

# Standard Methods for the Examination of Water and Wastewater

## 4500-NH<sub>3</sub> 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-NH<sub>3</sub>:I and Table 4500-NH<sub>3</sub>: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 NH<sub>3</sub>-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 NH<sub>3</sub>-N/L.

The manual phenate method is applicable to both fresh water and seawater and is linear to 0.6 mg NH<sub>3</sub>-N/L. Distill into sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 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 NH<sub>3</sub>-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-NH<sub>3</sub>.B.3d.

### 3. Storage of Samples

Most reliable results are obtained on fresh samples. If samples are to be analyzed within 24 h

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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-NH<sub>3</sub> B. Preliminary Distillation Step

### 1. General Discussion

The sample is buffered at pH 9.5 with a borate buffer to decrease hydrolysis of cyanates and organic nitrogen compounds. It is distilled into a solution of boric acid when titration is to be used or into H<sub>2</sub>SO<sub>4</sub> when the phenate method is used. The ammonia in the distillate can be determined either colorimetrically by the phenate method or titrimetrically with standard H<sub>2</sub>SO<sub>4</sub> and a mixed indicator or a pH meter. The choice between the colorimetric and the acidimetric methods depends on the concentration of ammonia. Ammonia in the distillate also can be determined by the ammonia-selective electrode method, using 0.04N H<sub>2</sub>SO<sub>4</sub> to trap the ammonia.

### 2. Apparatus

*a. Distillation apparatus:* Arrange a borosilicate glass flask of 800- to 2000-mL capacity attached to a vertical condenser so that the outlet tip may be submerged below the surface of the receiving acid solution. Use an all-borosilicate-glass apparatus or one with condensing units constructed of block tin or aluminum tubes.

*b. pH meter.*

### 3. Reagents

*a. Ammonia-free water:* Prepare by ion-exchange or distillation methods:

1) Ion exchange—Prepare ammonia-free water by passing distilled water through an ion-exchange column containing a strongly acidic cation-exchange resin mixed with a strongly basic anion-exchange resin. Select resins that will remove organic compounds that interfere with the ammonia determination. Some anion-exchange resins tend to release ammonia. If this occurs, prepare ammonia-free water with a strongly acidic cation-exchange resin. Regenerate the column

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according to the manufacturer's instructions. Check ammonia-free water for the possibility of a high blank value.

2) Distillation—Eliminate traces of ammonia in distilled water by adding 0.1 mL conc  $\text{H}_2\text{SO}_4$  to 1 L distilled water and redistilling. Alternatively, treat distilled water with sufficient bromine or chlorine water to produce a free halogen residual of 2 to 5 mg/L and redistill after standing at least 1 h. Discard the first 100 mL distillate. Check redistilled water for the possibility of a high blank.

It is very difficult to store ammonia-free water in the laboratory without contamination from gaseous ammonia. However, if storage is necessary, store in a tightly stoppered glass container to which is added about 10 g ion-exchange resin (preferably a strongly acidic cation-exchange resin)/L ammonia-free water. For use, let resin settle and decant ammonia-free water. If a high blank value is produced, replace the resin or prepare fresh ammonia-free water.

Use ammonia-free distilled water for preparing all reagents, rinsing, and sample dilution.

*b. Borate buffer solution:* Add 88 mL 0.1N NaOH solution to 500 mL approximately 0.025M sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) solution (9.5 g  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ /L) and dilute to 1 L.

*c. Sodium hydroxide, 6N.*

*d. Dechlorinating reagent:* Dissolve 3.5 g sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in water and dilute to 1 L. Prepare fresh weekly. Use 1 mL reagent to remove 1 mg/L residual chlorine in 500-mL sample.

*e. Neutralization agent.*

1) Sodium hydroxide, NaOH, 1N.

2) Sulfuric acid,  $\text{H}_2\text{SO}_4$ , 1N.

*f. Absorbent solution, plain boric acid:* Dissolve 20 g  $\text{H}_3\text{BO}_3$  in water and dilute to 1 L.

