

Standard Methods for the Examination of Water and Wastewater

4500-NH₃ NITROGEN (AMMONIA)*#(1)

4500-NH₃ A. Introduction

1. Selection of Method

The two major factors that influence selection of the method to determine ammonia are concentration and presence of interferences. In general, direct manual determination of low concentrations of ammonia is confined to drinking waters, clean surface or groundwater, and good-quality nitrified wastewater effluent. In other instances, and where interferences are present or greater precision is necessary, a preliminary distillation step (B) is required.

A titrimetric method (C), an ammonia-selective electrode method (D), an ammonia-selective electrode method using known addition (E), a phenate method (F), and two automated versions of the phenate method (G and H) are presented. Methods D, E, F, G, and H may be used either with or without sample distillation. The data presented in Table 4500-NH₃:I and Table 4500-NH₃:III should be helpful in selecting the appropriate method of analysis.

Nesslerization has been dropped as a standard method, although it has been considered a classic water quality measurement for more than a century. The use of mercury in this test warrants its deletion because of the disposal problems.

The distillation and titration procedure is used especially for NH₃-N concentrations greater than 5 mg/L. Use boric acid as the absorbent following distillation if the distillate is to be titrated.

The ammonia-selective electrode method is applicable over the range from 0.03 to 1400 mg NH₃-N/L.

The manual phenate method is applicable to both fresh water and seawater and is linear to 0.6 mg NH₃-N/L. Distill into sulfuric acid (H₂SO₄) absorbent for the phenate method when interferences are present.

The automated phenate method is applicable over the range of 0.02 to 2.0 mg NH₃-N/L.

2. Interferences

Glycine, urea, glutamic acid, cyanates, and acetamide hydrolyze very slowly in solution on standing but, of these, only urea and cyanates will hydrolyze on distillation at pH of 9.5. Hydrolysis amounts to about 7% at this pH for urea and about 5% for cyanates. Volatile alkaline compounds such as hydrazine and amines will influence titrimetric results. Residual chlorine reacts with ammonia; remove by sample pretreatment. If a sample is likely to contain residual chlorine, immediately upon collection, treat with dechlorinating agent as in Section 4500-NH₃.B.3d.

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3. Storage of Samples

Most reliable results are obtained on fresh samples. If samples are to be analyzed within 24 h of collection, refrigerate unacidified at 4°C. For preservation for up to 28 d, freeze at – 20°C unacidified, or preserve samples by acidifying to pH <2 and storing at 4°C. If acid preservation is used, neutralize samples with NaOH or KOH immediately before making the determination. CAUTION: Although acidification is suitable for certain types of samples, it produces interferences when exchangeable ammonium is present in unfiltered solids.

4. Bibliography

- THAYER, G.W. 1970. Comparison of two storage methods for the analysis of nitrogen and phosphorus fractions in estuarine water. *Chesapeake Sci.* 11:155.
- SALLEY, B.A., J.G. BRADSHAW & B.J. NEILSON. 1986. Results of Comparative Studies of Preservation Techniques for Nutrient Analysis on Water Samples. Virginia Institute of Marine Science, Gloucester Point.

4500-NH₃ D. Ammonia-Selective Electrode Method

1. General Discussion

a. Principle: The ammonia-selective electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an electrode internal solution of ammonium chloride. Dissolved ammonia (NH_{3(aq)} and NH₄⁺) is converted to NH_{3(aq)} by raising pH to above 11 with a strong base. NH_{3(aq)} diffuses through the membrane and changes the internal solution pH that is sensed by a pH electrode. The fixed level of chloride in the internal solution is sensed by a chloride ion-selective electrode that serves as the reference electrode. Potentiometric measurements are made with a pH meter having an expanded millivolt scale or with a specific ion meter.

b. Scope and application: This method is applicable to the measurement of 0.03 to 1400 mg NH₃-N/L in potable and surface waters and domestic and industrial wastes. High concentrations of dissolved ions affect the measurement, but color and turbidity do not. Sample distillation is unnecessary. Use standard solutions and samples that have the same temperature and contain about the same total level of dissolved species. The ammonia-selective electrode responds slowly below 1 mg NH₃-N/L; hence, use longer times of electrode immersion (2 to 3 min) to obtain stable readings.

c. Interference: Amines are a positive interference. This may be enhanced by acidification. Mercury and silver interfere by complexing with ammonia, unless the NaOH/EDTA solution (3c) is used.

d. Sample preservation: Refrigerate at 4°C for samples to be analyzed within 24 h. Preserve

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samples high in organic and nitrogenous matter, and any other samples for longer storage, by lowering pH to 2 or less with conc H_2SO_4 .

