INTERNATIONAL

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Standard Test Methods for Ammonia Nitrogen In Water[1]

This standard is issued under the fixed designation D1426; 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 U.S. Department of Defense.

ε[1] NOTE—The WTO caveat was editorially added in November 2021.

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 – 16
Test Method B—Ion Selective Electrode	17 – 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

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

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Flowing Process Streams
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

2.2 *APHA Standard:*[3]

Standard Methods for the Examination of Water and Waste Water

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

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

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

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from American Public Health Association, 800 I St. NW, Washington, DC 20001, http://www.apha.org.

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.[4] 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 specifications are available.[5] 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 D1193, 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 Practices D1066 and D3370, 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.

NOTE 1—This preservation procedure will convert cyanate to ammonia. The user must be cautioned not to acidify samples if they contain cyanates. The preservation can extend the holding time to 28 days; however, the user will need to confirm the actual holding time.

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[3] 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 E60. Spectrophotometers shall conform to Practice E275.

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 and Materials

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. A purchased ammonia nitrogen stock solution of appropriate known purity is also acceptable.

NOTE 2—Ammonia standards should be stored in an area free from ambient ammonia vapors.

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 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-μm membrane.

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

[5] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

11.4 *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. A purchased solution of appropriate known purity is also acceptable.

NOTE 3—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 D1193)) shortly before use.

NOTE 4—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.

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

11.6 *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.

11.7 *Zinc Sulfate Solution* (100 g/L)—Dissolve 100 g of zinc sulfate heptahydrate ($ZnSO_4·7H_2O$) 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 mL with water: 0.0, 1.0, 3.0, 5.0, 8.0, and 10.0 mL. Mix, add 1 mL of Nessler reagent (11.4), 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. Analyze at least three working standards containing concentrations of ammonia nitrogen that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

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 (11.1) 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 (11.4), and remix.

13. Procedure

13.1 If the sample contains turbidity, add 1 mL of $ZnSO_4$ solution (11.7) to a 100-mL aliquot and mix. Add NaOH solution (11.5) with gentle mixing until the pH is about 10.5. Allow to settle and filter (11.3) 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 (11.6) (or disodium dihydrogen ethylenediamine tetraacetate [11.2]) to prevent cloudy tubes, and mix. Add 1 mL of Nessler solution (11.4) 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 (11.4), 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:

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

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[6]

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/L NH_3-N, 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/L NH_3-N. Other precision data are shown in Table 1.

15.4 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

16. Quality Control

16.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1015. Contact ASTM Customer Service at service@astm.org.

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

confidence limits of the test, the following QC procedures must be followed when analyzing ammonia nitrogen.

16.2 *Calibration and Calibration Verification:*

16.2.1 Analyze at least three working standards containing concentrations of ammonia nitrogen that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument (see 12.1).

16.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

16.2.3 If calibration cannot be verified, recalibrate the instrument.

16.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

16.3 *Initial Demonstration of Laboratory Capability:*

16.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

16.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material covering a midrange concentration of ammonia nitrogen. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

16.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in 15.3. This study should be repeated until the recoveries are within the limits given in 15.3. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

16.4 *Laboratory Control Sample (LCS):*

16.4.1 To ensure that the test method is in control, prepare and analyze an LCS containing a mid-range concentration of ammonia nitrogen with each batch (laboratory defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ±15 % of the known concentration.

16.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.5 *Method Blank:*

16.5.1 Analyze a reagent water test blank with each laboratory defined batch. The concentration of ammonia nitrogen found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of ammonia nitrogen is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.6 *Matrix Spike (MS):*

16.6.1 To check for interferences in the specific matrix being tested, perform an MS on at least one sample from each laboratory defined batch by spiking an aliquot of the sample with a known concentration of ammonia nitrogen and taking it through the analytical method.

16.6.2 The spike concentration plus the background concentration of ammonia nitrogen must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is two to five times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

16.6.3 Calculate the percent recovery of the spike (P) using the following calculation:

$$P = \frac{100\left[A\left(V_s + V\right) - BV_s\right]}{CV} \quad (3)$$

where:

A = analyte known concentration (mg/L) in spiked sample,
B = analyte known concentration (mg/L) in unspiked sample,
C = known concentration (mg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

16.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 5—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

16.7 *Duplicate:*

16.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

16.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

16.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.8 *Independent Reference Material (IRM):*

16.8.1 n order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory

TEST METHOD B—ION SELECTIVE ELECTRODE

17. Scope

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

18. Summary of Test Method

18.1 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.

19. Interferences

19.1 Volatile amines are positive interferences.

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

19.3 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.

20. Apparatus

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

20.2 *Meter,* one of the following:

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

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

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

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

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

21. Reagents

21.1 *Ammonia, Solution, Stock* (1000 mg/L NH_3 as 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 in a 1-L volumetric flask. Dilute to volume with water. This solution is stable for at least three months. A purchased ammonia nitrogen stock solution of appropriate known purity is also acceptable. See Note 3.

21.2 *Ammonia, Solution, Intermediate* (100 mg/L NH_3 as N)—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.

21.3 *Ammonia, Solution, Working* (10, 1, and 0.1 mg/L NH_3 as N)—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.

21.4 *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.

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

22. Calibration

22.1 *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 21.3), bracketing the expected concentrations of the samples.

22.1.1 Treat the standards as directed in 23.1 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. Analyze at least three working standards containing concentrations of ammonia nitrogen that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

22.1.2 Prepare a semi-log plot and 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.

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

22.2 *ISE Meter*—Refer to the manufacturer's instruction manual for proper operation of the meter. Prepare calibration curves with three standard solutions (see 21.3), bracketing the expected concentrations of the samples. Analyze at least three