*g. Indicating boric acid solution:* See Section 4500-NH<sub>3</sub>.C.3a and *b*.

*h. Sulfuric acid, 0.04N:* Dilute 1.0 mL conc  $\text{H}_2\text{SO}_4$  to 1 L.

### 4. Procedure

*a. Preparation of equipment:* Add 500 mL water and 20 mL borate buffer, adjust pH to 9.5 with 6N NaOH solution, and add to a distillation flask. Add a few glass beads or boiling chips and use this mixture to steam out the distillation apparatus until distillate shows no traces of ammonia.

*b. Sample preparation:* Use 500 mL dechlorinated sample or a known portion diluted to 500 mL with water. When NH<sub>3</sub>-N concentration is less than 100 µg/L, use a sample volume of 1000 mL. Remove residual chlorine by adding, at the time of collection, dechlorinating agent equivalent to the chlorine residual. If necessary, neutralize to approximately pH 7 with dilute acid or base, using a pH meter.

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Add 25 mL borate buffer solution and adjust to pH 9.5 with 6*N* NaOH using a pH meter.

*c. Distillation:* To minimize contamination, leave distillation apparatus assembled after steaming out and until just before starting sample distillation. Disconnect steaming-out flask and immediately transfer sample flask to distillation apparatus. Distill at a rate of 6 to 10 mL/min with the tip of the delivery tube below the surface of acid receiving solution. Collect distillate in a 500-mL erlenmeyer flask containing 50 mL indicating boric acid solution for titrimetric method. Distill ammonia into 50 mL 0.04*N* H<sub>2</sub>SO<sub>4</sub> for the ammonia-selective electrode method and for the phenate method. Collect at least 200 mL distillate. Lower distillation receiver so that the end of the delivery tube is free of contact with the liquid and continue distillation during the last minute or two to cleanse condenser and delivery tube. Dilute to 500 mL with water.

When the phenate method is used for determining NH<sub>3</sub>-N, neutralize distillate with 1*N* NaOH solution.

*d. Ammonia determination:* Determine ammonia by the titrimetric method (C), the ammonia-selective electrode methods (D and E), or the phenate methods (F and G).

### 5. Bibliography

- NICHOLS, M.S. & M.E. FOOTE. 1931. Distillation of free ammonia from buffered solutions. *Ind. Eng. Chem., Anal. Ed.* 3:311.
- GRIFFIN, A.E. & N.S. CHAMBERLIN. 1941. Relation of ammonia nitrogen to breakpoint chlorination. *Amer. J. Pub. Health* 31:803.
- PALIN, A.T. 1950. Symposium on the sterilization of water. Chemical aspects of chlorination. *J. Inst. Water Eng.* 4:565.
- TARAS, M.J. 1953. Effect of free residual chlorination of nitrogen compounds in water. *J. Amer. Water Works Assoc.* 45:47.

## 4500-NH<sub>3</sub> C. Titrimetric Method

### 1. General Discussion

The titrimetric method is used only on samples that have been carried through preliminary distillation (see Section 4500-NH<sub>3</sub>.B). The following table is useful in selecting sample volume for the distillation and titration method.

Ammonia Nitrogen in Sample <i>mg/L</i>	Sample Volume <i>mL</i>
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Ammonia Nitrogen in Sample mg/L	Sample Volume mL
5–10	250
10–20	100
20–50	50.0
50–100	25.0

### 2. Apparatus

*Distillation apparatus:* See Section 4500-NH<sub>3</sub>.B.2a and Section 4500-NH<sub>3</sub>.B.2b.

### 3. Reagents

Use ammonia-free water in making all reagents and dilutions.

*a. Mixed indicator solution:* Dissolve 200 mg methyl red indicator in 100 mL 95% ethyl or isopropyl alcohol. Dissolve 100 mg methylene blue in 50 mL 95% ethyl or isopropyl alcohol. Combine solutions. Prepare monthly.

