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AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Method for Vanadium in Water[1]

This standard is issued under the fixed designation D 3373; 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 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 200µ g/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 *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.*

1.5 Former Test Method A (Catalytic) was discontinued. Refer to Appendix X1 for historical information.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[2]

D 1129 Terminology Relating to Water[2]

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]

D 1193 Specification for Reagent Water[2]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[2]

D 3370 Practices for Sampling Water from Closed Conduits[2]

D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry[2]

D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[2]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable vanadium*—dissolved vanadium plus that solubilized by acid digestion of particulates and organics in the sample.

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 D 3919.

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

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[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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

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.

6. Interferences

6.1 For a complete discussion on general interferences with furnace procedures, the analyst is referred to Practice D 3919.

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 *Pipets*, microlitre with disposable tips, ranging in size from 1 to 100 µL.

7.6 *Strip Chart Recorder*—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 (such as drift, incomplete atomization, change in sensitivity, etc.). A fast response recorder (0.2 s or less for full-scale deflection) is recommended 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.[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 D 1193, Type I.

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.

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.

9. Sampling

9.1 Collect the sample in accordance with Practice D 1066, Specification D 1192, and Practices D 3370, as applicable. The holding time for the sample may be calculated in accordance with Practice D 4841.

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.

10. Standardization

10.1 Initially, set the instrument in accordance with the manufacturer's specifications. Follow the general instructions as provided in Practice D 3919.

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 at 95°C on a steam bath or hotplate 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 3—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.

11.5 Cool and filter the sample through a suitable filter (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 4. The acid concentration at this point should be 5 % HNO_3.

NOTE 4—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 D 3919.

12. Calculation

12.1 Determine the concentration of vanadium in each sample in accordance with the Samples Analysis Procedure Section of Practice D 3919.

[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 *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

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.

TABLE 1 Determination of Precision and Bias for Vanadium

Amount Added, µg V/L[A]	Amount Found, µg V/L[A]	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

[A] Editorially corrected.

14. Keywords

14.1 atomic absorption; furnace; total recoverable vanadium; water

[4] Supporting data are available and on loan from ASTM Headquarters. Request RR: D19 – 1114.

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 D 2777.