

AMMONIA by IC

6016

NH₃

MW: 17.03

CAS: 7664-41-7

RTECS: BO0875000

METHOD: 6016, Issue 1

EVALUATION: FULL

Issue 1: 15 May 1996

OSHA : 50 ppm
NIOSH: 25 ppm; STEL 35 ppm; Group III Pesticide
ACGIH: 25 ppm; STEL 35 ppm
 (1 ppm = 0.697 mg/m³ @ NTP)

PROPERTIES: gas; MP -77.7 °C; BP -33.4 °C; VP 888 kPa (8.76 atm) @ 21.1 °C; vapor density 0.6 (air = 1); explosive range 16 to 25% v/v in air

SYNONYMS: none

SAMPLING	MEASUREMENT
<p>SAMPLER: SOLID SORBENT TUBE (sulfuric acid-treated silica gel) a 0.8-µm MCE prefilter may be used to remove particulate interferences.</p> <p>FLOW RATE: 0.1 to 0.5 L/min</p> <p>VOL-MIN: 0.1 L @ 50 ppm -MAX: 96 L @ 50 ppm [1]</p> <p>SHIPMENT: routine</p> <p>SAMPLE STABILITY: at least 35 days @ 5 °C [2]</p> <p>BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION</p> <p>ANALYTE: ammonium ion (NH₄⁺)</p> <p>EXTRACTION: 10 mL deionized water</p> <p>INJECTION VOLUME: 50 µL</p> <p>ELUENT: 48 mM HCl/4 mM DAP-HCl/4 mM L-histidine-HCl; 1 mL/min alternate: 12 mM HCl/0.25 mM DAP-HCl/0.25 mM L-histidine-HCl; 1 mL/min</p> <p>COLUMNS: HPIC-CS3 cation separator; HPIC-CG3 cation guard; CMMS-1 cation micromembrane suppressor</p> <p>CONDUCTIVITY SETTING: 30 µS full scale</p> <p>CALIBRATION: standard solutions of NH₄⁺ in deionized water</p> <p>RANGE: 4 to 100 µg per sample [3]</p> <p>ESTIMATED LOD: 2 µg per sample [3]</p> <p>PRECISION (S_r): 0.038 [2]</p>
ACCURACY	
<p>RANGE STUDIED: 17 to 68 mg/m³ [1] (30-L samples)</p> <p>BIAS: - 2.4% [1]</p> <p>OVERALL PRECISION (S_{rr}): 0.071 [1]</p> <p>ACCURACY: ± 14.5%</p>	

APPLICABILITY: The working range is 24 to 98 ppm (17 to 68 mg/m³) for a 30-L sample. This method is applicable to STEL measurements when sampled at ≥0.2 L/min.

INTERFERENCES: Ethanolamines (monoethanolamine, isopropanolamine, and propanolamine) have retention times similar to NH₄⁺. The use of the alternate (weak) eluent will aid in separating these peaks.

OTHER METHODS: This method combines the sampling procedure of methods S347 [4] and 6015 with an ion chromatographic analytical procedure similar to Method 6701 [5] and OSHA Method ID-188 [3].

REAGENTS:

1. Water, deionized, filtered.
2. Sulfuric acid (H_2SO_4), 0.01 N:*
Add 0.28 mL conc. H_2SO_4 to 500 mL deionized water in 1-L volumetric flask. Dilute to 1 L with deionized water.
3. Hydrochloric acid (HCl), 1 N:*
Add 82.5 mL conc. HCl to 500 mL deionized water in 1-L volumetric flask. Dilute to 1 L with deionized water.
4. 2,3-diaminopropionic acid monohydrochloride (DAP-HCl)
5. L-histidine monohydrochloride monohydrate (L-histidine-HCl)
6. Eluent (48 mM HCl/4 mM DAP-HCl/4 mM L-histidine-HCl): Place 0.560 g DAP-HCl and 0.840 g L-histidine-HCl in a 1-L volumetric flask. Add 48 mL of 1 N HCl, dilute to volume with deionized water. Prepare monthly.
7. Alternate eluent (12 mM HCl/0.25 mM DAP-HCl/0.25 mM L-histidine-HCl): Dilute 252 mL strong eluent and 36 mL 1 N HCl to 4 L with deionized water. Prepare fresh for each use.
8. Tetramethylammonium hydroxide (TMAOH), 25%, (Aldrich Chemical Co. Milwaukee, WI).
9. Regenerant solution: Dilute 57.4 mL of 25% TMAOH to 4 L with deionized water.
10. Ammonia stock solution, 1000 $\mu\text{g/mL}$ as NH_3 (1059 $\mu\text{g/mL}$ as NH_4^+): Dissolve 3.1409 g ammonium chloride in deionized water. Dilute to 1 L.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
 - a. Prefilter: 37-mm mixed cellulose ester membrane filter, 0.8- μm pore size, stainless steel or porous plastic screen in two piece cassette filter holder.
 - b. Sulfuric acid-treated silica gel, glass tube, unsealed and fire-polished, 6.0 cm long, 6-mm OD, 4-mm ID, containing two sections of 20/40 mesh sulfuric acid-treated silica gel (200 mg front/100 mg back) separated and held in place with plugs of silylated glass wool, and capped with plastic caps. Tubes are commercially available.
2. Personal sampling pump, 0.1 to 0.5 L/min, with flexible tubing.
3. Ion Chromatograph with conductivity detector, cation column and guard, and cation micromembrane suppressor (see p 6016-1).
4. Syringes, 10-mL, polyethylene, Luer tip.
5. Centrifuge tubes, 15-mL, graduated, plastic with screw caps.
6. Volumetric flasks, 10-, 50-, 100-mL, and 1-L.
7. Syringe filters, 13-mm, 0.8- μm , membrane filter.
8. Micropipets, disposable tips.
9. Analytical balance (sensitivity to 0.01 mg).

