METHOD #: 350.2	Approved for NPDES (Editorial Revision 1974)	
TITLE:	Nitrogen, Ammonia (Colorimetric, Titrimetric, Potentiometric Distillation Procedure)	
ANALYTE:	CAS # Nitrogen 7727-37-9, N CAS # Ammonium 7664-41-7, NH ₃	
INSTRUMENTATION:	Titration, Spectrophotometer	
STORET No.	Total 00610 Dissolved 00608	

1.0 Scope and Application

- 1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automatedequipment.
- 1.2 The method covers the range from about 0.05 to 1.0 mg NH_3 -N/L for the colorimetric procedure, from 1.0 to 25 mg/L for the titrimetric procedure, and from 0.05 to 1400 mg/L for the electrode method.
- 1.3 This method is described for macro glassware; however, microdistillation equipment may also be used.

2.0 Summary of Method

- 2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.
- 3.0 Sample Handling and Preservation
 - 3.1 Samples may be preserved with 2 mL of conc. H_2SO_4 per liter and stored at 4°C.
- 4.0 Interferences
 - 4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.
 - 4.2 Cyanate, which may be encountered in certain industrial emuents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried

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 ±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: $1.0 \text{ mL} = 1.0 \text{ mg NH}_3$ -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 H_3BO_3 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

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). Borate buffer: Add 88 mL of 0.1 N NaOH solution to 500 mL of 0.025 N

- 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 $Na_2B_4O_7$, or 9.5 g $Na_2B_4O_7$ •10H₂O per liter) and dilute to 1 liter.
- 6.8 Sulfuric acid, standard solution: (0.02 N, 1 mL = 0.28 mg NH_3 -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 $0.1 \text{ N H}_2\text{SO}_4$ solution against a $0.100 \text{ N Na}_2\text{CO}_3$ 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 Na₂CO₃ solution. This last solution is prepared by dissolving 1.060 g anhydrous Na₂CO₃, oven-dried at 140°C, and diluting to 1000 mL with CO₂-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:
 - a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g Na₂S₂O₃•5H₂O 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.
 - b. Sodium arsenite (1/70 N): Dissolve 1.0 g NaAsO₂ 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.

mL of Standard			
1.0 mL = mg NH ₃ -N	mg NH₃-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		

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

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 NH_3 -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

$$mg/L NH_3 - N = \frac{A \times 0.28 \times 1,000}{S}$$

where: $A = mL 0.02 \text{ N } H_2SO_4 \text{ used.}$ S = mL sample. 8.2 Spectrophotometric

$$mg/L NH_3 - N = \frac{A \times 1,000}{D} \times \frac{B}{C}$$

where:

A = mg NH_3 -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

$$mg/L NH_3 - N = \frac{500}{D} \times A$$

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	Precision as	Accuracy as	
Nitrogen, Ammonia	Standard Deviation	Bias	Bias
mg N/liter	mg N/liter	%	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).