



Designation: D3372 – 17

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

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 ( $\epsilon$ ) 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.<sup>2</sup>

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 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversion to inch-pound units that are provided for information only and are not considered 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 of regulatory limitations prior to use. For specific precautionary statements, see 8.16 and 11.12.*

1.6 *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>3</sup>

[D1129 Terminology Relating to Water](#)

<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 June 1, 2017. Published June 2017. Originally approved in 1975. Last previous edition approved in 2012 as D3372 – 12. DOI: 10.1520/D3372-17.

<sup>2</sup> 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.

<sup>3</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[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](#)

[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](#)

[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.

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

3.2.4 *total recoverable molybdenum, n*—a descriptive term relating to the metal forms of molybdenum recovered in the acid-digestion procedure specified in this test standard.

### 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.

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

## 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.

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 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.

## 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.<sup>4</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, 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.

<sup>4</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.

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<sub>3</sub>) 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<sub>3</sub>).

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. (**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.)

8.17 *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 this test method.

## 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<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 is required. If only dissolved molybdenum is to be determined, filter the samples at time of collection through a 0.45- $\mu$ m 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 Prepare in 200-mL volumetric flasks a blank and sufficient standards containing from 0.0 to 2.5  $\mu$ g 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 **11.6** to **11.12**.

10.3 Read directly in concentration if this capability is provided with the instrument or plot 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 An effective way to clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, is by soaking the glassware for 2 h first with HNO<sub>3</sub> (1 + 1) and then rinsing with reagent.

11.2 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 (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.

NOTE 5—When treating samples of brine or a sample containing a large amount of solids, the amount of reduction in volume is left to the discretion of the analyst.

NOTE 6—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.

11.3 If color in the digested solution indicates the presence of partially oxidized materials, add additional acid and approximately 90 mL of reagent water to the cooled solution and repeat the digestion.

11.4 Cool and filter the digested solution through a suitable filter (**8.17**) (such as a fine-textured, acid-washed, ashless paper) into a 100-mL volumetric flask. Wash the filter paper two to three times with reagent water, collecting washings in flask; make up to volume with reagent water.

NOTE 7—If only dissolved molybdenum is to be determined, filter portion of the sample through a 0.45- $\mu$ m membrane filter (**8.17**) and proceed with **11.5**.

11.5 Pipette a volume of sample containing less than 2.5  $\mu$ g of molybdenum (100 mL maximum) into a 200-mL volumetric flask and adjust the volume to 100 mL with water.

11.6 Add 5 mL of ascorbic acid solution (**8.3**) and mix.

11.7 Add 2 drops of bromphenol blue indicator solution (**8.4**) and mix.

11.8 Adjust the pH by addition of NaOH (**8.12**) solution (100 g/L) until a blue color persists. Add HCl (1 + 49) by drops until the blue color just disappears in both the standards and the sample; then add 2.5 mL of HCl (1 + 49) in excess. The pH at this point should be 2.3.

NOTE 8—The pH adjustment in **11.8** may be made with the use of a pH meter instead of using an indicator.

11.9 Add 5.0 mL of 8-hydroxyquinoline-MIBK solution (**8.6**) and shake vigorously for 15 min.

11.10 Allow the layers to separate; then carefully add water saturated with MIBK so as not to disturb the ketone layer until it is completely in the neck of the flask.

NOTE 9—The ketone layer should be centrifuged to remove all traces of water if the extract is to be stored for several hours before analysis.

11.11 Zero the instrument while aspirating the water-saturated MIBK (**8.13**).

11.12 Aspirate the ketone layer of standards and samples into the nitrous oxide-acetylene flame of the spectrophotometer and record the concentration or scale reading for each standard and sample against the blank. (**Warning**—Aspirating methyl isobutyl ketone into a nitrous oxide-acetylene flame can be dangerous. To minimize the chances of an accident, scrupulously follow recommended practices for using such a system.)

## 12. Calculation

12.1 If instrument readout is not in concentration, determine the weight of molybdenum in each sample by referring to the analytical curve. Calculate the concentration of molybdenum in micrograms per liter as follows:

$$\text{Molybdenum, } \mu\text{g/L} = (1000/A) \times B \quad (1)$$

where:

1000 = 1000 mL / L,

A = volume of sample, mL, and

B = weight of molybdenum in sample,  $\mu$ g.