Designation: D3372 – 12

Standard Test Method for Molybdenum in Water[1]

This standard is issued under the fixed designation D3372; 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 molybdenum in most waters, wastewaters, and brines by atomic absorption spectroscopy.[2]

1.2 This test method is applicable in the range from 1 to 25 µg/L of molybdenum. The range may be extended by dilution of the sample.

1.3 This test method has been used successfully with natural and reagent waters. 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 either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system are mathematical conversions and may not be exact equivalents; therefore, each system shall be used independently of the other.

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 of regulatory limitations prior to use.* For specific precautionary statements, see Note 3 *and Note 11*.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
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
D4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
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.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *laboratory control sample*—a solution with the certified concentration(s) of the analytes.

3.2.2 *total recoverable molybdenum*—an arbitrary analytical term relating to the forms of molybdenum that are determinable by the digestion procedure described in this test method.

4. Summary of Test Method

4.1 Molybdenum is determined by atomic-absorption spectrophotometry. The element is chelated with 8-hydroxyquinoline, extracted with methyl isobutyl ketone, and the extract aspirated into the nitrous oxide-acetylene flame of the spectrophotometer.

5. Significance and Use

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

5.2 National Pollution Discharge Elimination System (NPDES) 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 with those permits.

6. Interferences

6.1 Vanadium (V) and iron (III) enhance the absorption, while chromium (VI) and tungsten (VI) suppress it. These interferences are eliminated by the addition of ascorbic acid.

[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.

Current edition approved Sept. 1, 2012. Published October 2012. Originally approved in 1975. Last previous edition approved in 2002 as D3372 – 02 (2007)$^{\varepsilon 1}$. DOI: 10.1520/D3372-12.

[2] Chau, Y. K., and Lum-Shue-Chan, K., "Atomic Absorption Determination of Microgram Quantities of Molybdenum in Lake Waters," *Analytica Chimica Acta*, Vol 48, 1969, p. 205.

[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.

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

7. Apparatus

7.1 *Atomic-Absorption Spectrophotometer,* for use at 313.3 nm. A general guide for the use of flame atomic absorption applications is given in Practice D4691.

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

7.1.1 *Molybdenum Hollow-Cathode Lamp.*

7.2 *Pressure-Reducing Valves*—The supplies of fuel and oxidant shall be maintained at a pressure somewhat higher than the controlled operating pressure of the instrument by suitable valves.

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 the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] 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, II, or III water. Type I is preferred and more commonly used. Type II water was specified at the time of round robin testing of these test methods.

NOTE 2—The user must ensure the type of reagent water chosen is sufficiently free of interferences. The water should be analyzed using the test method.

8.3 *Ascorbic Acid Solution* (10 g/L)—Dissolve 1 g of ascorbic acid in water and dilute to 100 mL.

8.4 *Bromphenol Blue Indicator Solution* (1 g/L)—Dissolve 0.1 g of bromphenol blue in 100 mL of 50 % ethanol or isopropanol.

8.5 *Hydrochloric Acid* (1 + 49)—Mix 20.0 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) with water and dilute to 1 L.

8.6 *8-Hydroxyquinoline-Methyl Isobutyl Ketone Solution* (10 g/L)—Dissolve 1 g of 8-hydroxyquinoline in 100 mL of methyl isobutyl ketone. Prepare fresh daily.

8.7 *Methyl Isobutyl Ketone* (MIBK).

8.8 *Molybdenum Solution, Stock* (1.0 mL = 100 µg Mo)—Dissolve 0.1500 g of molybdenum trioxide (MoO_3) in 10 mL of water containing 1 mL of NaOH (100 g/L) (warm if necessary). Make just acid with HCl (1 + 49) and dilute to 1000 mL with water. A purchased molybdenum stock solution of appropriate known purity is also acceptable.

8.9 *Molybdenum Solution, Intermediate* (1.0 mL = 1.0 µg Mo)—Dilute 10.0 mL of molybdenum stock solution to 1000 mL with water.

8.10 *Molybdenum Solution, Standard* (1.0 mL = 0.1 µg Mo)—Immediately before use, dilute 10.0 mL of intermediate molybdenum solution of 100 mL with water. This standard is used to prepare working standards at the time of analysis.

8.11 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

8.12 *Sodium Hydroxide Solution* (100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

8.13 *MIBK-Saturated Water*—Thoroughly mix equal volumes of MIBK and water in a separatory funnel. Allow layers to separate. Collect and store water and MIBK, respectively, in properly marked containers.

8.14 *Water-Saturated MIBK*—Use MIBK prepared from 8.13.

8.15 *Nitrous Oxide*—Commercially available nitrous oxide is suitable as oxidant.

8.16 *Acetylene Fuel*—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, will affect analytical results. Generally, replacing the acetylene cylinder with 345 kPa (50 psi) remaining prevents acetone interference; however it has been reported that cylinders with pressure at 670 kPa (100 psi) or greater will cause interference.

NOTE 3—**Warning:** "Purified" grade acetylene contains a special proprietary solvent rather than acetone and should not be used. It can weaken the walls of poly(vinyl chloride) tubing that carries the acetylene to the burner, causing a potentially hazardous situation.

9. Sampling

9.1 Collect the sample in accordance with Practices D3370. The holding time for the samples may be calculated in accordance with Practice D4841.

9.2 To preserve the samples add concentrated HNO_3 (sp gr 1.42) to a pH of 2 or less immediately at the time of collection; normally about 2 mL/L is required. If only dissolved molybdenum is to be determined, filter the samples at time of collection through a 0.45-µm membrane filter before acidification.

NOTE 4—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. This could reduce hazards of working with acids in the field when appropriate.

10. Standardization

10.1 Prepare in 200-mL volumetric flasks a blank and sufficient standards containing from 0.0 to 2.5 µg of molybdenum by diluting 0.0 to 25.0-mL portions of the standard molybdenum solution to 100 mL with water.

10.2 Proceed as directed in 11.5 to 11.11.

10.3 Construct an analytical curve by plotting the absorbances of standards versus micrograms of molybdenum.

NOTE 5—The burner must be conditioned just prior to standardization and running of sample extracts by aspirating water-saturated MIBK until

[4] *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.