Designation: D 3867 – 99

Standard Test Methods for Nitrite-Nitrate in Water[1]

This standard is issued under the fixed designation D 3867; 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.

1. Scope *

1.1 These test methods cover the determination of nitrite nitrogen, nitrate nitrogen, and combined nitrite-nitrate nitrogen in water and wastewater in the range from 0.05 to 1.0 mg/L nitrogen. Two test methods[2] are given as follows:

	Sections
Test Method A—Automated Cadmium Reduction	9 to 16
Test Method B—Manual Cadmium Reduction	17 to 24

1.2 These test methods are applicable to surface, saline, waste, and ground waters. It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

1.3 *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.* For specific hazard statements, see Note 1 and Note 2.

2. Referenced Documents

2.1 *ASTM Standards:*

D 992 Test Method for Nitrate Ion in Water[3]

D 1129 Terminology Relating to Water[4]

D 1141 Specification for Substitute Ocean Water[5]

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[4]

D 1193 Specification for Reagent Water[4]

D 1254 Test Method for Nitrite Ion in Water[6]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[4]

D 3370 Practices for Sampling Water from Closed Conduits[4]

E 60 Practices for Photometric and Spectrometric Methods for Chemical Analysis of Metals[7]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[8]

3. Terminology

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

4. Summary of Test Methods

4.1 A filtered sample is passed through a column containing copper-coated cadmium granules to reduce nitrate ion to nitrite ion. The combined nitrite-nitrate nitrogen is determined by diazotizing the total nitrite ion with sulfanilamide and coupling with *N*-(1-naphthyl)ethylenediamine dihydrochloride to form a highly colored azo dye that is measured spectrophotometrically.

4.2 The nitrite ion originally present in the sample can be determined separately by carrying out the procedure and omitting the cadmium reduction step.

4.3 The nitrate ion can be calculated as the difference between the combined nitrite-nitrate nitrogen and the nitrite nitrogen.

5. Significance and Use

5.1 Both test methods use identical reagents and sample processing. The only difference between the two methods is that one test method is automated and the other is manual. The ranges and interferences are identical.

5.2 The automated test method is preferred when large numbers of samples are to be analyzed. The manual test method is used for fewer samples or when automated instrumentation is not available.

5.3 These test methods replace Test Methods D 1254 (Nitrite) and D 992 (Nitrate). The nitrite test method (Test Method D 1254) used a reagent which is considered to be a potential carcinogen. The nitrate test method (Test Method D 992) has been shown to have relatively large errors when used in wastewaters and also has greater manipulative difficulties than the test method described herein.

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

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[2] Methods similar to these appear in *Methods of Chemical Analysis of Water and Wastes*, 2nd edition, U.S. Environmental Protection Agency.

[3] Discontinued; see 1983 *Annual Book of ASTM Standards*, Vol 11.01.

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

[5] *Annual Book of ASTM Standards*, Vol 11.02.

[6] Discontinued; see 1980 *Annual Book of ASTM Standards*, Part 31.

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

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

***A Summary of Changes section appears at the end of this standard.**

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6. Interferences

6.1 Turbid samples must be filtered prior to analysis to eliminate particulate interference. Furthermore, sample turbidity results in a buildup on the reduction column that restricts sample flow.

6.2 Sample color that absorbs at wavelengths between 520 and 540 nm interferes with the absorbance measurements. When color is suspect, analyze a sample blank, omitting the *N*-(1-naphthyl)ethylenediamine dihydrochloride from the color reagent.

6.3 Oil and grease in the sample coat the surface of the cadmium and prevent complete reduction of nitrate to nitrite. This interference is usually removed by filtration prior to analysis. If filtration is not adequate, the interference can be removed by preextracting the sample with an *n*-hexane or a solid phase extraction (SPE) filter.

6.4 Certain metal ions, in concentrations above 35 mg/L, may cause an interference. For example, Hg (II) and Cu (II) may form colored complex ions having absorption bands in the region of color measurement. Iron and manganese are other reported examples of interference.

6.5 Excessive amounts of chlorine will deactivate the reducing column. Chlorine might be present in some Type II water. The use of chlorine-containing Type II water will lead to a negative interference because nitrite and chlorine do not normally coexist. This is of particular importance when preparing standards or spiked samples.

6.6 In acid samples (pH less than 4.5) nitrate is not reduced in the cadmium column. To overcome this interference, the sample must be neutralized to a pH of between 6 and 8 prior to analysis.

7. Purity of Reagents

7.1 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, when such specifications are available.[9] Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. Other reagent water types may be used, provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of these test methods. Type II water was specified at the time of round-robin testing of these test methods.

