

AMMONIUM DETERMINATION IN AQUEOUS SOLUTIONS BY ION CHROMATOGRAPHY

UOP Method 959-98

SCOPE

This method is for determining the concentration of ammonium ion in aqueous solutions by Ion Chromatography (IC). The limit of quantitation of the method is 0.0001 mass-% (1 mass-ppm). Sodium and potassium interfere with the analysis when they are present at concentrations greater than 0.1 mass-%. Acidic samples that contain greater than 50-mM hydronium ion concentration (pH less than 1.3) deteriorate the performance of the analysis (through loss of resolution). Organic contamination should also be kept to a minimum (to lengthen column life). Sample matrix effects can be avoided or minimized by sample dilution, but only at the expense of the analysis limit of quantitation. When used in conjunction with UOP Method 958 (an extraction procedure), ammonia can also be determined in hydrocarbon samples.

OUTLINE OF METHOD

For analysis, the sample is diluted by mass in water to an analyte concentration between 0.0001 and 0.0015 mass-%. A reproducible volume of diluted sample is injected into an ion chromatograph equipped with a cation exchange column, conductivity suppressor device and conductivity detector. The ammonium is separated from other ions by cation exchange with hydronium ions supplied by the chromatographic system mobile phase, methanesulfonic acid. A mobile phase step-gradient elutes off highly retained cations such as aliphatic amines, calcium and magnesium. The column effluent enters a conductivity suppressor device, where the background conductivity of the column effluent is reduced and the ammonium ion is simultaneously converted into ammonium hydroxide. The analyte effluent from the conductivity suppressor device then flows to a conductivity detector where solution conductance is continuously measured. The solution conductance at any given time is proportional to ionic concentration and the inherent mobility of each type of ion present in the detector flow cell. The method is calibrated by an external standard procedure using calibration standards prepared from pure ammonium chloride.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Balance, readability 0.1-mg

Cation self-regenerating suppressor, conductivity suppressor device, Model CSRS-II (4-mm), Dionex, Cat. No. 46079

Chromatographic column, Model IonPac CS12A Analytical, dimensions 250-mm length by 4-mm ID, Dionex, Cat. No. 46073

Conductivity cell, with shield, Dionex, Cat. No. 44132

Flask, volumetric, Class A, 2-L Pyrex™, serialized with stopper, Fisher Scientific, Cat. No. 5680-2L

Ion chromatography system, equipped with a PeakNet Chromatography Workstation (includes the integrator), LC10 chromatography organizer with injection valve, GP40 gradient pump with degas, CD20 electrochemical detector and E01 eluent/solvent organizer, Dionex, Model DX 500

Mobile phase reservoirs, 2-L, Dionex, Cat. No. 39163, 2 required

Pipets, volumetric, Class A, serialized, 6- and 40-mL, Fisher Scientific, Cat. Nos. 13-650-3G and 13-650-3R, respectively

Refrigerator, laboratory, explosion proof, Fisher Scientific, Cat. No. 97-950-1

Syringe, HPLC, 250-μL, Fisher Scientific, Cat. No. 14-815-291. An autosampler may be used.

Water purification system, Barnstead NANOpure II, three module, equipped with Pretreatment (D0835), Ultrapure (D0809) and Organic Free (D0820) replacement cartridges, Fisher Scientific, Cat Nos. 09-050-254, 09-034-104, 09-034-3 and 09-034-175K, respectively

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized and distilled water that is subsequently treated with a Barnstead NANOpure II water purification system to produce ionically pure, 18 megohm-cm, organic-free, water.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Ammonium chloride, 99.998 % pure, Aldrich Chemical, Cat. No. 25,413-4

1.0-M Methanesulfonic acid solution. Prepare two liters by adding 192.2 ± 0.01 g of methanesulfonic acid to a 2-L volumetric flask containing about 1500 mL of water. Dilute to volume and mix thoroughly.

3.0-mM Methanesulfonic acid solution (Mobile Phase A). Prepare two liters by pipeting 6 mL of 1.0-M methanesulfonic acid into a 2-L volumetric flask containing about 1500 mL of water. Dilute to volume and mix thoroughly.

20.0-mM Methanesulfonic acid solution (Mobile Phase B). Prepare two liters by pipeting 40 mL of 1.0-M methanesulfonic acid into a 2-L volumetric flask containing about 1500 mL of water. Dilute to volume and mix thoroughly.