*b. Indicating boric acid solution:* Dissolve 20 g H<sub>3</sub>BO<sub>3</sub> in water, add 10 mL mixed indicator solution, and dilute to 1 L. Prepare monthly.

*c. Standard sulfuric acid titrant, 0.02N:* Prepare and standardize as directed in Alkalinity, Section 2320B.3c. For greatest accuracy, standardize titrant against an amount of Na<sub>2</sub>CO<sub>3</sub> that has been incorporated in the indicating boric acid solution to reproduce the actual conditions of sample titration; 1.00 mL = 14 × normality × 1000 µg N. (For 0.02N, 1.00 mL = 280 µg N.)

### 4. Procedure

*a.* Proceed as described in Section 4500-NH<sub>3</sub>.B using indicating boric acid solution as absorbent for the distillate.

*b. Sludge or sediment samples:* Rapidly weigh to within ±1% an amount of wet sample, equivalent to approximately 1 g dry weight, in a weighing bottle or crucible. Wash sample into a 500-mL kjeldahl flask with water and dilute to 250 mL. Proceed as in ¶ 4a but add a piece of paraffin wax to distillation flask and collect only 100 mL distillate.

*c.* Titrate ammonia in distillate with standard 0.02N H<sub>2</sub>SO<sub>4</sub> titrant until indicator turns a pale lavender.

*d. Blank:* Carry a blank through all steps of the procedure and apply the necessary correction to the results.

### 5. Calculation

*a. Liquid samples:*

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$$\text{mg NH}_3\text{-N/L} = \frac{(A - B) \times 280}{\text{mL sample}}$$

b. Sludge or sediment samples:

$$\text{mg NH}_3\text{-N/kg} = \frac{(A - B) \times 280}{\text{g dry wt sample}}$$

where:

$A$  = volume of  $\text{H}_2\text{SO}_4$  titrated for sample, mL, and

$B$  = volume of  $\text{H}_2\text{SO}_4$  titrated for blank, mL.

### 6. Precision and Bias

Three synthetic samples containing ammonia and other constituents dissolved in distilled water were distilled and analyzed by titration.

Sample 1 contained 200  $\mu\text{g NH}_3\text{-N/L}$ , 10 mg  $\text{Cl}^-/\text{L}$ , 1.0 mg  $\text{NO}_3^-/\text{L}$ , 1.5 mg organic N/L, 10.0 mg  $\text{PO}_4^{3-}/\text{L}$ , and 5.0 mg silica/L. The relative standard deviation and relative error for the 21 participating laboratories were 69.8% and 20%, respectively.

Sample 2 contained 800  $\mu\text{g NH}_3\text{-N/L}$ , 200 mg  $\text{Cl}^-/\text{L}$ , 1.0 mg  $\text{NO}_3^-/\text{L}$ , 0.8 mg organic N/L, 5.0 mg  $\text{PO}_4^{3-}/\text{L}$ , and 15.0 mg silica/L. The relative standard deviation and relative error for the 20 participating laboratories were 28.6% and 5%, respectively.

Sample 3 contained 1500  $\mu\text{g NH}_3\text{-N/L}$ , 400 mg  $\text{Cl}^-/\text{L}$ , 1.0 mg  $\text{NO}_3^-/\text{L}$ , 0.2 mg organic N/L, 0.5 mg  $\text{PO}_4^{3-}/\text{L}$ , and 30.0 mg silica/L. The relative standard deviation and relative error for the 21 participating laboratories were 21.6%, and 2.6%, respectively.

### 7. Bibliography

- MEEKER, E.W. & E.C. WAGNER. 1933. Titration of ammonia in the presence of boric acid. *Ind. Eng. Chem., Anal. Ed.* 5:396.
- WAGNER, E.C. 1940. Titration of ammonia in the presence of boric acid. *Ind. Eng. Chem., Anal. Ed.* 12:711.

## 4500-NH<sub>3</sub> D. Ammonia-Selective Electrode Method

### 1. General Discussion