8. Sampling and Sample Preservation

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

8.2 When nitrite ion is to be determined separately, analyze as soon as possible after sampling. Even when sterile bottles are used, bacteria naturally present in the water may cause conversion of all or part of nitrite ion to other forms such as nitrate or ammonia. Ammonia and natural amines, which are frequently present in natural waters, may react with nitrites to form nitrogen. If samples are to be stored for 24 h or less, preserve the sample by refrigeration at 4°C. If the sample must be stored for more than 24 h, preserve it by the addition of 2 mL of chloroform per litre (11.8 and 11.9) in addition to refrigeration at 4°C.

NOTE 1—**WARNING**: Chloroform is toxic and is a suspected human carcinogen. Use with adequate ventilation or in a fume hood. Wear prescribed protective equipment. Use of chloroform is discouraged, since its use renders the solution a hazardous waste.

NOTE 2—**CAUTION**: The common prescribed use of sulfuric acid or mercury compounds as preservatives is discouraged. Sulfuric acid does not necessarily inhibit oxidation and mercury compounds should be avoided to prevent environmental pollution. Mercuric chloride is known to deactivate the column.

TEST METHOD A—AUTOMATED CADMIUM REDUCTION

9. Scope

9.1 The applicable range of this test method is from 0.05 to 1 mg/L of nitrite or nitrate nitrogen. The range may be extended upward by dilution of an appropriate aliquot. Many workers have found that this test method is reliable for nitrite and combined nitrite-nitrate levels to 0.01 mg N/L. However, the precision and bias data presented in this test method are insufficient to justify application of this test method in the 0.01 to 0.05 mg/L-N range.

9.2 This test method is applicable to surface, saline, waste, and ground waters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

10. Apparatus

10.1 *Automated Analysis System* [10] consisting of:

10.1.1 *Sampler.*

10.1.2 *Manifold or Analytical Cartridge.*

10.1.3 *Colorimeter* equipped with a 15- or 50-mm tubular flow cell and 540 ± 10-nm filters.

10.1.4 *Recorder or Electronic Data Acquisition Device.*

10.1.5 *Digital Printer (Optional).*

10.1.6 *Continuous Filter (Optional).*

10.2 *Reduction Columns*—Choose the appropriate reduction column for the manifold system. A schematic drawing of the manifold system is shown in Fig. 1 and the cartridge system is shown in Fig. 2.

10.2.1 *Reduction Column*, a glass tube 8 by 50 mm with the ends reduced in diameter to permit insertion into the system (see Fig. 1).

10.2.2 *Reduction Column*, a U-shaped glass tubing, 350-mm length and 2-mm inside diameter.

[9] "Reagent Chemicals. American Chemical Society Specifications," American Chemical Society, Washington, D.C. 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.

[10] The apparatus described is commercially available. ASTM does not undertake to ensure anyone utilizing an automated analysis system against liability of infringement of patent or assume such liability.

