



Designation: **D3373—12 D3373 – 17**

## Standard Test Method for Vanadium in Water<sup>1</sup>

This standard is issued under the fixed designation D3373; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

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

### 1. Scope\*

1.1 This test method covers the determination of dissolved and total recoverable vanadium in most waters and wastewater by graphite furnace atomic absorption spectrophotometry.

1.2 The optimum range of this test method is 10 to 200  $\mu\text{g/L}$  of vanadium based on a 20- $\mu\text{L}$  sample size. Concentrations higher than ~~200  $\mu\text{g/L}$~~  200  $\mu\text{g/L}$  may be determined by proper dilution of sample. A detection level as low as 4  $\mu\text{g/L}$  of vanadium has been reported.

1.3 This test method has been used successfully with reagent water, lake water, tap water, river water, condensate from a medium Btu coal gasification process, and well water. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 or regulatory limitations prior to use.*

1.6 Former Test Method A (Catalytic) was discontinued. Refer to [Appendix X1](#) for historical information.

1.7 *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:*<sup>2</sup>

[D1066 Practice for Sampling Steam](#)

[D1129 Terminology Relating to Water](#)

[D1193 Specification for Reagent Water](#)

[D1976 Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy](#)

[D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)

[D3370 Practices for Sampling Water from Closed Conduits](#)

[D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry](#)

[D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents](#)

[D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry](#)

[D5810 Guide for Spiking into Aqueous Samples](#)

[D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)

### 3. Terminology

3.1 *Definitions:* For definitions of terms used in this test method refer to Terminology [D1129](#).

3.1.1 For definitions of terms used in this standard, refer to Terminology [D1129](#).

3.2 *Definitions of Terms Specific to This Standard:*

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee [D19](#) on Water and is the direct responsibility of Subcommittee [D19.05](#) on Inorganic Constituents in Water. Current edition approved ~~Sept. 1, 2012~~ June 1, 2017. Published ~~September 2012~~ June 2017. Originally approved in 1975. Last previous edition approved in ~~2007~~ 2012 as [D3373 – 03 \(2007\) D3373 – 12](#). DOI: [10.1520/D3373-12.10.1520/D3373-17](#).

<sup>2</sup> 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.

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

3.2.1 continuing calibration blank, *n*—a solution containing no analytes (of interest) which is used to verify blank response and freedom from carryover.

3.2.2 continuing calibration verification, *n*—a solution (or set of solutions) of known concentration used to verify freedom from excessive instrumental drift; the concentration is to cover the range of calibration curve.

3.2.3 total recoverable vanadium, *n*—~~dissolved vanadium plus that solubilized by acid digestion of particulates and organics in the sample;~~ a descriptive term relating to the metal forms of vanadium recovered in the acid-digestion procedure specified in this test standard.

#### 4. Summary of Test Method

4.1 Vanadium is determined by an atomic absorption spectrophotometer utilizing a graphite furnace for sample atomization.

4.2 A sample volume of several microlitres, depending upon the concentration of the analyte, is transferred to a graphite tube housed within an electrical furnace and the system is heated in an inert or reducing atmosphere. The sample is evaporated to dryness, charred (pyrolyzed or ashed) and atomized.

4.3 Ground state atoms, produced in atomization, absorb the light of their spectrum emanating from a source and passing through the sample vapor. The amount of light absorbed is proportional to the concentration of the analyte in the sample.

4.4 Since the graphite furnace uses the sample much more efficiently than does flame atomization, the detection of low concentrations of the elements of interest in small volumes is possible.

4.5 Finally, the absorption signal produced during atomization is recorded and compared to those of standards, taken through the same process, by means of an analytical curve.

4.6 A general guide for graphite furnace applications is given in Practice [D3919](#).

4.7 Dissolved vanadium is determined after filtration and addition of HNO<sub>3</sub> to a pH of  $\leq 2$ .

4.8 Total recoverable vanadium is determined following acid digestion and filtration.

#### 5. Significance and Use

5.1 Vanadium can be found in waste that result from chemical cleaning of components in which the metal is alloyed.

5.2 National Pollutant Discharge Elimination Systems permits or other standards, or both, require monitoring pollutants in waste discharged onto the water shed of, or into, navigable waters, and those disposed of in such a manner that eventual contamination of underground water could result.

5.3 This test method affords an accurate and sensitive means of determining compliance or noncompliance, or both, with those permits.

5.4 ICP-MS or ICP-AES may also be appropriate but at a higher instrument cost. See Test Methods [D5673](#) and [D1976](#).