Methanesulfonic acid, 99% pure, Aldrich Chemical, Cat. No. M860-6

Pipet, Pasteur, disposable, borosilicate glass, 146-mm length, Fisher Scientific, Cat. No. 13-678-20A

Sample vials and caps, 6-dram, Fisher Scientific, Cat. No. 03-339-10H. The vials and caps must be rinsed five times with water, dried in air and stored with the caps on.

PROCEDURE

Chromatographic Technique

1. Assemble and test all ion chromatographic system components as per the manufacturer's specifications.
2. Install the analytical column and suppressor device (configured in the auto-suppression recycle mode).
3. Fill Mobile Phase A reservoir with two liters of 3.0-mM methanesulfonic acid solution. Fill Mobile Phase B reservoir with two liters of 20.0-mM methanesulfonic acid solution. Pump mobile phase at a flow rate of 1.0 mL/min and set the mobile phase composition to 83 vol-% Mobile Phase A and 17 vol-% Mobile Phase B. Immediately turn on power to the Cation Self-Regenerating Suppressor.
4. Set the conductivity detector sensitivity to 10 μ S. The detector baseline should level off to a steady flat baseline within 20 minutes.
 - When the system is fully equilibrated, the background conductivity should be at a steady level less than 3 μ S.

Operating Conditions

Table 1 summarizes the recommended chromatographic operating conditions for the convenience of the method user. Other conditions may be used, provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (see Figure).

Table 1
Recommended Chromatographic Conditions

Analytical column	Dionex IonPac CS12A		
Suppressor	Dionex CSRS-II (4-mm) configured in auto-suppression recycle mode		
Mobile Phase A	3.0-mM methanesulfonic acid		
Mobile Phase B	20.0-mM methanesulfonic acid		
Mobile phase flow rate	1.0 mL/min		
Mobile phase gradient	<u>Time (min.)</u>	<u>%Mobile Phase A</u>	<u>%Mobile Phase B</u>
	initial	83	17
	12.00	83	17
	12.01	0	100
	24.99	0	100
	25.00	83	17
	30.00	83	17
Injection volume	25 µL		
Column temperature	ambient		
Detector	conductivity		
Detector Sensitivity	10 µS		

Calibration

Prepare a fresh calibration standard and calibrate the system each day samples are to be analyzed. A calibration factor is required to relate the conductivity detector response to ammonium concentration. Detector response is measured in µS units of conductivity.

1. Weigh approximately 0.1 g ammonium chloride into a 6-dram sample vial and record the mass to the nearest 0.1-mg.
2. Dissolve the salt with approximately 19.9 g of Mobile Phase B and record the total mass to the nearest 0.1-mg. Cap the solution and shake vigorously until all of the solid is totally dissolved. Label the mixture "Standard Stock Solution". Calculate the ammonium concentration in this solution using Eq. 1 in *CALCULATIONS*.
3. Transfer approximately 0.1 g of the Standard Stock Solution, with a Pasteur pipet, to a separate 6-dram vial. Weigh and record the mass of the Standard Stock Solution aliquot to the nearest 0.1-mg.
4. Dilute the aliquot with approximately 19.9 g of Mobile Phase B and record the total mass to the nearest 0.1-mg. Label the mixture "Standard Calibration Solution". Cap the vial and shake the solution vigorously for approximately 15 seconds.
 - The Standard Calibration Solution should contain approximately 0.00084 mass-% ammonium. Calculate the actual concentration using Eq. 2 in *CALCULATIONS*.
5. Using a syringe, inject 25 µL of the Standard Calibration Solution into the ion chromatograph and immediately start the mobile phase gradient and integrator. The chromatographic analysis should run for 30 minutes.

6. Identify the ammonium peak by comparing the chromatogram obtained with the Typical Chromatogram (see Figure).
7. Repeat Steps 5 and 6 to obtain a duplicate analysis of the Standard Calibration Solution.
 - If the area counts from the duplicates are within 5% of each other, proceed with the analysis. If not, repeat injections until the desired repeatability is attained on two consecutive runs, or repair the instrument, as necessary.
8. Calculate the mean response factor for ammonium using Eq. 3 in *CALCULATIONS*.

Sample Analysis

Ammonium ion has an acid dissociation constant of 9.24 ($-\log_{10}$), so samples must be kept slightly acidic (about pH 5) to avoid dissociation of ammonium and evaporation of ammonia. Samples should be stored in a refrigerator prior to analysis and analyzed within 24 hours.