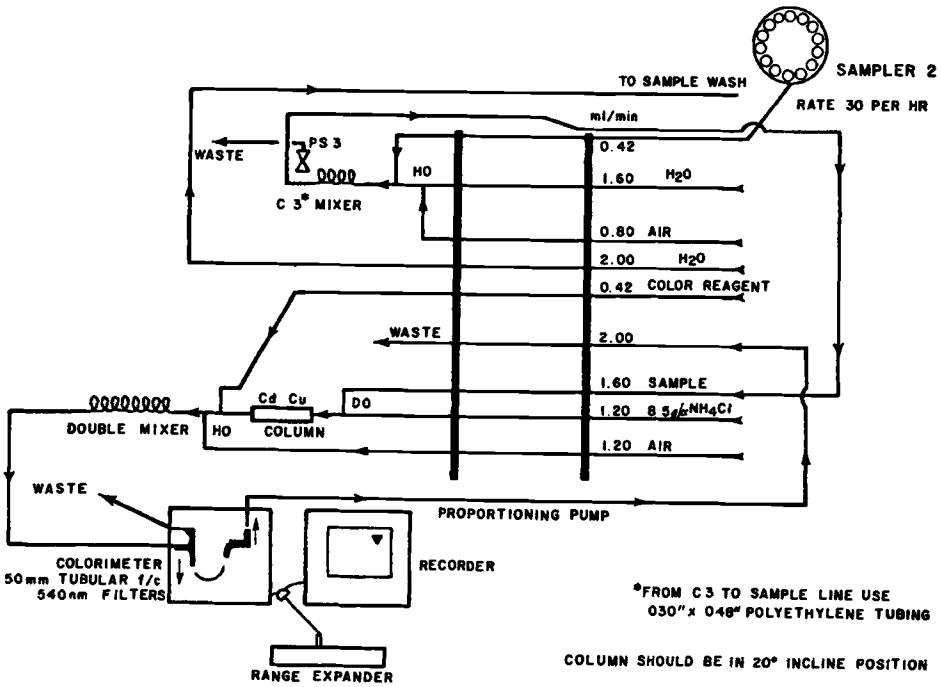

FIG. 1 Nitrite-Nitrate Manifold

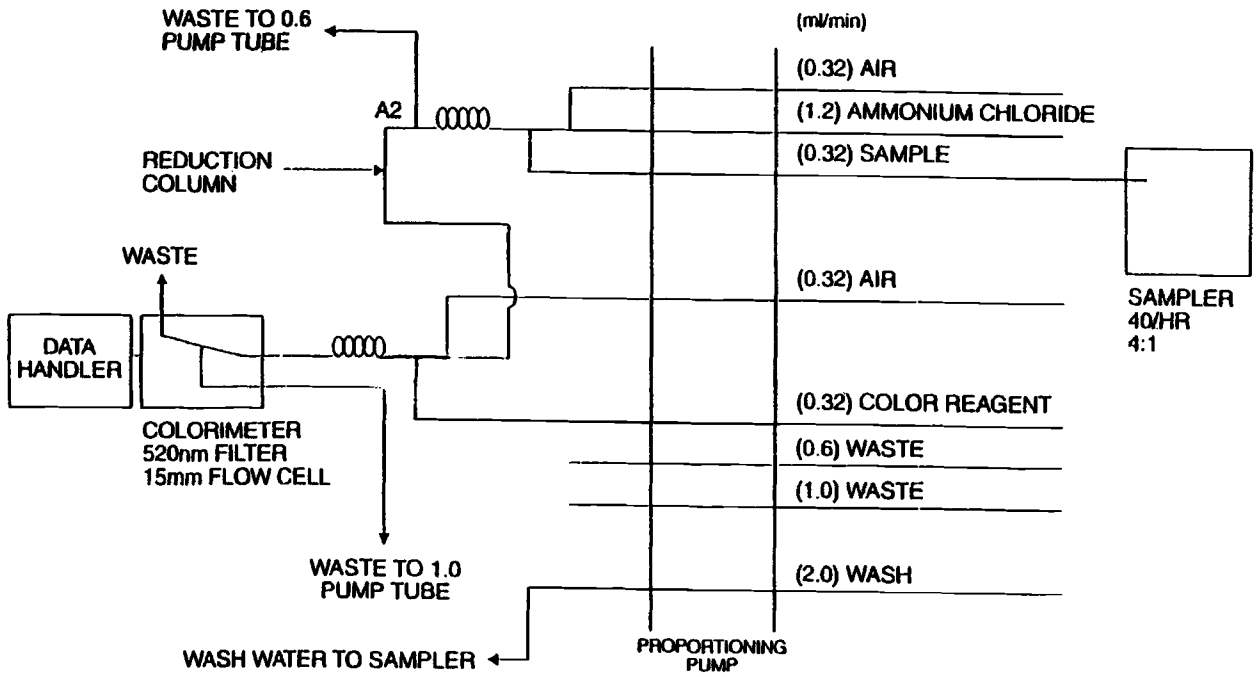

FIG. 2 Nitrite-Nitrate Cartridge

NOTE 3—A pump tube with 0.081-in. (2.1-mm) inside diameter can be used in place of the 2-mm glass tube.

11. Reagents

11.1 *Ammonium Chloride Solution* (85 g/L)—Dissolve 85 g of ammonium chloride (NH_4Cl) in water and dilute to 1 L. Add 0.5 mL wetting agent.[11]

11.2 *Cadmium*, 40 to 60 mesh, granulated.[12]

[11] A 30 % aqueous solution of Brij® 35, a polyoxyethylene compound with dodecyl alcohol (sp gr 1.18 to 1.22) has been found satisfactory for this purpose.

[12] Different sizes of granulated cadmium may be used. The analyst should ensure that adequate reduction occurs with the size chosen.

11.3 *Color Reagent*— Add the following to 800 mL of water, while stirring constantly: 100 mL of concentrated phosphoric acid (H_3PO_4), 10 g of sulfanilamide, and 0.5 g of *N*-1-(naphthyl)ethylenediamine dihydrochloride. Stir until dissolved. Add 1 mL of wetting agent,[11] and dilute to 1 L with water. This solution is stable for about a month when stored in a brown bottle in a dark cool place.

11.4 *Copper Sulfate Solution* (20 g/L)—Dissolve 20 g of copper sulfate pentahydrate ($CuSO_4 \cdot 5\ H_2O$) in 500 mL of water. Dilute to 1 L.