#### 6. Interferences

6.1 For a complete discussion on general interferences with furnace procedures, the analyst is referred to Practice [D3919](#).

#### 7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*; for use at 318.4 nm with background correction.

NOTE 1—The manufacturer's instructions should be followed for all instrumental parameters.

7.2 *Vanadium Hollow Cathode Lamp*.

7.3 *Graphite Furnace* capable of reaching temperature sufficient to atomize the element of interest.

7.4 *Graphite Tubes*, pyrolytically coated, compatible with furnace device are recommended.

7.5 *Pipettes*, microlitre with disposable tips, ranging in size from 1 to 100  $\mu$ L.

7.6 *Strip Chart Recorder—Data Storage and Reduction Devices, Computer- and Microprocessor-Controlled Devices, or Strip Chart Recorders* A recorder is strongly recommended. The tracings can be used as permanent records and are of diagnostic value in the identification and analysis of instrument problems shall be utilized for collection, storage, reduction, and problem recognition (such as drift, incomplete atomization, ~~changechanges~~ changes in sensitivity, etc.). A fast response recorder (0.2 s or less for full-scale deflection) is recommended. Strip chart recorders shall have a full scale deflection time of 0.2 s or less to ensure accuracy. ~~Electronic peak-measuring devices have also been found useful.~~

7.7 *Automatic Sampling Accessory* is recommended, if available.

#### 8. Reagents and Materials

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

specifications are available.<sup>3</sup> 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.

8.2 *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 precision and bias of the test method.

8.3 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO<sub>3</sub>).

8.4 *Vanadium Solution, Stock* (1.0 mL = 100 µg vanadium). Dissolve 0.2296 g of ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) in water and dilute to 1000 mL. A purchased vanadium stock solution of appropriate known purity is also acceptable.

8.5 *Vanadium Solution, Intermediate* (1.0 mL = 1.0 µg vanadium)—Dilute 5 mL of vanadium stock solution to 500 mL with water.

8.6 *Vanadium Solution, Standard* (1.0 mL = 0.100 µg vanadium)—Dilute 10.0 mL of vanadium intermediate solution to 100 mL with water.

8.7 *Nitrogen Gas*—standard, welders grade, commercially available.

NOTE 2—It is probable that argon or some other inert gas can be used in place of nitrogen. It is the analyst's responsibility to verify suitability.

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

## 9. Sampling

9.1 Collect the sample in accordance with Practices **D1066** and **D3370**, as applicable. The holding time for the sample may be calculated in accordance with Practice **D4841**.

9.2 Preserve samples with nitric acid (HNO<sub>3</sub>, sp gr 1.42) to a pH of 2 or less immediately at the time of collection, normally about 2 mL/L. If only dissolved vanadium is to be determined, filter the sample through a 0.45-µm (No. 325) membrane filter before acidification.

NOTE 3—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days of collection. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

## 10. Standardization

10.1 Initially, set the instrument in accordance with the manufacturer's specifications. Follow the general instructions as provided in Practice **D3919**.

## 11. Procedure

11.1 Clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, by rinsing first with HNO<sub>3</sub> (1 + 1) and then with water. Alternatively, soaking the glassware overnight in HNO<sub>3</sub> (1 + 1) is useful for low levels.

11.2 Measure 100.0 mL of each standard and well-mixed sample into a 125-mL beaker or flask. For total recoverable vanadium, add 5 mL of HNO<sub>3</sub> (sp gr 1.42) to each sample and proceed as directed in **11.4** through **11.6**.

11.3 If only dissolved vanadium is to be determined, proceed to **11.6**.

11.4 Heat the samples at 95°C (between 65°C and 95°C) on a steam bath or ~~hotplate~~ hot plate below boiling in a well-ventilated fume hood until the volume has been reduced to 15 to 20 mL making certain that the samples do not boil.

NOTE 4—When analyzing samples of brines or samples containing appreciable amounts of suspended matter or dissolved solids, the amount of reduction in volume is left to the discretion of the analyst.

NOTE 5—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. The digestion block must be capable of maintaining a temperature between 65°C and 95°C. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least ~~0.5%~~ 0.5%. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

11.5 Cool and filter the sample through a suitable filter (**8.8**) (such as fine-textured, acid washed, ashless paper) into a 100-mL volumetric flask. Wash the filter paper 2 or 3 times with water and bring to volume. See **Note 6**. The acid concentration at this point should be 5 % HNO<sub>3</sub>.

<sup>3</sup> *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 *Annual 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.