



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

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 ( $\epsilon$ ) 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<sup>2</sup> 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 Water<sup>3</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D-19 on Water<sup>3</sup>
- D 3370 Practices for Sampling Water from Closed Conduits<sup>3</sup>
- D 4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry<sup>3</sup>
- D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents<sup>3</sup>
- D 5810 Guide for Spiking into Aqueous Samples<sup>3</sup>

<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.

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<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> *Annual Book of ASTM Standards*, Vol 11.01.

D 5847 Practice for the Writing Quality Control Specifications for Standard Test Methods for Water Analysis<sup>4</sup>

## 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.

<sup>4</sup> *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.<sup>5</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 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 (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.<sup>6</sup>

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 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 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-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

<sup>5</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 *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.

<sup>6</sup> Commercial Stock Standards may also be purchased.

amount of solids, the amount of reduction in volume is left to the discretion of the analyst.

11.2 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.

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

NOTE 6—If only dissolved molybdenum is to be determined, filter portion of the sample through a 0.45- $\mu$ m membrane filter and proceed with 11.4.

11.4 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.

11.5 Add 5 mL of ascorbic acid solution and mix.

11.6 Add 2 drops of bromphenol blue indicator solution and mix.

11.7 Adjust the pH by addition of NaOH 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 7—The pH adjustment in 11.7 may be made with the use of a pH meter instead of using an indicator.

11.8 Add 5.0 mL of 8-hydroxyquinoline-MIBK solution and shake vigorously for 15 min.

11.9 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 8—The ketone layer should be centrifuged to remove all traces of water if the extract is to be stored for several hours before analysis.

11.10 Zero the instrument while aspirating the water-saturated MIBK.

11.11 Aspirate the ketone layer of standards and samples into the nitrous oxide-acetylene flame of the spectrophotometer and record the scale reading for each standard and sample against the blank.

NOTE 9—**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 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:

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

where:

$A$  = volume of sample, mL, and

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

## 13. Precision and Bias <sup>7</sup>

13.1 The single-operator and overall precision of this test method within its designated range based on data from four laboratories, which includes a total of five operators analyzing each sample on three different days, may be expressed as follows:

$$S_T = 0.072X + 0.450$$

$$S_O = 0.039X + 0.610$$

where:

$S_T$  = overall precision,  $\mu$ g/L,

$S_O$  = pooled single-operator precision,  $\mu$ g/L, and

$X$  = concentration of molybdenum,  $\mu$ g/L.

13.2 Recoveries of known amounts of molybdenum (from  $\text{MoO}_3$ ) added to a series of natural waters for the same laboratories and operators were as follows:

Amount Added, $\mu$ g/L	Amount Found, $\mu$ g/L	Bias	% Bias	Statistically Significant (95 % Confidence Level)
3.0	3.07	0.07	2.3	no
9.5	9.38	-0.12	-1.3	no
18.0	16.86	-1.14	-6.3	yes

13.3 This test method was evaluated with reagent and natural water matrices. These data may not apply to waters of other matrices.

13.4 Practice D 2777 requires a minimum of six independent laboratories and analysts, respectively, for a collaborative study of a test method. Since the numbers listed for this study do not meet these requirements, that deficiency is recorded here for the benefit of the user of this test method.

NOTE 10—The nitric acid digestion steps were not performed in the round robin of this test method. It is an approved and recommended practice for determining total recoverable metals by atomic absorption spectrometry; however, its use can be expected to increase the variability of the final results. The user should verify its suitability for a matrix of interest by evaluating recovery for spikes that have been taken through the digestion process. (Guide D 5810)

13.5 Precision and bias for this test method conforms to Practice D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777-98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

## 14. Quality Control (QC)

14.1 The following quality control information is recommended for the determination of molybdenum in water.

14.2 The instrument shall be calibrated using a minimum of four calibration standards and a calibration blank. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank shall be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

14.3 An instrument check standard shall be analyzed at a minimum frequency of 10 % throughout the batch analysis.

<sup>7</sup> Supporting data are available from ASTM Headquarters. Request RR: D-19-1025.

The value of the instrument check standard shall fall between 80 % and 120 % of the true value.

14.4 Two method blanks shall be prepared ensuring that an adequate method blank volume is present for a minimum of seven repetitive analysis. The standard deviation of the method blank is used to determine the minimum detectable concentration of each sample and control in the batch.

14.5 A Laboratory Control Sample shall be analyzed with each batch of sample at a minimum frequency of 10 %.

14.6 If the QC for the sample batch is not within the established control limits, reanalyze the samples or qualify the results with the appropriate flags, or both. (Practice D 5847)

14.7 Blind control samples should be submitted by an outside agency in order to determine the laboratory performance capabilities.

## **15. Keywords**

15.1 atomic absorption; molybdenum; water

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