11.5 *n-Hexane.*

11.6 *Hydrochloric Acid* (1 + 1)—Slowly add 50 mL of concentrated hydrochloric acid (HCl) to 40 to 45 mL of water and dilute to 100 mL.

11.7 *Nitrate Solution, Stock* (1.0 mL = 1.0 mg NO_3-N)—Dry potassium nitrate (KNO_3) in an oven at 105°C for 24 h. Dissolve 7.218 g in water in a 1-L volumetric flask. Dilute to the mark with water. This solution is stable for up to 1 month with refrigeration. If longer stability is required or refrigeration is not available, add 2 mL of chloroform as a preservative and store in a dark bottle. This solution is stable for 6 months. (See Note 1.)

11.8 *Nitrate Solution, Standard* (1.0 mL = 0.01 mg NO_3-N)—Dilute 10 mL of stock nitrate solution (11.7) to 1 L with water and store in a dark bottle. Prepare fresh as needed.

11.9 *Nitrite Solution, Stock* (1.0 mL = 1.0 mg NO_2-N)—Place about 7 g of potassium nitrite (KNO_2) in a tared 125-mL beaker and dry for about 24 h to a constant weight in a desiccator containing a suitable dessicant. Adjust the weight of the dry potassium nitrite to 6.072 g. Add 50 mL of water to the beaker, stir until dissolved, and transfer quantitatively to a 1000-mL volumetric flask. Dilute to the mark with water store in a sterilized bottle under refrigeration. Prepare fresh as needed.

NOTE 4—Potassium nitrite is easily oxidized, so use only fresh bottles of this reagent.

11.10 *Nitrite Solution, Standard* (1.0 mL = 0.01 mg NO_2-N)—Dilute 10 mL of stock nitrite solution (11.9) to 1 L with water. This solution is unstable; prepare fresh as needed.

12. Preparation of Reduction Column

12.1 *Cadmium Granules Treatment*—Clean and copperize new or used cadmium granules in the following manner:

12.1.1 Clean about 10 g of cadmium granules by washing with dilute HCl (11.6) and rinsing with water.

12.1.2 Swirl the clean cadmium in 100-mL portions of copper sulfate solution (11.4) in a beaker for 5 min or until the blue color partially fades. Decant and repeat with fresh copper sulfate until the first visible brown colloidal precipitate appears.

12.1.3 Wash the granules with water at least 10 times to remove all of the precipitated copper.

12.2 *Filling the Reduction Column*:

12.2.1 Insert a small plug of glass wool in one end of the column (10.2).

12.2.2 Fill the column with water to prevent the entrapment of air bubbles during the filling operation.

12.2.3 Fill the column with copper-cadmium granules, tap to pack the granules, and plug the open end with glass wool.

12.3 *Installation of Reduction Column*—Install the copper-cadmium reduction column in the automatic analyzer system. Purge the system with ammonium chloride solution (11.1) using water in the sample line. Observe the following precautions while installing the reduction column:

12.3.1 Place the column in the manifold system in an upflow 20° incline to minimize channeling (see Fig. 1).

12.3.2 Fill all pump tubes with reagents before inserting the column in the cartridge system to prevent the entrapment of air bubbles.

12.4 *Reduction Column Storage*—When it is not in use, put the sample line in water and purge the column with ammonium chloride solution and water.

NOTE 5—Do not allow air to enter the column and do not let the cadmium granules become dry. If this occurs, refill the column with freshly treated cadmium granules.

13. Calibration

13.1 Using the standard nitrate solution (11.8) prepare calibration standards by pipetting specified volumes of the standard solution into 100-mL volumetric flasks and diluting to the mark with water. Table 1 specifies the millilitres of standard solution required.

13.2 Prepare at least one calibration standard from the standard nitrite solution at the same concentration as one of the nitrate standards to verify the efficiency of the reduction column. Repeat this when a suspected loss in NO_3-N reduction is observed.

NOTE 6—When the sample to be analyzed is a saline water, use substitute ocean water (SOW) to prepare the standards (Specification D 1141). Run a reagent water blank in addition to a SOW blank because the reagents used to prepare SOW frequently contain nitrite or nitrate, or both. Adjust this curve for the contaminant level in SOW.

13.3 Develop the color and determine the absorbance of each standard as directed in the procedure (14.5).

13.4 Prepare a standard curve by plotting the peak heights of each processed calibration standard against its known concentrations.

