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AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Methods for Ammonia Nitrogen In Water [1]

This standard is issued under the fixed designation D 1426; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the determination of ammonia nitrogen, exclusive of organic nitrogen, in water. Two test methods are included as follows:

	Sections
Test Method A—Direct Nesslerization	7 to 15
Test Method B—Ion Selective Electrode	16 to 24

1.2 Test Method A is used for the routine determination of ammonia in steam condensates and demineralizer effluents.

1.3 Test Method B is applicable to the determination of ammonia nitrogen in the range from 0.5 to 1000 mg NH_3N/L directly in reagent and effluent waters. Higher concentrations can be determined following dilution. The reported lower range is based on multiple-operator precision. Lower limits have been obtained by two of the twelve laboratories participating in the round robin.

1.4 Both test methods A and B are applicable to surface and industrial waters and wastewaters following distillation. The test method for distillation given in Appendix X1 has been used in the past to meet requirements for predistillation of samples being analyzed for ammonia.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.6 The distillation method now appears as Appendix X1 and is provided as nonmandatory information only. The automated colorimetric phenate method has been discontinued.

2. Referenced Documents

2.1 *ASTM Standards:*

D1066 Practice for Sampling Steam[2]
D1129 Terminology Relating to Water[2]
D1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]
D1193 Specification for Reagent Water[2]
D2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[2]
D3370 Practices for Sampling Water[2]
E60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[3]
E275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[4]

2.2 *APHA Standard*:

Standard Methods for the Examination of Water and Waste Water [5]

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1129.

4. Significance and Use

4.1 Nitrogen is a nutrient in the environment and is necessary to sustain growth of most organisms. It exists in several forms such as nitrate, nitrite, organic nitrogen such as proteins or amino acids, and ammonia.

4.2 Ammonia is a colorless, gaseous compound with a sharp distinctive odor. It is highly soluble in water where it exists in a molecular form associated with water and in an ionized form as NH_4^+. The extent of association or ionization is dependent on the temperature and pH. It may also be toxic to aquatic life. The extent of toxicity is dependent upon species and extent of dissociation.[6] Ammonia may occur in water as a product of anaerobic decomposition of nitrogen containing compounds or from waste streams containing ammonia.

5. Purity of Reagents

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such

[1] These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 03.05.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

[5] Available from American Public Health Association, 1015 15th St. N.W., Washington, DC 20005.

[6] *Quality Criteria for Water*, USEPA-440/9-76-023, July 26, 1976, pp. 16–24.

specifications are available.[7] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. In addition, this water shall be free of ammonia nitrogen. Such water is best prepared by the passage of distilled water through an ion-exchange resin. These resins should also be selected so that organic compounds which might subsequently interfere with the ammonia determination will be removed. Regeneration of the ion-exchange materials should be carried out in accordance with the instructions of the manufacturer.

6. Sampling

6.1 Collect the sample in accordance with Practice D 1066, Specification D 1192, and Practices D 3370, as applicable.

6.2 Preserve the samples by the addition of 1 mL of concentrated sulfuric acid per litre and store at 4°C. The pH should be 2.0 or less. Analyze the samples within 24 h of sampling. Do not use mercuric chloride as a preservative.

TEST METHOD A—DIRECT NESSLERIZATION

7. Scope

7.1 This test method is suitable for the rapid routine determination of ammonia nitrogen in steam condensates and demineralized water. See Appendix X1 for the distillation test method.

8. Summary of Test Method

8.1 A sample aliquot is Nesslerized directly and the ammonia content determined colorimetrically.

9. Interferences

9.1 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 a pH of 9.5. Glycine, hydrazine, and some amines will react with Nessler's reagent to give the characteristic yellow color in the time required for the test. Similarly, volatile alkaline compounds such as hydrazine and the amines will influence titrimetric results. Some organic compounds such as ketones, aldehydes, alcohols, and some amines may cause an off color on Nesslerization. Some of these, such as formaldehyde may be eliminated by boiling off at a low pH prior to Nesslerization. Residual chlorine must be removed prior to the ammonia determination by pretreatment of the sample.