1. Inject 25 μL of sample into the ion chromatograph and immediately start the mobile phase gradient and integrator. The chromatographic analysis should run for 30 minutes.
2. Identify the ammonium peak by comparing the chromatogram obtained with the Typical Chromatogram (see Figure).
3. Prepare quantitative serial dilutions of the sample, if the value obtained for ammonium is above 0.0015 mass-%. This is done by diluting the sample in water on a mass/mass basis until the resulting chromatographic ammonium peak area closely matches that of the Standard Calibration Solution (-50 to +150% of the Standard Calibration Solution peak area). Record the masses of the sample aliquot and the final diluted sample solution to the nearest 0.1-mg.
 - Several serial dilutions may be required in order to obtain the appropriate peak area response. Make sure that each sample dilution is thoroughly mixed before proceeding with the next dilution. Use Mobile Phase B as the diluent.

Analysis of the Blank

A sample of the laboratory water is analyzed each day an analysis of a sample is to be performed. The water must contain less than 0.00005 mass-% ammonium for a valid sample analysis. If not, check first for errors due to dirty glassware by rerunning the blank in a fresh set of glassware. If this does not solve the problem, replace the cartridges in the water purification unit and try again.

1. Inject 25 μL of the blank into the ion chromatograph and immediately start the mobile phase gradient and integrator. The chromatographic analysis should run for 30 minutes.
2. Identify and integrate the peak area of ammonium by comparing the chromatogram obtained with the Typical Chromatogram (see Figure).

CALCULATIONS

Any mass-% value calculated using the following equations can be converted to mass-ppm by multiplying the mass-% value by 10,000. Calculate the concentration of ammonium in the Standard Stock Solution to three significant figures using Eq. 1.

$$A = \frac{33.72 B}{C} \quad (1)$$

where:

A = concentration of ammonium in Standard Stock Solution, mass-%

B = mass of ammonium chloride weighed, g

C = total mass of Standard Stock Solution, g

33.72 = mass fraction ammonium in pure solid (0.3372) times 100 (factor to convert g/g to mass-%), mass-%

Calculate the concentration of ammonium in the Standard Calibration Solution to three significant figures using Eq. 2.

$$D = \frac{AE}{F} \quad (2)$$

where :

A = defined in Eq. 1

D = concentration of ammonium in Standard Calibration Solution, mass-%

E = mass of aliquot of Standard Stock Solution, g

F = total mass of Standard Calibration Solution, g

Eqs. 3 and 4 assume that the densities of the Standard Calibration Solution and the injected sample are essentially the same. That assumption is considered adequate for this use. Calculate the mean response factor for ammonium in the Standard Calibration Solution to three significant figures using Eq. 3.

$$H = \frac{2D}{G} \quad (3)$$

where:

D = defined in Eq. 2

G = sum of ammonium area responses in duplicate injections

H = mean response factor for ammonium

2 = number of injections

Calculate ammonium concentration in the original sample to two significant figures using Eq. 4.

$$L = \frac{MHK}{J} \quad (4)$$

where:

H = defined in Eq. 3

J = mass of sample weighed (*Sample Analysis*, Step 3), g

K = total diluted sample solution mass (*Sample Analysis*, Step 3), g

L = concentration of ammonium in sample, mass-%

M = ammonium peak area of injected sample

Note: **K/J** = 1 if sample dilution is not required.

PRECISION

ASTM Repeatability

A nested design was carried out by two analysts at three different concentration levels on two separate days. Each analyst performed two analyses at each concentration level each day for a total of 24 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the mean concentrations and are shown in Table 2. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the ASTM allowable differences shown at the concentrations listed in Table 2 with 95% confidence.

UOP Repeatability

A nested design was carried out by two analysts at three different concentration levels on two separate days. Each analyst performed two analyses at each concentration level each day for a total of 24 analyses. Using a stepwise analysis of variance procedure, the within-lab estimated standard deviations (esd) were calculated at the mean concentrations and are shown in Table 2. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable differences shown at the concentrations listed in Table 2 with 95% confidence.