14. Procedure

14.1 *Removal of Interferences*—Remove interferences (Section 6) by the following procedures:

14.1.1 For turbidity removal, when suspended solids are present, filter the sample through a glass-fiber filter or a 0.45-µm filter. Alternatively, use a continuous filter (10.1.6) as an integral part of the system to remove particulate matter. Centrifugation can be used as an option.

TABLE 1 Concentration of Calibration Standards, Automated Cadmium Reduction

NO_3-N or NO_2-N, mg/L	mL Standard Solution/100 mL
0.01	0.1
0.02	0.2
0.04	0.4
0.1	1.0
0.2	2.0
0.4	4.0
0.7	7.0
1.0	10.0

14.1.2 For oil and grease removal, if necessary after filtration, adjust the pH of the sample to 2 with concentrated HCl. Extract with two 25-mL portions of *n*-hexane (11.5) in a separatory funnel. Discard the *n*-hexane layer after each extraction. Alternatively, solid-phase extraction filters may be used.

14.1.3 For pH adjustment, determine the pH of the sample with a pH meter. Adjust the pH to within the range from 6 to 8 with concentrated HCl or concentrated NH_4OH, if needed.

14.1.4 For correction for color interferences, if there is a possibility that the color of the sample might absorb in the photometric range from 530 ± 10 nm, determine the background absorbance. Replace the color reagent with a similar reagent where just the *N*-1-(naphthyl) ethylenediamine dihydrochloride is omitted and analyze the sample for background color absorbance as directed in the following procedure. Repeat the analysis using the complete color reagent.

14.2 Depending on the model of analysis system available, set up the manifold and complete the system as shown in Fig. 1 or Fig. 2.

NOTE 7—When determining nitrite alone, omit the reduction column from the manifold system.

14.3 Turn on the colorimeter and the recorder and allow them both to warm up for 30 min.

14.4 Obtain a stable baseline with all reagents, feeding water through the sample line.

14.5 Place the appropriate nitrate and nitrite calibration standards in the sampler in order of decreasing concentration of nitrogen. Fill the remainder of the sample tray with unknown samples.

14.6 For the manifold system, sample at a rate of 30/h, 1 + 1 cam. For the cartridge system, use a 40/h, 4 + 1 cam and a common wash.

14.7 Switch the sample line from water to sampler and begin the analysis, continuing until all unknowns have been analyzed.

15. Calculation

15.1 Determine the concentration of nitrate or nitrite nitrogen in the samples in milligrams per litre by comparing the peak heights of the samples with the standard curves (13.4) manually or by a computer-based data handler.

NOTE 8—If the background color absorbance has been measured (14.1.4), calculate the net absorbance by subtracting the background absorbance from the measured absorbance of the color developed sample. Use the net absorbance to determine the concentration of nitrogen in the sample.

15.2 Where separate values are required for nitrite-nitrogen and nitrate-nitrogen, calculate the nitrate-nitrogen by subtracting the nitrite-nitrogen from the total nitrate-nitrite nitrogen content.

16. Report

16.1 Report the following information:

16.1.1 Report the nitrogen content in milligrams per litre as:

16.1.1.1 Nitrite-Nitrogen (NO_2-N), mg/L,

16.1.1.2 Nitrate-Nitrogen (NO_3-N), mg/L, and

16.1.1.3 Combined Nitrate-Nitrite Nitrogen (NO_3, NO_2-N), mg/L.

17. Precision and Bias [13]

17.1 *Precision Statement:*

17.1.1 *Nitrite*—Based on the results of six operators in five laboratories, the overall and single-operator precision of this test method for nitrite within its designated range for reagent water and selected water matrices (including surface, saline, waste, and ground waters) varies with the quantity being tested in accordance with Table 2. No data were rejected as outliers for this statistical evaluation.

17.1.2 *Nitrate*—The precision of this test method for nitrate within its designated range for reagent water and selected water matrices may be expressed as follows (concentrations are given in mg/L):

Reagent Water	S_T = 0.0400
	S_O = 0.0296
Water Matrix	S_T = 0.0437
	S_O = 0.0300

17.2 This section on precision and bias conforms to Practice D 2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.5 of Practice D 2777 – 86, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D-19 test methods.

17.3 *Bias Statement*— Recoveries of known amounts of nitrites-nitrates from reagent water and selected water matrices are shown in Table 3.

17.4 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

TEST METHOD B—MANUAL CADMIUM REDUCTION

18. Scope

18.1 The applicable range of this test method is from 0.05 to 1 mg/L of nitrite or nitrate nitrogen. The range may be extended upward by dilution of an appropriate aliquot. Many workers have found that this test method is reliable for nitrite and combined nitrite-nitrate levels to 0.01 mg N/L. However, the precision and accuracy data presented in this test method are insufficient to justify application of this test method in the 0.01 to 0.05 mg/L-N range.

