hydroxide** (Reagent 1). Dilute to the mark with **DI water**. Degas this solution by filtering it through a 0.45 μm filter. The **pH** of this solution will be approximately **13**. This solution can be stored in a plastic bottle (polyethylene) at room temperature. This solution is stable for one month.

Reagent 10. 2 M KCl (Standard Diluent)

By Volume: In a **1 L** volumetric flask, add about **800 mL DI water**, then add **150 g potassium chloride** (KCl). Dilute to the mark with **DI water** and invert three times to mix. This solution will be used for standard preparation, scale up volume if necessary.

5.2. PREPARATION OF STANDARDS

To prepare the stock and working standards, the following containers will be required:

By Volume: One 1 L and five 100 mL volumetric flasks per working range.

By Weight: One 1 L and five 100 mL containers per working range.

Standard 1. Stock Standard 1000 mg N/L as NH_3

By Volume: In a **1 L** volumetric flask dissolve **3.819 g ammonium chloride** (NH_4Cl) in approximately **500 mL of Reagent 10**. Dilute to the mark with **Reagent 10** and mix with a magnetic stirrer. This solution may be stored in a refrigerator for at least three months.

Standard 2. Stock Standard 100 mg N/L as NH_3

By Volume: In a **1 L** volumetric flask add **100 mL Standard 1** (1000 mg N/L). Dilute to the mark with **Reagent 10** and invert to mix. This solution may be stored in a refrigerator for at least a week.

Working Standards (Prepare Daily)	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**
Concentration mg N/L as NH_3	20.0	10.0	5.0	2.0	1.0	0.5	0.25	0.10	0.0

By Volume

Volume (mL) of **stock standard 2** diluted to 100 mL with **Reagent 10.**	20	10	5.0	2.0	1.0	---	---	---	---
Volume (mL) of **working standard A** diluted to 100 mL with **Reagent 10.**	---	---	---	---	---	2.5	1.25	0.5	---

By Weight

Weight (g) of **stock standard 2** diluted to final weight (~100 g) divided by **factor** below with **Reagent 10.**	20	10	5.0	2.0	1.0	---	---	---	---
Weight (g) of **working standard A** diluted to final weight (~100 g) divided by **factor** below with **Reagent 10.**	---	---	---	---	---	2.5	1.25	0.5	---
Division Factor Divide exact weight of the standard by this **factor** to give the final weight	0.2	0.1	0.05	0.02	0.01	0.025	0.0125	0.005	---

6. SAMPLE COLLECTION, PRESERVATION AND STORAGE

6.1. Containers of glass, polyalkylenes and polytetrafluoroethylene (PTFE) are suitable for sample collection. All containers coming in contact with the sample shall be thoroughly cleaned with hydrochloric acid (Reagents 3,4, or 5) and shall be rinsed several times with DI water.

6.2. Analyze the samples immediately after collection. Alternatively, add sulfuric acid to adjust to a pH of approximately 2, store at 2 to 5°C in the dark, and analyze within the next 24 hours.

6.3. In exceptional cases, the sample may be stored up to two weeks, provided the sample has been membrane-filtered after acidification. The applicability of this preservation procedure shall be checked for each individual case of examination.

6.4. If there is a risk of clogging the pump or the manifold tubing the samples shall be filtered before analysis.

7. PROCEDURE

7.1. SAMPLE PRETREATMENT PROCEDURE

7.1.1. Interferences may occur in exceptional cases when the sample does not reach a pH of at least 12 after the addition of the alkaline reagent, since then ammonium will not be converted quantitatively into ammonia. In particular, this may occur strongly acidic or buffered samples. In such cases, the pH of the sample should be adjusted to 3 to 5 by the addition of sodium hydroxide solution (Reagents 1 or 2).

7.1.2. Particulates in the samples must be filtered before analysis.

7.2. CALIBRATION PROCEDURE

7.2.1. Prepare reagent and standards as described in Section 5.

7.2.2. Set up manifold as shown in Section 11.

7.2.3. Input data system parameters as shown in Section 11.

7.2.4. Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

7.2.5. Place samples and/or standards in the sampler. Input the information required by the data system, such as concentration, replicates and QuikChem scheme (See Section 11).

