



Designation: D 3372 – 02

Standard Test Method for Molybdenum in Water¹

This standard is issued under the fixed designation D 3372; 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 approval. 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 method² covers the determination of dissolved and total recoverable molybdenum in most waters, wastewaters, and brines by atomic absorption spectroscopy.

1.2 This test method is applicable in the range from 1 to 25 $\mu\text{g/L}$ 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 *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 9**.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water³

D 1193 Specification for Reagent Water³

D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water³

D 3370 Practices for Sampling Water from Closed Conduits³

D 4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry³

D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents³

D 5810 Guide for Spiking into Aqueous Samples³

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 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 *Annual Book of ASTM Standards*, Vol 11.01.

D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis⁴

3. Terminology

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

3.2 *Definition of Term 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 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.

⁴ *Annual Book of ASTM Standards*, Vol 11.02.

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 **D 4691**.

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.⁵ 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, 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 (MoO₃) 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.⁶

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 (HNO₃).

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 50 psig (345 kPa) remaining prevents acetone interference; however it has been reported that cylinders with pressure at 100 psig (670 kPa) 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 **D 3370**. The holding time for the samples may be calculated in accordance with Practice **D 4841**.

9.2 To preserve the samples add concentrated HNO₃(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.

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 4—The burner must be conditioned just prior to standardization and running of sample extracts by aspirating water-saturated MIBK until the flame stabilizes. Some systems have required as long as 10 min for conditioning.

11. Procedure

11.1 For total recoverable molybdenum, add 5 mL of concentrated nitric acid to 100 mL of the sample in a 250-mL Erlenmeyer flask and mix well. Heat the sample, without boiling, on a steam bath or hot plate in a well-ventilated fume hood until the volume has been reduced to 15 to 20 mL.

NOTE 5—When treating samples of brine or a sample containing a large

⁵ *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 Pharmacopoeia and National Formulary*, U.S. Pharmacopoeia Convention, Inc. (USPC), Rockville, MD.

⁶ Commercial Stock Standards may also be purchased.