18.2 This test method is applicable to surface, saline, waste, and ground waters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

19. Apparatus

19.1 *Reduction Column* as shown in Fig. 3. The column

[13] Precision and bias data are available from ASTM Headquarters. Request Research Report RR:D19-1058.

TABLE 2 Interlaboratory Precision for Nitrite Found in Selected Matrices

Water Matrix:				
Concentration (x),mg/L	0.05	0.09	0.42	0.80
S_T	0.024	0.006	0.033	0.049
S_O	0.012	0.005	0.029	0.043
Reagent Water:				
Concentration (x), mg/L	0.05	0.09	0.42	0.80
S_T	0.021	0.005	0.019	0.032
S_O	0.009	0.002	0.011	0.006

TABLE 3 Reagent Water, Automated Cadmium Reduction

Radical	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Statistically Significant 95 % Level
Nitrite-nitrogen	0.050	0.042	−16	no
	0.090	0.096	+6	yes
	0.420	0.416	−1	no
	0.800	0.798	0	no
Nitrate-nitrogen	0.050	0.044	−11	no
	0.090	0.092	+2	no
	0.420	0.404	−4	yes
	0.850	0.828	−3	no
Water Matrix				
Radical	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Statistically Significant 95 % Level
Nitrite-nitrogen	0.050	0.060	+20	no
	0.090	0.097	+8	yes
	0.420	0.427	+2	no
	0.800	0.790	−1	no
Nitrate-nitrogen	0.050	0.053	+6	no
	0.090	0.081	−10	no
	0.420	0.396	−6	yes
	0.850	0.828	−3	no

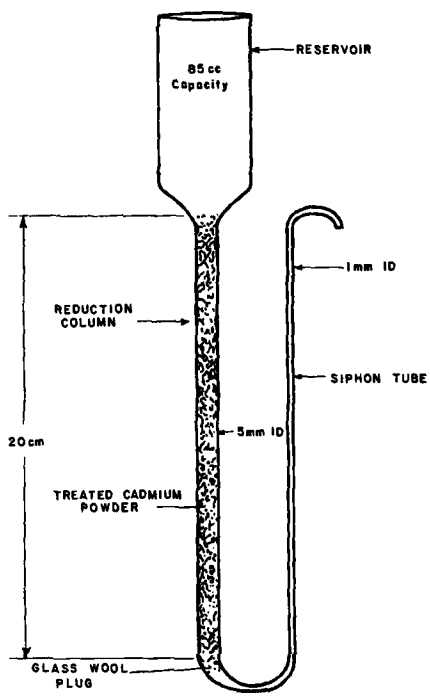

FIG. 3 Cadmium Reduction Column

shall be laboratory fabricated from the following:

19.1.1 *Pipet*, volumetric, 100-mL capacity, with 200-mm delivery stem. The top of the bulb shall be cut off before the constriction for the entry stem and the delivery tip curved to form a shallow hook.

19.1.2 *Tubing*, glass or vinyl, 1-mm inside diameter (1/16in.) and about 350-mm (14 in.) in length.

NOTE 9—If glass tubing is used, it must be bent at the lower end to connect with the curved tip of the pipet and parallel to the pipet. Its upper end is then bent over to form an inverted U-siphon. This last bend should be level with the top of the lower stem of the pipet. With this arrangement, liquid placed in the reservoir flows out of the system and stops when the level of the liquid just covers the cadmium powder packing.

19.2 *Cylinders*, graduated, 50-mL capacity.

19.3 *Test Tubes*, 15-mL capacity.

19.4 *Photometer*—A spectrophotometer or filter photometer suitable for use at 543 nm and equipped with absorption cells providing a light-path length of 1 cm. Spectrophotometers shall conform to Practice E 275. Filter photometers and photometric practices prescribed in this method shall conform to Practice E 60.

19.5 *Pipets*, serological, 1 and 10-mL capacity, calibrated to 0.1 mL, to deliver with ejection.

20. Reagents

20.1 *Ammonium Chloride Solution* (85 g/L)—Dissolve 85 g of ammonium chloride (NH_4Cl) in water and dilute to 1 L.

20.2 *Cadmium*, 40 to 60 mesh granulated.[12]

20.3 *Color Reagent*— Add the following to 800 mL of water, while stirring constantly: 100 mL of concentrated phosphoric acid (H_3PO_4), 10 g of sulfanilamide, and 0.5 g of *N*-(1-naphthyl)ethylenediamine dihydrochloride. Stir until dissolved. Dilute to 1 L with water. This solution is stable for about a month when stored in a brown bottle in a dark cool place.