7.2.6. Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the instrument responses for each standard.

7.3. SYSTEM NOTES

7.3.1. For information on system maintenance and troubleshooting refer to the Troubleshooting Guide in the System Operation Manual. This guide is also available on request from Lachat.

7.3.2. **Placement of the Teflon membrane in the diffusion cell:**

7.3.2.1. Cut a piece of Teflon membrane 12 cm long. This Teflon membrane should be at least 1 and 1/2 inches wide.

7.3.2.2. Place the Teflon membrane over the bottom half of the diffusion cell, making sure that the serpentine path is completely covered with the membrane. Wearing gloves, place the membrane on the cell. NOTE: Tape one end of the membrane to the opposite side of the bottom half of the cell. This helps hold the membrane in place. Then smooth the membrane toward the other end. Tape that end of the membrane to the opposite side of the bottom half of the cell.

7.3.2.3. Carefully place the top half of the diffusion cell on top of the bottom half, lining up the serpentine paths (with the membrane in between).

7.3.2.4. Holding the top and bottom halves together, place them inside the black holder. Place the black plate on top of the now sandwiched membrane cell.

7.3.2.5. Turn this holder on its side so that the membrane cells and plate are all aligned along one edge. While holding the diffusion cell and plate in place in the holder, finger tighten the three screws on top of the black holder. Using an allen wrench, make sure the screws are all securely tightened. The membrane is now firmly set in the diffusion cell.

7.3.3. Place the reagent lines in the appropriate reservoirs. Allow 10 minutes for reagents to circulate through the manifold before starting the analysis.

7.3.4. The Teflon membranes are very durable and seldom have to be changed. Symptom of failure – Color change in recipient stream.

7.3.5. Shut down procedure:

Remove all transmission lines from the reagents and place them in deionized water. Pump water through the system for 10 minutes.

Remove the transmission lines from the water and pump air through the system for 5 minutes.

Stop the pump and release tension on the pump tubing.

8. DATA ANALYSIS AND CALCULATIONS

8.1. Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

8.2. Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

8.3. Report results in mg N/L.

9. METHOD PERFORMANCE

9.1. The method support data are presented in Section 11. This data was generated according to a Lachat Work Instruction during development of the method.

9.2. Although Lachat Instrument publishes method performance data, including MDL, precision, accuracy and carryover studies, we cannot guarantee that each laboratory will be capable of meeting such performance. Individual laboratory and instrument conditions, as well as laboratory technique play a major role in determining method performance. The support data serves as a guide of the potential method performance. Some labs may not be able to reach this level of performance for various reasons, while other labs may exceed it.

10. REFERENCES

10.1. International Organization for Standardization, Draft International Standard ISO/DIN 11732, Water Quality – Determination of ammonium nitrogen by flow analysis and spectrometric detection.

11. TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

11.1. DATA SYSTEM PARAMETERS FOR QUIKCHEM 8500/8000

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput: 30 samples/h, 120 s/sample
Pump Speed: 35
Cycle Period: 120

Analyte Data:

Concentration Units: mg N/L
Inject to Peak Start: 20.6 s
Peak Base Width: 102.3 s
Chemistry: Direct/Bipolar

Calibration Data:

Standards	1	2	3	4	5	6	7	8	9
Concentration mg N/L	20	10	5.0	2.0	1.0	0.5	0.25	0.1	0.0

Calibration Fit Type: 2nd Order Polynomial
Weighting Method: 1/X
Force through zero: no

Sampler Timing:

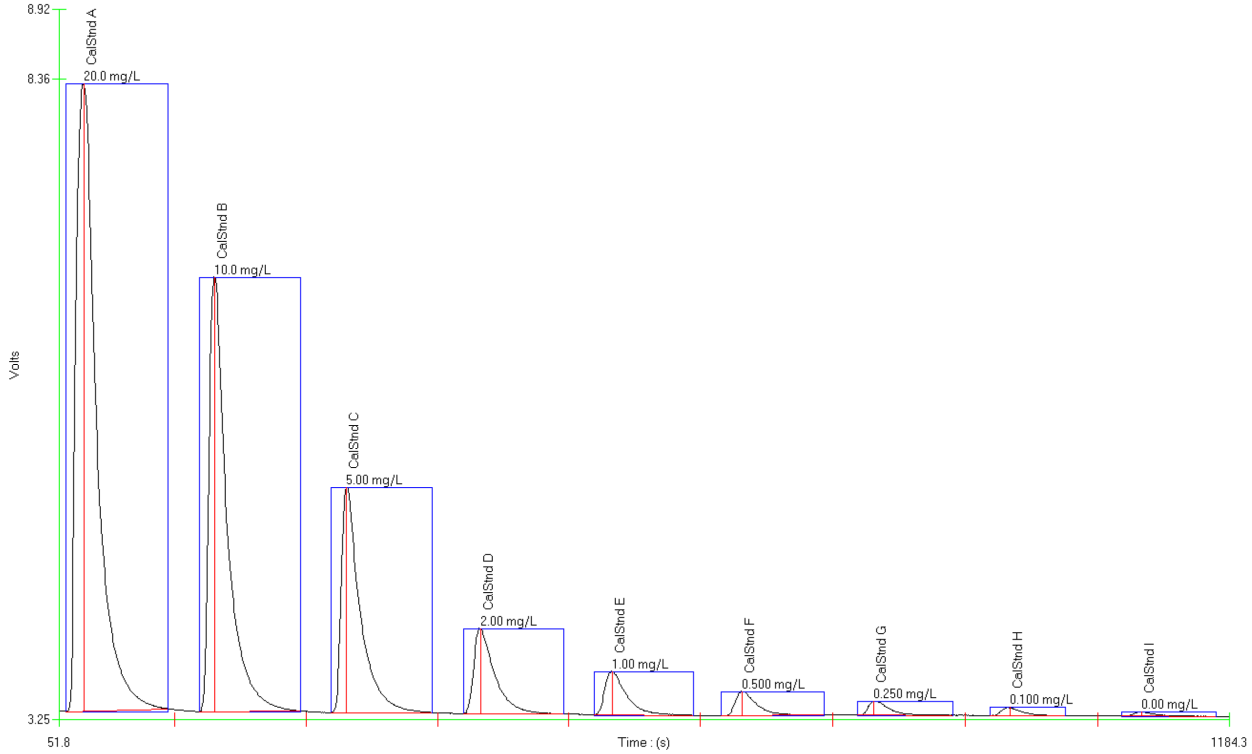
Min. Probe in Wash Period: 15 s
Probe in Sample Period: 25 s

Valve Timing:

Load Period: 20 s
Inject Period: 100 s

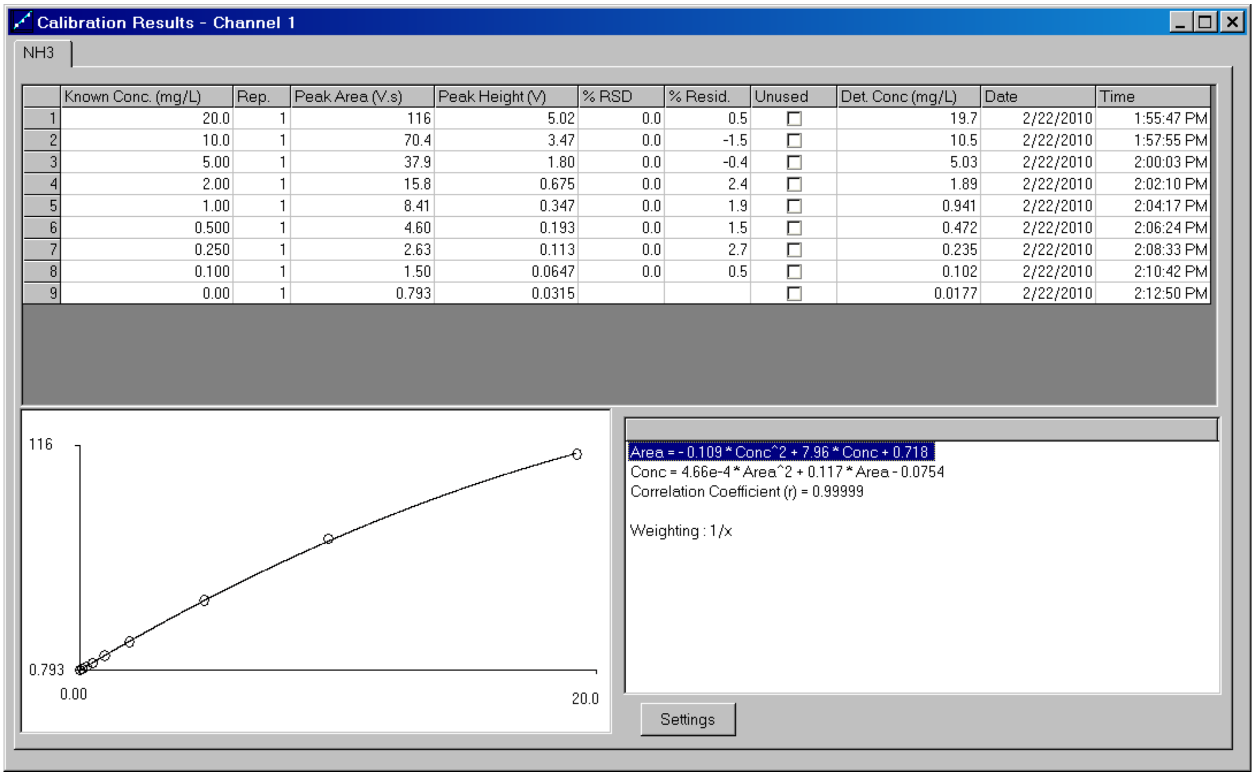
11.2. SUPPORT DATA FOR QUIKCHEM 8500/8000

Calibration Data for Ammonia



File Name: OM_2-22-2010_01-55-09PM.OMN
Acq. Date: 22 February 2010

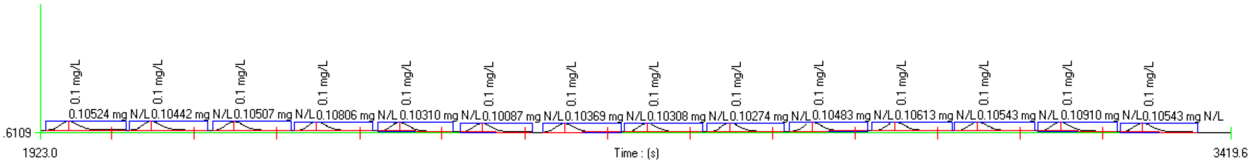
Calibration Graph and Statistics



	Known Conc. (mg/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	20.0	1	116	5.02	0.0	0.5	☐	19.7	2/22/2010	1:55:47 PM
2	10.0	1	70.4	3.47	0.0	-1.5	☐	10.5	2/22/2010	1:57:55 PM
3	5.00	1	37.9	1.80	0.0	-0.4	☐	5.03	2/22/2010	2:00:03 PM
4	2.00	1	15.8	0.675	0.0	2.4	☐	1.89	2/22/2010	2:02:10 PM
5	1.00	1	8.41	0.347	0.0	1.9	☐	0.941	2/22/2010	2:04:17 PM
6	0.500	1	4.60	0.193	0.0	1.5	☐	0.472	2/22/2010	2:06:24 PM
7	0.250	1	2.63	0.113	0.0	2.7	☐	0.235	2/22/2010	2:08:33 PM
8	0.100	1	1.50	0.0647	0.0	0.5	☐	0.102	2/22/2010	2:10:42 PM
9	0.00	1	0.793	0.0315			☐	0.0177	2/22/2010	2:12:50 PM

Area = - 0.109 * Conc^2 + 7.96 * Conc + 0.718
Conc = 4.66e-4 * Area^2 + 0.117 * Area - 0.0754
Correlation Coefficient (r) = 0.99999