9.2 Turbid samples may be clarified with $ZnSO_4$ and NaOH solution; the precipitated $Zn(OH)_2$ is filtered off, discarding the first 25 mL of filtrate, and the ammonia is determined on an aliquot of the remaining clear filtrate by direct Nesslerization. Ammonia can be lost in basic conditions. Check procedure with a standard solution.

10. Apparatus

10.1 *Nessler Tubes*— Matched Nessler tubes[5] about 300 mm long, 17-mm inside diameter, and marked for 50 mL at 225 ± 1.5 mm from inside the bottom.

10.2 *Photometer*—Filter photometer or spectrophotometer suitable for absorbance measurements at 425 nm. Filter photometers and photometric practices used in this test method shall conform to Practice E 60. Spectrophotometers shall conform to Practice E 275.

10.3 *Stoppers*—Rubber, size No. 2, to fit Nessler tubes. These stoppers shall be boiled in H_2SO_4(1 + 99), rinsed, boiled in NaOH solution (1 g/L), rinsed, allowed to stand in dilute Nessler reagent for 30 min, and then rinsed again.

11. Reagents

11.1 *Ammonia Nitrogen Solution, Standard* (1 mL = 0.01 mg N)—Dry reagent grade ammonium sulfate ($(NH_4)_2SO_4$) for 1 h at 100°C. Accurately weigh 4.718 g and dissolve in water. Dilute to 1 L in a volumetric flask. Pipet 10 mL of this stock solution to a 1-L volumetric flask and dilute to volume with water.

11.2 *Disodium Dihydrogen Ethylenediamine Tetraacetate Solution* (500 g/L)—Dissolve 500 g of disodium dihydrogen ethylenediamine tetraacetate dihydrate in water containing 100 g of NaOH. Gently heat to complete dissolution. Cool and dilute to 1 L.

11.3 *Nessler Reagent*— Dissolve 100 g of anhydrous mercuric iodide (HgI_2) and 70 g of anhydrous potassium iodide (KI) in a small volume of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of sodium hydroxide (NaOH) in 500 mL of water. Dilute the mixture to 1 L. Store the solution in the dark for five days and filter twice, either through a fritted glass crucible or glass fiber filter before using. If this reagent is stored in a chemically resistant bottle out of direct sunlight, it will remain stable up to a period of 1 year.

NOTE 1—This reagent should give the characteristic color with ammonia within 10 min after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50-mL volume). The solution may be used without 5-day storage if it is filtered through a 0.45 µm membrane (previously rinsed with reagent water Type I (see Specification D 1193)) shortly before use.

NOTE 2—Mercury and its salts are hazardous materials. They should be stored, handled and dispensed accordingly. Disposal of solutions must be made by legally acceptable means.

11.4 *Sodium Hydroxide Solution* (240 g/L)—Dissolve 240 g of NaOH in water and dilute to 1 L.

11.5 *Sodium Potassium Tartrate Solution* (300 g/L)—Dissolve 300 g of sodium-potassium tartrate tetrahydrate in 1 L of water. Boil until ammonia-free and dilute to 1 L.

11.6 *Zinc Sulfate Solution* (100 g/L)—Dissolve 100 g of zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) in water and dilute to 1 L.

12. Calibration

12.1 Prepare a series of standards containing the following volumes of standard ammonia nitrogen solution diluted to 50

[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

mL with water: 0.0, 1.0, 3.0, 5.0, 8.0, and 10.0 mL. Mix, add 1 mL of Nessler reagent, and remix. After 20 to 30 min, using a photometer suitable for absorbance measurement at 425 nm and a compensatory blank (Nesslerized ammonia-free water), prepare a calibration curve based on a series of these standards.

12.2 If a visual comparison method is used, prepare a series of 14 Nessler tubes containing the following volumes of standard ammonia nitrogen solution diluted to 50 mL with water: 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.7, 2.0, 2.5, 3.0, 3.5, and 4.0 mL. Mix, add 1 mL of Nessler reagent, and remix.

13. Procedure

13.1 If the sample contains turbidity, add 1 mL of $ZnSO_4$ solution to a 100-mL aliquot and mix. Add NaOH solution with gentle mixing until the pH is about 10.5. Allow to settle and filter using a water-washed, moderately-retentive filter paper, discarding the first 25 mL of the filtrate. Dilute a portion of the filtrate or clear sample, containing not more than 0.1 mg of ammonia nitrogen, to 50 mL in a Nessler tube. Add 2 drops of sodium potassium tartrate solution (or disodium dihydrogen ethylenediamine tetraacetate) to prevent cloudy tubes, and mix. Add 1 mL of Nessler solution and measure photometrically at a wavelength of 425 nm.