20.4 *Copper Sulfate Solution* (20 g/L)—See 11.4.

20.5 *n-Hexane*..

20.6 *Hydrochloric Acid* (1 + 1)—See 11.6.

20.7 *Nitrate Solution, Stock* (1.0 mL = 1.0 mg NO_3-N)—See 11.7.

20.8 *Nitrate Solution, Standard* (1.0 mL = 0.01 mg NO_3-N)—See 11.8.

20.9 *Nitrite Solution, Stock* (1.0 mL = 1.0 mg NO_2-N)—See 11.9.

NOTE 10—Potassium nitrite is easily oxidized, and only fresh bottles of this reagent are to be used.

20.10 *Nitrite Solution, Standard* (1.0 mL = 0.01 mg NO_2-N)—See 11.10.

21. Preparation of Reduction Column

21.1 *Cadmium Granules Treatment*—Clean and copperize new or used cadmium granules in accordance with 12.1.

21.2 *Filling the Reduction Column*:

21.2.1 Insert a small plug of glass wool in the tip of the pipet.

21.2.2 Fill the column with water to prevent the entrapment of air bubbles during the filling operations.

21.2.3 Pour sufficient cadmium powder into the apparatus to produce a column 300 mm in length; tap to pack the powder.

21.2.4 Wash the column thoroughly with ammonium chloride solution (20.1).

NOTE 11—Use a flow rate no greater than 8 mL/min. If the rate is too fast, slow it down by constricting the end of the siphon outlet or by raising the height of the siphon tube. Flow rates of less than 5 mL/min unnecessarily increase the time for analysis and may cause low results.

21.3 *Storing the Column*—When not in use, cover the cadmium in the column with ammonium chloride solution. Do

not allow air to enter the packing, nor the packing to dry out. If this occurs, prepare another column.

22. Calibration

22.1 Using the nitrate standard solution (20.8) prepare calibration standards by pipetting specified volumes of the standard solution into 100-mL volumetric flasks and diluting to the mark with water. Table 4 specifies the millilitres of standard solution required.

22.2 Prepare at least one calibration standard from the nitrite standard solution (20.10) at the same concentration as one of the nitrate standards to verify the efficiency of the reduction column.

NOTE 12—When the sample to be analyzed is a saline water, use substitute ocean water (SOW) to prepare the standards (Specification D 1141). A reagent water blank should be run in addition to a SOW blank because the reagents used to prepare SOW frequently contain nitrite or nitrate, or both. Adjust this curve for the contaminant level in SOW.

22.3 Treat the standards as directed in 23.2.

22.4 Develop the color and measure the absorbance of each standard as directed in 23.3 for nitrite standards or in 23.4 for nitrate standards.

22.5 Prepare a standard curve by plotting the absorbance of each processed calibration standard against its known concentration.

NOTE 13—The nitrite standard will fall on the nitrate standard curve if the reduction of nitrate was complete. If the nitrite standard is 5 % higher, prepare a fresh reduction column and repeat the analysis of the nitrate standards. Analyze a nitrate standard every 4 hours of continuous testing. The reduction column will usually last for several weeks of continuous analysis.

23. Procedure

23.1 *Removal of Interferences*—Remove interferences (Section 6) by the following procedures:

23.1.1 For turbidity removal, when suspended solids are present, filter the sample through a glass fiber filter or 0.45-μm filter.

23.1.2 For oil and grease removal, adjust the pH of the sample to 2 with concentrated HCl. Extract with two 25-mL portions of trichloro-trifluoroethane (20.5) in a separatory funnel. Discard the lower trichlorotrifluoroethane layer after each extraction.

23.1.3 For pH adjustment, determine the pH of the sample with a pH meter. If the pH is less than 6 or greater than 8, adjust the pH to within the range from 6 to 8 with concentrated HCl or concentrated NH_4OH.

23.1.4 For correction for color interferences, if there is a possibility that the sample might absorb at 543 nm, determine the background absorbance. Dilute the sample as directed in 23.2. Replace the color reagent with a similar reagent where just the *N*-(1-naphthyl)-ethylenediamine dihydrochloride is omitted and follow the procedure as directed in 23.3. Using the complete color reagent, repeat the analysis as directed in 23.3 for nitrite determination or in 23.4 for combined nitrite-nitrate determination.

TABLE 4 Concentration of Calibration Standards, Manual Cadmium Reduction

NO_3-N or NO_2-N, mg/L	mL Standard Solution/100 mL
0.04	0.4
0.1	1
0.2	2
0.4	4
0.7	7
1.0	10

23.2 *Sample Treatment*— To a 20-mL sample add 80 mL of ammonium chloride solution (20.1). Mix well.

