AMMONIA by IC

6016

NH_3 MW: 17.03 CAS: 7664-41-7 RTECS: BO0875000

METHOD: 6016, Issue 2 **EVALUATION:** FULL **Issue 1:** 15 May 1996
Issue 2: 3 March 2016

OSHA: 50 ppm
NIOSH: 25 ppm; STEL 35 ppm

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

SAMPLER: SOLID SORBENT TUBE (sulfuric acid-treated silica gel); a 0.8-µm MCE prefilter may be used to remove particulate interferences.

FLOW RATE: 0.1 - 0.5 L/min

VOL-MIN: 0.1 L @ 50 ppm
-MAX: 96 L @ 50 ppm {1}

SHIPMENT: routine

SAMPLE STABILITY: at least 35 days @ 5 °C [2]

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 17 to 68 mg/m^3 [1] (30-L samples)

BIAS: -2.4%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.071 [1]

ACCURACY: ± 14.5%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION

ANALYTE: ammonium ion (NH_4^+)

EXTRACTION ION: 10 mL deionized water

INJECTION VOLUME: 50 µL

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

COLUMNS: cation separator; cation guard; cation micromembrane suppressor

CONDUCTIVITY SETTING: 30 µS full scale

CALIBRATION: standard solutions of NH_4^+ in deionized water

RANGE: 8 to 100 µg/sample [3]

ESTIMATED LOD: 2 µg/sample [3]

PRECISION ($\bar{S}_r$): 0.038 [2]

APPLICABILITY: The working range is 24 to 98 ppm (17 to 68 mg/m^3) for a 30-L sample [1]. 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 NH_4^+. 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 [5] with an ion chromatographic analytical procedure similar to Method 6701 [6] 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% in water.
9. Regenerant solution: Dilute 57.4 mL of 25% TMAOH to 4 L with deionized water.
10. Ammonia stock solution, 1000 µg/mL as NH_3 (1059 µg/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.
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 Evaluation).
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.
7. Transfer samples to 10-mL syringes fitted with inline syringe filters for manual injection or transfer to autosampler vials.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards over the range of 1 to 110 µg NH_3 per sample (about 0.11 to 12 µg/mL NH_4^+).
9. 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.
10. Analyze working standards together with samples and blanks (steps 9 through 11).
11. Prepare calibration graph (peak height vs. µg NH_3).

MEASUREMENT:

12. Set ion chromatograph to conditions given on page 6016-1, according to manufacturer's instructions.
13. 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.
14. 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:

15. 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.
16. Calculate concentration, C, of NH_3 in the air volume sampled, V (L):

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

EVALUATION OF METHOD:

This method combines the sampling procedure of NIOSH Methods S347 [4] and 6015 [5] with the ion chromatographic analytical procedure of NIOSH Method 6701 [6] and OSHA Method ID-188 [3]. This method used HPIC-CS3 cation separator, HPIC-CG3 cation guard and CMMS-1 cation micromembrane suppressor. This method will serve as an alternate analytical procedure to the automated spectrophotometric procedure of NIOSH Method 6015 [5]. 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 [6]. 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 [3]. When stored at room temperature for five days and then

refrigerated for 21 days, silica gel samples had a mean recovery of 102 ± 3.8% (n = 8), while carbon beads had a mean recovery of 95 ± 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 ± 3.8% for silica gel (n = 12), and 108 ± 7.0% for carbon beads (n = 12) [2].

REFERENCES:

[1] NIOSH [1977]. Ammonia: Backup data report No. S347. Ten NIOSH analytical methods, set 6. SRI International Contract No. 210-76-0123. (NTIS PB-288629)

[2] Copenhafer RB, Dearden PA [1995]. User check of method 6015 for ammonia. Sequence 8321-J, K, L, M. Salt Lake City, UT: DataChem Labaratories. Unpublished.

[3] OSHA [1991]. Ammonia in workplace atmospheres - solid sorbent: Method ID-188. In: OSHA analytical methods manual, 2nd ed., Part 2, Inorganic substances. Salt Lake City, UT: U.S. Department of Labor, Occupational Safety and Health Administration.

[4] NIOSH [1979]. Ammonia: Method S347. In: Taylor DG, ed. NIOSH manual of analytical methods, 2nd ed., volume 5. Cincinnati, OH: U.S. Department of Health, Education and Welfare, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 79-141.

[5] NIOSH [1994]. Ammonia: Method 6015. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods, 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS(NIOSH) Publication No. 94-113 [www.cdc.gov/niosh/nmam].

[6] NIOSH [1984]. Ammonia: Method 6701. In: Eller PM, Cassinelli ME, eds. NIOSH manual of analytical methods, 3rd ed. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 84-100.

METHOD WRITTEN BY:

Mary Ellen Cassinelli, NIOSH