Table 2
ASTM and UOP Repeatability, mass-%

<u>Component</u>	<u>Mean</u>	<u>ASTM Repeatability</u>		<u>UOP Repeatability</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Ammonium	0.00068	0.000004	0.00002	0.000006	0.00002
	0.050	0.0005	0.002	0.0009	0.007
	3.0	0.01	0.1	0.07	0.5

The data in Table 2 are short-term estimates of the repeatability. When the test is run routinely in the field, a control standard and chart should be used to develop a better estimate of the long-term repeatability. An autosampler was used to collect the data shown in Table 2.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

TIME FOR ANALYSIS

The elapsed time for the preparation and analysis of one sample, including the analysis of a blank and calibration, is 2 hours. The labor requirement is 1 hour.

REFERENCE

UOP Method 958, "Ammonia in Hydrocarbons"

SUGGESTED SUPPLIERS

Aldrich Chemical Co., 1001 W. St. Paul Ave., Milwaukee, WI 53233 (414-273-3850)

Dionex Corp., 1228 Titan Way, P.O. Box 3603, Sunnyvale, CA 94088-3603 (408-737-0700)

Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-562-8300)

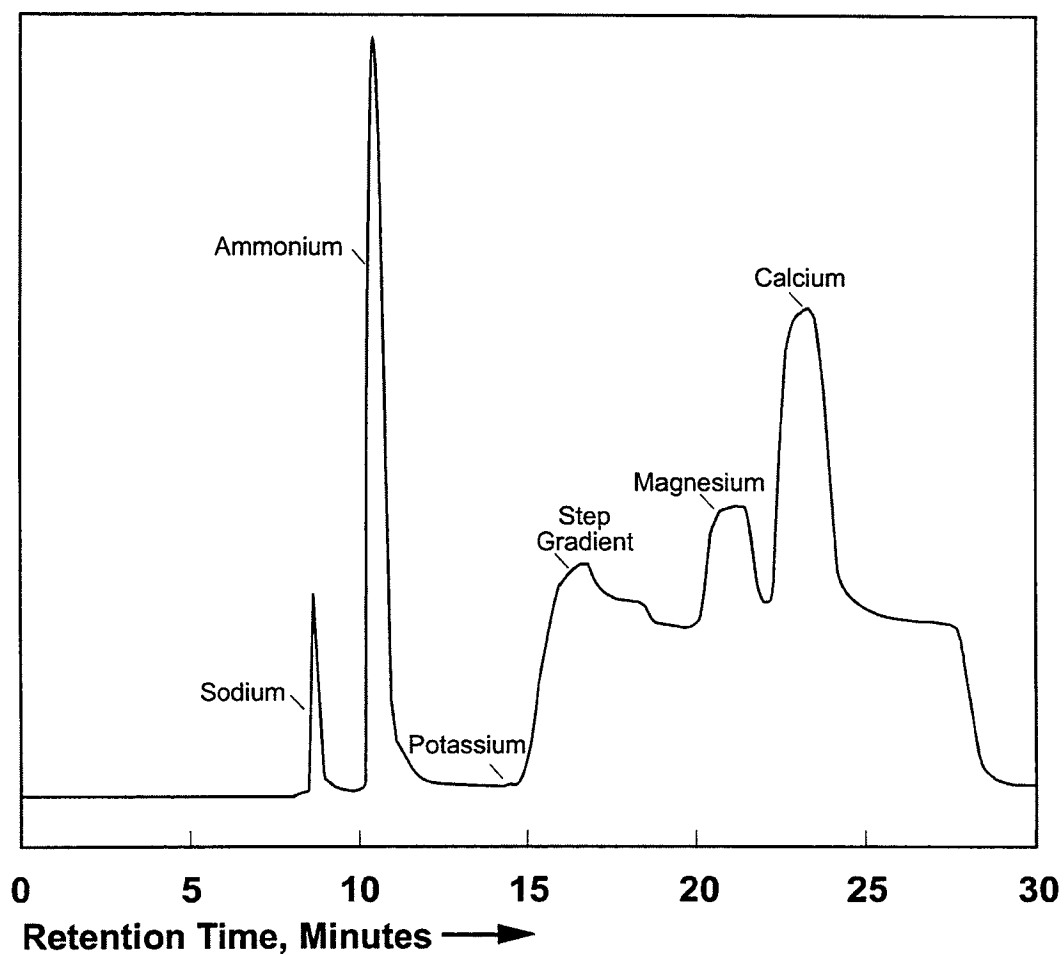


Figure
Typical Chromatogram