Designation: D3373 − 17

Standard Test Method for Vanadium in Water[1]

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 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.

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 µg/L of vanadium based on a 20-µL sample size. Concentrations higher than 200 µg/L may be determined by proper dilution of sample. A detection level as low as 4 µg/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:*[2]

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:*

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

3.2 *Definitions of Terms Specific to 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.

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[1] 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.

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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.

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

3.2.3 *total recoverable vanadium, n*—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_3 to a pH of ≤ 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 µL.

7.6 *Data Storage and Reduction Devices, Computer- and Microprocessor-Controlled Devices, or Strip Chart Recorders* shall be utilized for collection, storage, reduction, and problem recognition (such as drift, incomplete atomization, changes in sensitivity, etc.). Strip chart recorders shall have a full scale deflection time of 0.2 s or less to ensure accuracy.

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.[3] 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_3).

8.4 *Vanadium Solution, Stock* (1.0 mL = 100 µg vanadium). Dissolve 0.2296 g of ammonium metavanadate (NH_4VO_3) 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.

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[3] *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.

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_3, 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 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_3 (1 + 1) and then with water. Alternatively, soaking the glassware overnight in HNO_3 (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_3 (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 (between 65°C and 95°C) on a steam bath or 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 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

TABLE 1 Determination of Precision and Bias for Vanadium

Amount Added, µg V/L	Amount Found, µg V/L	S_T, µg/L	Bias, µg/L	% Bias	Statistically Significant
Reagent Water Type II					
25	24	2.6	−1.0	4.0	no
70	73.4	4.8	+3.4	4.9	no
240	232.7	25.5	−7.3	3.0	no
Water of Choice					
25	25.9	3.6	+0.9	3.6	no
70	70	7.6	0	0	no
240	247.3	27.7	+7.3	3.0	no

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_3.

NOTE 6—If suspended material is not present, this filtration may be omitted, however, digested sample must still be diluted to 100 mL.

11.6 Inject a measured aliquot of sample into the furnace device following the directions as provided by the particular instrument manufacturer. Refer to Practice D3919.

12. Calculation

12.1 Determine the concentration of vanadium in each sample in accordance with the Samples Analysis Procedure Section of Practice D3919.

13. Precision and Bias[4]

13.1 Based on data from twelve participating laboratories, the overall precision of this test method and recoveries from a series of standards containing known amounts of vanadium, were as given in Table 1.

13.2 Because of the large number of metals analyzed in this study the requirement for replicate tests have been waived; therefore, single-operator precision is not available.

13.3 Each participating laboratory evaluated this test method in reagent water. Individual laboratories selected one water of choice as an additional matrix of interest in which to test recovery. Listed among those choices were: lake water, tap water, river water, well water, and condensate from a medium Btu coal gasification process.

13.4 These data may not apply to waters of other matrices.

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

14. Quality Control (QC)

14.1 To ensure that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing vanadium.

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1114. Contact ASTM Customer Service at service@astm.org.

14.2 *Calibration and Calibration Verification:*

14.2.1 Analyze at least three working standards containing concentrations of vanadium that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument. The calibration correlation coefficient shall be equal to or greater than 0.990.

14.2.2 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. The blank result should be less than the method reporting limit.

14.2.3 If calibration cannot be verified, recalibrate the instrument.

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

14.3 *Initial Demonstration of Laboratory Capability:*

14.3.1 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.

14.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a midrange concentration of vanadium. 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.

14.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. 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.

14.4 *Laboratory Control Sample (LCS):*

14.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of vanadium 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 a mid-range LCS shall fall within ±15 % of the known concentration.

14.4.2 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.

14.5 *Method Blank:*

14.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of vanadium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of vanadium 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.

14.6 *Matrix Spike (MS):*

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

14.6.2 The spike concentration plus the background concentration of vanadium must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

14.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100\left[A\left(V_s+V\right) - BV_s\right]/CV \qquad (1)$$

where:

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

14.6.4 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 7—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

14.7 *Duplicate:*

14.7.1 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.

14.7.2 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.

14.7.3 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.

14.8 *Independent Reference Material (IRM):*

14.8.1 In order to verify the quantitative value produced by the test method, analyze an 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.

15. Keywords

15.1 atomic absorption; furnace; total recoverable vanadium; water

APPENDIX

(Nonmandatory Information)

X1. RATIONALE FOR DISCONTINUATION OF TEST METHODS

X1.1 Former Test Method A—Catalytic

X1.1.1 This test method was discontinued in 1988. The test method may be found in its entirety in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X1.1.2 This test method covers the determination of dissolved and total recoverable vanadium found in concentrations of 1.0 to 8.0 µg/L.

X1.1.3 Trace amounts of vanadium are determined by measuring the catalytic effect it exerts on the rate of oxidation of gallic acid by persulfate in acid solution. Under given conditions of reactant concentration, temperature, and reaction time, the extent of oxidation of gallic acid is proportional to the concentration of vanadium present. Depending on the amount of vanadium present, the reaction produces a yellow-to-red color. Vanadium is determined by measuring the absorbance of the sample at 415 nm and comparing it with standard solutions treated in an identical manner.

X1.1.4 This test method was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D2777.

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3373 – 12) that may impact the use of this standard. (Approved June 1, 2017.)

(1) Revised Section 2 to include D1976 and D5673.
(2) Revised Section 3 to update and add terms.
(3) Added 5.4 to inform the user of the possibility of using an ICP-MS or ICP-AES.
(4) Revised 7.6.
(5) Added 8.8 to include information on filter paper.
(6) Revised Note 3 to include information on pH of the samples.
(7) Revised Note 5 to include information on the block digestion systems.
(8) Revised 14.2.2, 14.2.4, 14.4.1, and 14.6.3.