13.2 If a visual comparison method is used, select a volume containing not more than 0.04 mg of ammonia nitrogen and dilute to 50 mL. Mix, add 1 mL of Nessler reagent, and remix. Compare the color developed after 10 min with the previously prepared standards. If the ammonia nitrogen concentration is below 0.008 mg (in the 50-mL tube) compare after 30 min.

14. Calculation

14.1 Calculate the ammonia concentration in mg/L of nitrogen in the original sample, using Eq 1:

$$\text{Ammonia nitrogen, mg/L} = [(A \times 1000)/S] \quad (1)$$

where:
A = ammonia nitrogen observed, mg, and
S = sample, mL.

14.2 Calculate the ammonia concentration in mg/L of ammonia in the original sample, using Eq 2:

$$\text{Ammonia, mg/L} = E \times 1.22 \quad (2)$$

where:
E = ammonia nitrogen, mg/L.

15. Precision and Bias [8]

15.1 The precision of this test method was measured without the use of any distillation procedure by nine laboratories in reagent water only at four levels in the range from 30 to 100 mg NH_3-N/L, and each concentration was done in triplicate. The test method was tested in reagent water because steam condensates and demineralized effluents are similar to reagent water.

15.2 Analysts using Test Method A in any matrix other than a steam condensate or demineralized effluent must show the applicability of this test method to that matrix.

15.3 The precision of Test Method A in reagent water was 0.04 mg/L at 1.0 mg NH_3-N/L. Other precision data are shown in Table 1.

15.4 *Bias*—Recoveries of known amounts of ammonia from reagent water are shown in Table 1. No distillation procedure was used in this test.

TEST METHOD B—ION SELECTIVE ELECTRODE

16. Scope

16.1 This test method is applicable to the measurement of ammonia in reagent and effluent water.

17. Summary of Test Method

17.1 The sample is made alkaline with sodium hydroxide to convert ammonium ion to ammonia. The ammonia thus formed diffuses through a gas-permeable membrane of an ion selective electrode (ISE) and alters the pH of its internal solution which, in turn, is sensed by a pH electrode. The potential is measured by means of a pH meter or an ISE meter. If the pH meter is used, the ammonia content is determined from a calibration curve; if the ISE meter is used, the ammonia content is read directly from the meter.

18. Interferences

18.1 Volatile amines are positive interferences.

18.2 Mercury, if present, forms ammonia complexes, thus causing negative interference.

18.3 Organic compounds that form ammonia readily (within 5 min) under alkaline conditions are a positive interference. In general, this should not be a problem because the interfering concentrations may have to be greater than 100 mg/L. Among the inorganic compounds, hydrazine sulfate has yielded a reading of 0.2 mg/L of NH_3 as N when its concentration was 100 mg/L as N.

19. Apparatus

19.1 *Electrode*, gas-sensing, ammonia, incorporating an internal reference electrode and a diffusion-type membrane.

19.2 *Meter*, one of the following:

19.2.1 *pH Meter*, digital or expanded millivolt scale, accurate to ±0.1 mV.

19.2.2 *ISE Meter*, with direct-reading concentration scale.

19.3 *Electrode Holder*, for mounting the electrode at 20° to the vertical.

19.4 *Stirrer*, magnetic, with TFE-fluorocarbon-coated stirring bars.

19.5 *Heat Barrier*, 6-mm thick cork board placed underneath the beaker to insulate the sample solution from heat generated by the magnetic stirrer.

TABLE 1 Determination of Precision and Bias for Test Method A—Direct Nesslerization Method (Photometric at 425 nm)

Amount Added, mg/L	Matrix Water	Mean Recovery, %	Precision, mg/L		Bias, %
			S_t	S_o	
0.120	Reagent	89	0.011	0.003	−10.8
0.200	Reagent	98	0.013	0.002	−2.5
0.350	Reagent	98	0.021	0.002	−1.7
1.000	Reagent	101	0.042	0.014	+ 1.4

[8] Supporting data are available from ASTM Headquarters. Request RR:D19-1015.

