

out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.

- 4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

5.0 Apparatus

- 5.1 An all-glass distilling apparatus with an 800-1000 mL flask.
- 5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.
- 5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm \pm 1.5 mm inside measurement from bottom.
- 5.4 Erlenmeyer flasks: The distillate is collected in 500 mL glass-stoppered flasks. These flasks should be marked at the 350 and the 500 mL volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6.0 Reagents

- 6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.
- NOTE 1:** All solutions must be made with ammonia-free water.
- 6.2 Ammonium chloride, stock solution: 1.0 mL = 1.0 mg NH₃-N. Dissolve 3.819 g NH₄Cl in distilled water and bring to volume in a 1 liter volumetric flask.
- 6.3 Ammonium chloride, standard solution: 1.0 mL = 0.01 mg. Dilute 10.0 mL of stock solution (6.2) to 1 liter in a volumetric flask.
- 6.4 Boric acid solution (20 g/L): Dissolve 20 g H₃BO₃ in distilled water and dilute to 1 liter.
- 6.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.
- NOTE 2:** Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95% ethanol.
- 6.6 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 mL of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.
- NOTE 3:** This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 mL volume).
- 6.7 Borate buffer: Add 88 mL of 0.1 N NaOH solution to 500 mL of 0.025 M sodium tetraborate solution (5.0 g anhydrous Na₂B₄O₇, or 9.5 g Na₂B₄O₇•10H₂O per liter) and dilute to 1 liter.
- 6.8 Sulfuric acid, standard solution: (0.02 N, 1 mL = 0.28 mg NH₃-N). Prepare a

stock solution of approximately 0.1 N acid by diluting 3 mL of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2 -free distilled water. Dilute 200 mL of this solution to 1 liter with CO_2 -free distilled water.

NOTE 4: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can then be prepared.

6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3 , oven-dried at 140°C , and diluting to 1000 mL with CO_2 -free distilled water.

- 6.9 Sodium hydroxide 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.
- 6.10 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:
- Sodium thiosulfate (1/70 N): Dissolve 3.5 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in distilled water and dilute to 1 liter. One mL of this solution will remove 1 mg/L of residual chlorine in 500 mL of sample.
 - Sodium arsenite (1/70 N): Dissolve 1.0 g NaAsO_2 in distilled water and dilute to 1 liter.

7.0 Procedure

- 7.1 Preparation of equipment: Add 500 mL of distilled water to an 800 mL Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.
- 7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 mL of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.
- 7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 mL Kjeldahl flask and add 25 mL of the borate buffer (6.7). Distill 300 mL at the rate of 6-10 mL/min. into 50 mL of 2% boric acid (6.4) contained in a 500 mL Erlenmeyer flask.
- NOTE 5:** The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution. Dilute the distillate to 500 mL with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/L the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically. The electrode method may also be used.
- 7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.
- 7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4 , matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

mL of Standard	
1.0 mL = mg NH ₃ -N	mg NH ₃ -N/50.0 mL
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 mL with distilled water, add 2.0 mL of Nessler reagent (6.6) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained plot absorbance vs. mg NH₃-N for the standard curve. Determine the ammonia in the distillate by nesslerizing 50 mL or an aliquot diluted to 50 mL and reading the absorbance at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Selective Ion Electrode Method (Method 350.3) in this manual.

7.5 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

8.0 Calculations

8.1 Titrimetric

$$\text{mg/L NH}_3 - \text{N} = \frac{A \times 0.28 \times 1,000}{S}$$

where:

A = mL 0.02 N H₂SO₄ used.

S = mL sample.

8.2 Spectrophotometric

$$\text{mg/L NH}_3 - \text{N} = \frac{\text{A} \times 1,000}{\text{D}} \times \frac{\text{B}}{\text{C}}$$

where:

A = mg NH₃-N read from standard curve.

B = mL total distillate collected, including boric acid and dilution.

C = mL distillate taken for nesslerization.

D = mL of original sample taken.

8.3 Potentiometric

$$\text{mg/L NH}_3 - \text{N} = \frac{500}{\text{D}} \times \text{A}$$

where:

A = mg NH₃-N/L from electrode method standard curve.

D = mL of original sample taken.

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

Increment as Nitrogen, Ammonia mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as Bias %	Bias mg N/liter
0.21	0.122	-5.54	-0.01
0.26	0.070	-18.12	-0.05
1.71	0.244	+0.46	+0.01
1.92	0.279	-2.01	-0.04

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 410, Method 418A and 418B (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1426-74, Method A, p 237 (1976).