2. Apparatus

a. *Electrometer*: A pH meter with expanded millivolt scale capable of 0.1 mV resolution between -700 mV and $+700$ mV or a specific ion meter.

b. *Ammonia-selective electrode*. *#(2)

c. *Magnetic stirrer*, thermally insulated, with TFE-coated stirring bar.

3. Reagents

a. *Ammonia-free water*: See Section 4500-NH₃.B.3a. Use for making all reagents.

b. *Sodium hydroxide*, 10N.

c. *NaOH/EDTA solution*, 10N: Dissolve 400 g NaOH in 800 mL water. Add 45.2 g ethylenediaminetetraacetic acid, tetrasodium salt, tetrahydrate ($\text{Na}_4\text{EDTA}\cdot 4\text{H}_2\text{O}$) and stir to dissolve. Cool and dilute to 1000 mL.

d. *Stock ammonium chloride solution*: Dissolve 3.819 g anhydrous NH_4Cl (dried at 100°C) in water, and dilute to 1000 mL; 1.00 mL = 1.00 mg N = 1.22 mg NH_3 .

e. *Standard ammonium chloride solutions*: See ¶ 4a below.

4. Procedure

a. *Preparation of standards*: Prepare a series of standard solutions covering the concentrations of 1000, 100, 10, 1, and 0.1 mg NH_3 -N/L by making decimal dilutions of stock NH_4Cl solution with water.

b. *Electrometer calibration*: Place 100 mL of each standard solution in a 150-mL beaker. Immerse electrode in standard of lowest concentration and mix with a magnetic stirrer. Limit stirring speed to minimize possible loss of ammonia from the solution. Maintain the same stirring rate and a temperature of about 25°C throughout calibration and testing procedures. Add a sufficient volume of 10N NaOH solution (1 mL usually is sufficient) to raise pH above 11. If the presence of silver or mercury is possible, use NaOH/EDTA solution in place of NaOH solution. If it is necessary to add more than 1 mL of either NaOH or NaOH/EDTA solution, note volume used, because it is required for subsequent calculations. Keep electrode in solution until a stable millivolt reading is obtained. Do not add NaOH solution before immersing electrode, because ammonia may be lost from a basic solution. Repeat procedure with remaining standards, proceeding from lowest to highest concentration. Wait until the reading has stabilized (at least 2 to 3 min) before recording millivolts for standards and samples containing ≤ 1 mg NH_3 -N/L.

c. *Preparation of standard curve*: Using semilogarithmic graph paper, plot ammonia concentration in milligrams NH_3 -N per liter on the log axis vs. potential in millivolts on the

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linear axis starting with the lowest concentration at the bottom of the scale. If the electrode is functioning properly a tenfold change of $\text{NH}_3\text{-N}$ concentration produces a potential change of about 59 mV.

d. Calibration of specific ion meter: Refer to manufacturer's instructions and proceed as in ¶s 4a and b.

e. Measurement of samples: Dilute if necessary to bring $\text{NH}_3\text{-N}$ concentration to within calibration curve range. Place 100 mL sample in 150-mL beaker and follow procedure in ¶ 4b above. Record volume of 10N NaOH added. Read $\text{NH}_3\text{-N}$ concentration from standard curve.

5. Calculation

$$\text{mg NH}_3\text{-N/L} = A \times B \times \left[\frac{100 + D}{100 + C} \right]$$

where:

A = dilution factor,

B = concentration of $\text{NH}_3\text{-N/L}$, mg/L, from calibration curve,

C = volume of 10N NaOH added to calibration standards, mL, and

D = volume of 10N NaOH added to sample, mL.