20. Reagents

20.1 *Ammonia, Solution, Stock* (1000 mg NH_3 as N/L)—Dry reagent-grade ammonium sulfate ($(NH_4)_2SO_4$) for 1 h at 100°C. Accurately weigh 4.718 g and dissolve in water in a 1-L volumetric flask. Dilute to volume with water. This solution is stable for at least three months.

20.2 *Ammonia, Solution, Intermediate* (100 mg NH_3 as N/L)—Pipet 100 mL of the 1000-mg/L standard solution to a 1-L volumetric flask and dilute to volume with water. This solution is stable for one month.

20.3 *Ammonia, Solution, Working* (10, 1, and 0.1 mg NH_3 as N/L)— Quantitatively transfer 100, 10, and 1 mL of the 100-mg/L standard solution into separate 1-L volumetric flasks. Dilute each to volume with water. Prepare these solutions daily before use.

20.4 *Ammonium Chloride Solution* (5.4 g/L)—Dissolve 5.4 g of ammonium chloride (NH_4Cl) in water and dilute to 1 L. This solution is used only for soaking the electrode.

20.5 *Sodium Hydroxide Solution* (400 g/L)—Dissolve 400 g of sodium hydroxide (NaOH) in water. Cool and dilute to 1 L.

21. Calibration

21.1 *pH Meter*—Refer to the manufacturer's instruction manual for proper operation of the pH meter. Prepare calibration curves using a minimum of three standard solutions (see 20.3), bracketing the expected concentrations of the samples.

21.1.1 Treat the standards as directed in 22.1 and measure the potential of each standard and record in millivolts. The standards and the sample must be at the same temperature, preferably about 25°C.

21.1.2 Using semilogarithmic graph paper, plot the concentration of ammonia nitrogen in milligrams per litre on the log axis against the corresponding electrode potential, in millivolts, on the linear axis.

21.1.3 Check the calibration curve every 3 h when analyzing a series of samples.

21.2 *ISE Meter*—Refer to the manufacturer's instruction manual for proper operation of the meter. Prepare calibration curves with three standard solutions (see 20.3), bracketing the expected concentrations of the samples.

21.2.1 Check the calibration curve every 3 h when analyzing a series of samples; otherwise, calibrate daily.

22. Procedure

22.1 *Sample Treatment*:

22.1.1 Transfer 100 mL of the sample (or an aliquot diluted to 100 mL) to a 150-mL beaker. The sample temperature must be the same as that of the standards used in calibration (see 21.1 and 21.2).

22.1.2 Add the stirring bar and mix on the magnetic stirrer. Do not mix so rapidly that air bubbles are drawn into the solution.

22.1.3 Immerse the electrode into the sample, positioning it at an angle 20° to the vertical, making sure that no air bubbles are trapped on the membrane of the electrode. All precautions recommended by the manufacturer should be observed to ensure accurate measurements.

22.1.4 Add 1.0 mL of NaOH solution (see 20.5) to the sample. The NaOH solution should be added just prior to measurement because ammonia may be lost to the atmosphere from a stirred alkaline solution.

22.1.5 Check the pH of the sample with pH paper. The pH must be greater than 11.0. If less than 11.0, add additional NaOH solution (see 20.5) in 0.1-mL increments until the pH of the solution exceeds 11.0.

22.1.6 When the electrode comes to equilibrium, measure the electrode potential of the ammonia nitrogen concentration as directed in 22.2 (see Note 3).

NOTE 3—The time required for the electrode to come to equilibrium is dependent on the ammonia content of the sample. For concentrations above 0.5 mg/L, the response time is about 30 s.

22.2 *Sample Measurement*—Determine the ammonia nitrogen concentration by means of a pH meter or a specific-ion meter.

22.2.1 *pH Meter*—Record the observed potential in millivolts and convert to milligrams per litre of ammonia nitrogen by means of the calibration curve (see 21.1.2).

22.2.2 *ISE Meter*—Record the concentration reading directly from the logarithmic scale as milligrams of ammonia nitrogen per litre.

23. Calculation

23.1 Report the ammonia nitrogen content in milligrams per litre. If necessary calculate for dilution of original sample.