Weighting : 1/x



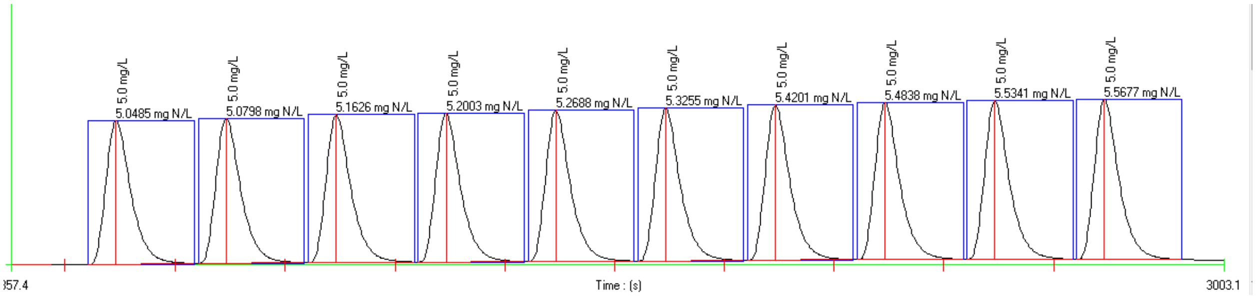
Method Detection Limit for ammonia using 0.1 mg N/L standard

MDL= determined 0.0056 mg, claiming 0.02 mg N/L

Standard Deviation (s) = 0.002 mg N/L, Mean (x) = 0.1043 mg N/L, Known value = 0.10 mg N/L

File Name: Ammonia_MDL_2015_April_15.OMN

Acq. Date: 15 April 2015



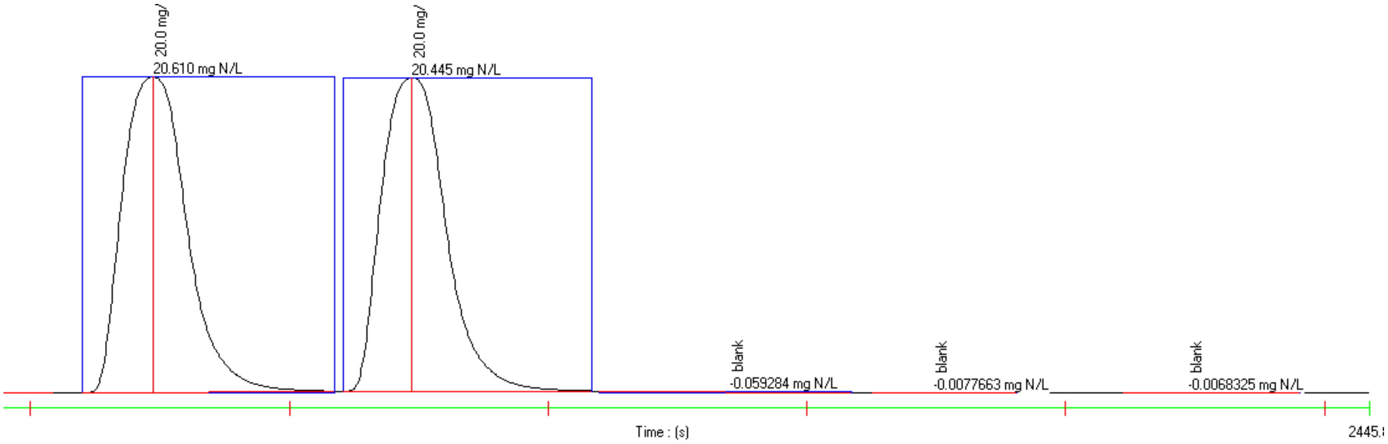
Precision data for ammonia using 5.0 mg N/L standard

% RSD = 3.52

Standard Deviation (s) = 0.187 mg N/L, Mean (x) = 5.31 mg N/L, Known value = 5.0 mg N/L

File Name: Ammonia_precision_2015_April_15.OMN

Acq. Date: 15 April 2015



Carryover Study: Two 20 mg N/L standards followed by 3 blanks

Carryover Passed

File Name: Ammonia_carryover_2015_April_15.OMN

Acq. Date: 15 April 2015