



Designation: D3867 – 16 (Reapproved 2021)^{ε1}

Standard Test Methods for Nitrite-Nitrate in Water¹

This standard is issued under the fixed designation D3867; 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.

^{ε1} NOTE—The WTO caveat was editorially added and warning notes were editorially updated throughout in November 2021.

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 methods² are given as follows:

Test Method A—Automated Cadmium Reduction	Sections 9 to 18
Test Method B—Manual Cadmium Reduction	19 to 28

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 The values stated in either SI or inch-pound units are to be regarded as the standard. No other units of measurement are included in this standard.

1.4 *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.* For specific hazard statements, see 8.2.

1.5 *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:³

D992 Method of Test for Nitrate Ion in Water (Withdrawn 1983)⁴

D1129 Terminology Relating to Water

D1141 Practice for Preparation of Substitute Ocean Water

D1193 Specification for Reagent Water

D1254 Method of Test for Nitrite Ion in Water (Withdrawn 1980)⁴

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

D7781 Test Method for Nitrite-Nitrate in Water by Nitrate Reductase

E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry

E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

3.1 Definitions:

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

4. Summary of Test Methods

4.1 *Total Oxidized Nitrogen*—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

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

Current edition approved Nov. 1, 2021. Published December 2021. Originally approved in 1979. Last previous edition approved in 2016 as D3867 – 16. DOI: 10.1520/D3867-16R21E01.

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

³ 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.

⁴ The last approved version of this historical standard is referenced on www.astm.org.

sulfanilamide and coupling with *N*-(1-naphthyl)ethylenediamine dihydrochloride to form a highly colored azo dye that is measured spectrophotometrically.

4.2 Nitrite—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 Nitrate—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 **D1254** (Nitrite) and **D992** (Nitrate). The nitrite test method (Test Method **D1254**) used a reagent that is considered to be a potential carcinogen. The nitrate test method (Test Method **D992**) has been shown to have relatively large errors when used in wastewaters and also has greater manipulative difficulties than the test method described herein.

5.4 Test Method **D7781** uses a nitrate reductase enzyme for the reduction of nitrate to nitrite. Cadmium is considered a toxic metal. Also, the heterogeneous cadmium reductant creates greater difficulty than the reduction described in this test method.

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 extracting 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 interferences. 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 (Guide **D5810**).

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.⁵ 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 **D1193**, 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 Practices **D3370**.

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 (**11.7 and 11.9**) in addition to refrigeration at 4°C. (**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.) (**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.)

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.