6. Precision and Bias

For the ammonia-selective electrode in a single laboratory using surface water samples at concentrations of 1.00, 0.77, 0.19, and 0.13 mg $\text{NH}_3\text{-N/L}$, standard deviations were ± 0.038 , ± 0.017 , ± 0.007 , and ± 0.003 , respectively. In a single laboratory using surface water samples at concentrations of 0.10 and 0.13 mg $\text{NH}_3\text{-N/L}$, recoveries were 96% and 91%, respectively. The results of an interlaboratory study involving 12 laboratories using the ammonia-selective electrode on distilled water and effluents are summarized in Table 4500-NH3:I.

7. Bibliography

- BANWART, W.L., J.M. BREMNER & M.A. TABATABAI. 1972. Determination of ammonium in soil extracts and water samples by an ammonia electrode. *Comm. Soil Sci. Plant Anal.* 3:449.
- MIDGLEY, C. & K. TERRANCE. 1972. The determination of ammonia in condensed steam and boiler feed-water with a potentiometric ammonia probe. *Analyst* 97:626.
- BOOTH, R.L. & R.F. THOMAS. 1973. Selective electrode determination of ammonia in water and wastes. *Environ. Sci. Technol.* 7:523.
- U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, National Environmental Research Center, Cincinnati, Ohio.
- AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1979. Method 1426-79. American Soc.

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4500-NH₃ E. Ammonia-Selective Electrode Method Using Known Addition

1. General Discussion

a. Principle: When a linear relationship exists between concentration and response, known addition is convenient for measuring occasional samples because no calibration is needed. Because an accurate measurement requires that the concentration at least double as a result of the addition, sample concentration must be known within a factor of three. Total concentration of ammonia can be measured in the absence of complexing agents down to 0.8 mg NH₃-N/L or in the presence of a large excess (50 to 100 times) of complexing agent. Known addition is a convenient check on the results of direct measurement.

b. See Section 4500-NH₃.D.1 for further discussion.

2. Apparatus

Use apparatus specified in Section 4500-NH₃.D.2.

3. Reagents

Use reagents specified in Section 4500-NH₃.D.3.

Add standard ammonium chloride solution approximately 10 times as concentrated as samples being measured.

4. Procedure

a. Dilute 1000 mg/L stock solution to make a standard solution about 10 times as concentrated as the sample concentrate.

b. Add 1 mL 10*N* NaOH to each 100 mL sample and immediately immerse electrode. When checking a direct measurement, leave electrode in 100 mL of sample solution. Use magnetic stirring throughout. Measure mV reading and record as E_1 .

c. Pipet 10 mL of standard solution into sample. Thoroughly stir and immediately record new mV reading as E_2 .

5. Calculation

a. $\Delta E = E_1 - E_2$.

b. From Table 4500-NH₃:II find the concentration ratio, Q , corresponding to change in potential, ΔE . To determine original total sample concentration, multiply Q by the concentration of the added standard:

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$$C_o = Q C_s$$

where:

C_o = total sample concentration, mg/L,

Q = reading from known-addition table, and

C_s = concentration of added standard, mg/L.

c. To check a direct measurement, compare results of the two methods. If they agree within $\pm 4\%$, the measurements probably are good. If the known-addition result is much larger than the direct measurement, the sample may contain complexing agents.

6. Precision and Bias

In 38 water samples analyzed by both the phenate and the known-addition ammonia-selective electrode method, the electrode method yielded a mean recovery of 102% of the values obtained by the phenate method when the $\text{NH}_3\text{-N}$ concentrations varied between 0.30 and 0.78 mg/L. In 57 wastewater samples similarly compared, the electrode method yielded a mean recovery of 108% of the values obtained by the phenate method using distillation when the $\text{NH}_3\text{-N}$ concentrations varied between 10.2 and 34.7 mg N/L. In 20 instances in which two to four replicates of these samples were analyzed, the mean standard deviation was 1.32 mg N/L. In three measurements at a sewer outfall, distillation did not change statistically the value obtained by the electrode method. In 12 studies using standards in the 2.5- to 30-mg N/L range, average recovery by the phenate method was 97% and by the electrode method 101%.

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Endnotes

1 (Popup - Footnote)

* APPROVED BY STANDARD METHODS COMMITTEE, 1997.

2 (Popup - Footnote)

* Orion Model 95-12, EIL Model 8002-2, Beckman Model 39565, or equivalent.