SPECIAL PRECAUTIONS: Concentrated acids are corrosive to skin. Handle acid in a fume hood. Wear protective gloves.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 0.1 and 0.5 L/min for a total sample size of 0.1 to 96 L.
3. Cap the sampling tubes with plastic (not rubber) caps immediately after sampling.
4. Pack securely for shipment.

SAMPLE PREPARATION:

5. Remove caps from sampling tubes. Transfer the front and back sections of sulfuric acid-treated silica gel to separate 15-mL graduated centrifuge tubes.
NOTE: Firm tapping of the tube may be necessary to effect complete transfer of the sulfuric acid-treated silica gel.
6. Add 10 mL of deionized water to each centrifuge tube. Cap and shake vigorously. Allow to stand 45 minutes with occasional shaking. (Desorption is complete in 45 minutes.)

NOTE: Analyses should be completed within one day after the ammonia is desorbed.

- Transfer samples to 10-mL syringes fitted with inline syringe filters for manual injection or transfer to autosampler vials.

CALIBRATION AND QUALITY CONTROL:

- Calibrate daily with at least six working standards over the range of 1 to 110 $\mu\text{g NH}_3$ per sample (about 0.11 to 12 $\mu\text{g/mL NH}_4^+$).
 - Add known aliquots of ammonia stock solution to 0.01 N H_2SO_4 in 10-mL volumetric flasks.

NOTE: Prepare standards just before use.
 - Analyze working standards together with samples and blanks (steps 9 through 11).
 - Prepare calibration graph (peak height vs. $\mu\text{g NH}_3$).

MEASUREMENT:

- Set ion chromatograph to conditions given on page 6016-1, according to manufacturer's instructions.
- Inject 50- μL sample aliquot manually or with autosampler. For manual operation, inject 2 to 3 mL of sample from filter/syringe to ensure complete rinse of sample loop.
- Measure peak height.

NOTE: If peak height exceeds linear calibration range, dilute with 0.01 N H_2SO_4 , reanalyze and apply the appropriate dilution factor in calculations.

CALCULATIONS:

- Determine the mass, μg , of ammonia found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
- Calculate concentration, C , of NH_3 in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3$$

EVALUATION OF METHOD:

This method combines the sampling procedure of NIOSH Methods S347 [4] and 6015 with the ion chromatographic analytical procedure of NIOSH Method 6701 [5] and OSHA Method ID-188 [3]. This method will serve as an alternate analytical procedure to the automated spectrophotometric procedure of method 6015. Although the methods from which this method is derived are fully evaluated methods, the combination of the sulfuric acid-treated silica gel sampler and IC analysis has not received a full evaluation as such. During the development of the passive monitor method for ammonia (6701), sulfuric acid-treated silica gel tubes were used as one of the reference methods [5]. The silica gel samples with IC analysis showed good agreement with the other reference methods, bubbler collection with colorimetric analysis using Nessler's Reagent, and bubbler collection with IC analysis.

A storage stability study compared the sulfuric acid-treated silica gel tube and sulfuric acid-treated carbon beads used in OSHA Method ID-188. When stored at room temperature for five days and then refrigerated for 21 days, silica gel samples had a mean recovery of $102 \pm 3.8\%$ ($n = 8$), while carbon beads had a mean recovery of $95 \pm 1.6\%$ ($n = 8$). The samples stored on carbon beads for 35 days showed significantly lower (although still acceptable) recovery compared to samples stored for 14 days: $103 \pm 3.8\%$ for silica gel ($n = 12$), and $108 \pm 7.0\%$ for carbon beads ($n = 12$) [2].

REFERENCES:

- NIOSH [1977]. Ammonia: Backup data report No. S347. Ten NIOSH analytical methods, set 6. SRI

- International Contract No. 210-76-0123. Available NTIS PB-288629.
- [2] DataChem [1995]. User check of method 6015 for ammonia. Sequence 8321-J, K, L, M. Unpublished report.
 - [3] OSHA [1991]. Ammonia in workplace atmospheres - solid sorbent: Method ID-188, OSHA analytical methods manual, 2nd ed., Part 2, Inorganic substances.
 - [4] NIOSH [1979]. Ammonia: Method S347. In: Taylor DG, Ed. NIOSH manual of analytical methods, 2nd ed., volume 5. Cincinnati, OH: National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 79-141.
 - [5] NIOSH [1984]. Ammonia: Method 6701. In: Eller PM, Ed. NIOSH manual of analytical methods, 3rd ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.

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