23.3 *Nitrite Determination*:

23.3.1 Pipet a 10-mL portion of the treated sample into a 15-mL test tube.

23.3.2 Pipet 3 mL of color reagent (20.3) into the test tube, mix, and let stand for 15 min.

23.3.3 Using water in the reference cell, determine the absorbance of the solution at 543 nm and record.

23.4 *Combined Nitrite-Nitrate Determination*:

23.4.1 Pour about 60 mL treated sample (23.2) into the reservoir of the reduction column on top of any liquid in the column.

NOTE 14—The cadmium in the reduction column will be covered by the ammonium chloride storage solution or by a previous sample because it should *never* be allowed to dry out.

23.4.2 Place a clean 50-mL graduate under the siphon outlet and allow approximately 30 mL of effluent to collect. Discard this initial 30 mL.

23.4.3 Place a clean 50-mL graduate under the siphon outlet and collect an additional 25 mL of effluent. Do not remove all the liquid from the column. Allow enough solution to remain in the column to completely cover the copper-cadmium granules.

23.4.4 Pipet a 10-mL portion of the collected effluent into a 15-mL test tube.

23.4.5 Pipet 3.0 mL of color reagent (20.3) into the test tube, mix, and let stand for 15 min.

23.4.6 Using water in the reference cell, determine the absorbance of the solution at 543 nm and record.

24. Calculation

24.1 From the standard curve (22.5) obtain the nitrogen content in mg/L which corresponds to the absorbance.

NOTE 15—If the background color absorbance has been measured (23.1.4), calculate the net absorbance by subtracting the background absorbance from the measured absorbance of the color developed sample. Use the net absorbance to determine the concentration of nitrogen in the sample.

24.2 Where separate values are required for nitrite-nitrogen and nitrate-nitrogen, calculate the nitrate-nitrogen by subtracting the nitrite-nitrogen (23.3) from the combined nitrite-nitrate nitrogen content (23.4).

25. Report

25.1 Report the following information:

25.1.1 Report the nitrogen content in milligrams per litre as:

25.1.1.1 Nitrite-Nitrogen (NO_2-N), mg/L,

25.1.1.2 Nitrate-Nitrogen (NO_3-N), mg/L, and

25.1.1.3 Combined Nitrite-Nitrate Nitrogen (NO_2, NO_3-N), mg/L.

26. Precision and Bias [13]

26.1 Based on the results from eight operators from seven laboratories, the precision of this test method within its designated range for reagent water and water matrices selected (see 17.1.1) may be expressed as follows (concentrations are given in mg/L):

Reagent Water

Nitrite-Nitrogen	$S_T = 0.039\ X + 0.0108$
	$S_O = 0.010$
Nitrate-Nitrogen	$S_T = 0.033$
	$S_O = 0.014$

Water Matrix

Nitrite-Nitrogen	$S_T = 0.0901\ X + 0.035$
	$S_O = 0.0841\ X + 0.019$
Nitrate-Nitrogen	$S_T = 0.057$
	$S_O = 0.038$

26.2 *Bias Statement*—Recoveries of known amounts of nitrite and nitrate from reagent water and water matrices selected are shown in Table 5.

26.3 One set of nitrate results were rejected as outliers. The nitrite results from this laboratory were acceptable.

26.4 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

TABLE 5 Reagent Water, Manual Cadmium Reduction

Radical	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Statistically Significant 95 % Level
Nitrite	0.05	0.05	0	no
	0.09	0.09	0	no
	0.42	0.42	0	no
	0.80	0.82	+2	yes
Nitrate	0.05	0.03	−40	yes
	0.09	0.08	−11	no
	0.42	0.43	+2	no
	0.85	0.81	−5	yes
		Water Matrix		
Radical	Amount Added, mg/L	Amount Found, mg/L	Bias, %	Statistically Significant 95 % Level
Nitrite	0.05	0.04	−20	no
	0.09	0.06	−33	yes
	0.42	0.36	−10	no
	0.80	0.75	−6	yes
Nitrate	0.05	0.04	−20	no
	0.09	0.10	−11	no
	0.42	0.41	−2	no
	0.85	0.79	−7	yes

27. Keywords

27.1 cadmium reduction method; groundwater; nitrate; nitrite; saline water; waste water; water

SUMMARY OF CHANGES

This section identifies the location of selected changes to these test methods that have been incorporated since the last issue. For the convenience of the user, Committee D-19 has highlighted those changes that may impact the use of these test methods. This section may also include descriptions of the changes or reasons for the changes, or both.

(1) Techniques for the removal of interferences due to oil and grease were revised.

(2) Techniques for preservation of samples were revised.

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