24. Precision and Bias [9]

24.1 The precision of this test method was tested without the use of any distillation procedure by twelve laboratories in reagent water and effluent waters at six levels in the range from 0.04 to 750 mg NH_3-N/L, and each concentration was done in triplicate.

24.2 Analysts using Test Method B in any matrix other than reagent water or effluent waters must show the applicability of this test method to that matrix.

24.3 The precision of Test Method B in reagent water was 0.11 mg/L at 0.8 mg NH_3-N/L and 0.3 mg/L at 0.8 mg NH_3-N/L in effluent waters. Other precision data are shown in Table 2.

[9] Supporting data are available from ASTM Headquarters. Request RR:D19-1052.

TABLE 2 Precision and Bias of Test Method B—Ion Selective Electrode

Amount Added, mg/L	Matrix Water	Mean Recovery,%	Precision, mg/L		Bias, %
			S_t	S_o	
0.04	Reagent	200	0.05	0.01	+ 100
	Effluent	100	0.03	0.00	0
0.10	Reagent	180	0.05	0.01	+ 80
	Effluent	470	0.61	0.01	+ 370
0.80	Reagent	105	0.11	0.04	+ 5
	Effluent	105	0.30	0.06	+ 5
20	Reagent	95	2	1	−5
	Effluent	95	3	2	−5
100	Reagent	98	5	2	−2
	Effluent	97	...	...	...
750	Reagent	97	78	12	−3
	Effluent	99	106	10	−1

24.4 *Bias*—Recoveries of known amounts of ammonia, without the use of any distillation procedure, from both reagent water and effluent water were 95 % at 0.8 mg NH_3-N/L. Other recovery data are shown in Table 2.

25. Keywords

25.1 ammonia; analysis; calorimetric; electrode; water

APPENDIX

(Nonmandatory Information)

X1. DISTILLATION TEST METHOD

X1.1 Distillation Apparatus

X1.1.1 An all-glass still consisting of a 1- or 2-L flask, preferably double-necked to facilitate sample addition. The center neck is connected in series with a spray trap (Kjeldahl), a water-cooled condenser, and a long narrow delivery tube which extends nearly to the bottom of a suitable receiver marked at 300 or 350 mL. The outer neck carries a glass-stoppered funnel to facilitate sample addition. The outlet of this funnel shall extend below the liquid level in the flask. In the distillation of ammonia it is also permissible to use the regular Kjeldahl distillation apparatus. When using such apparatus, the 800-mL Kjeldahl flask shall be used.

X1.2 Reagents

X1.2.1 *Borate Buffer Solution*—Add 88 mL of a 4 g/L (see X1.2.5) NaOH solution to 500 mL of a 5.04-g/L sodium tetraborate ($Na_2B_4O_7$) solution and dilute to 1 L.

X1.2.2 *Boric Acid Solution* (20 g/L)—Dissolve 20 g of boric acid (H_3BO_3) in water and dilute to 1 L.

X1.2.3 *Dechlorinating Agent*—Dissolve 1.0 g of sodium arsenite ($NaAsO_2$) in ammonia-free water and dilute to 1 L. One millilitre of this solution will remove 1 mg/L of residual chlorine from the 500-mL sample.

X1.2.4 *Sodium Hydroxide Solution* (240 g/L)—Dissolve 240 g of NaOH in 1 L of water.

X1.2.5 *Sodium Hydroxide Solution* (4 g/L)—Dissolve 4 g of NaOH in 1 L of water.

X1.3 Procedure

X1.3.1 *Distillation*— Remove residual chlorine by adding the appropriate quantity of dechlorinating agent (see X1.2.3). To 500 mL of water add 25 mL of borate buffer and adjust the pH to 9.5 with 6 *N* NaOH solution (see X1.2.4) using a pH meter. Distill until two 50-mL portions of the distillate are shown to be ammonia-free. After the still has cooled, add sample containing not more than 0.4 mg of ammonia nitrogen and water to attain a final volume of about 550 mL. Distill 300 mL at a rate of 6 to 10 mL/min into 50 mL of H_3BO_3 solution (see X1.2.2). Remove the receiver and mix. Collect an additional 50 mL to check for complete ammonia removal.

X1.4 Ammonia Determination

X1.4.1 The distillation procedure (see X1.3) should be followed by the use of either Test Method A or B.