Designation: D3372 – 17

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 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:*[3]

D1129 Terminology Relating to Water

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.

[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] 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

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.[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. (**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

[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.

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_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 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 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 11.6 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_3 (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-µm membrane filter (8.17) and proceed with 11.5.

11.5 Pipette a volume of sample containing less than 2.5 µg 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:

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

where:

1000 = 1000 mL / L,
A = volume of sample, mL, and
B = weight of molybdenum in sample, µg.

13. Precision and Bias[5]

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:

$$S_T = 0.072X + 0.450 \quad (2)$$

$$S_O = 0.039X + 0.610 \quad (3)$$

where:

S_T = overall precision, µg/L,
S_O = pooled single-operator precision, µg/L, and
X = concentration of molybdenum, µg/L.

13.2 Recoveries of known amounts of molybdenum (from MoO_3) added to a series of natural waters for the same laboratories and operators were as follows:

Amount Added, µg/L	Amount Found, µg/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 D2777 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 D5810).

13.5 Precision and bias for this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

14. Quality Control (QC)

14.1 To ensure that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing molybdenum.

14.2 *Calibration and Calibration Verification:*

14.2.1 Analyze at least three working standards containing concentrations of molybdenum that bracket the expected sample concentration, prior to analysis of samples, to calibrate the instrument (see 11.1). The calibration correlation coefficient shall be equal to or greater than 0.990.

14.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness. The blank result should be less than the method reporting limit.

14.2.3 If calibration cannot be verified, recalibrate the instrument.

14.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The CCB result should be less than the method reporting limit. The CCV results should fall within the expected precision of the method or ±15 % of the known concentration.

14.3 *Initial Demonstration of Laboratory Capability:*

14.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

14.3.2 Analyze seven replicates of a standard solution prepared from an independent reference material containing a midrange concentration of molybdenum. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

14.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in accordance with the appropriate table in the method of analysis. This study should be repeated until the recoveries are within the limits given in that table. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

14.4 *Laboratory Control Sample (LCS):*

14.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a known concentration of molybdenum with each batch (laboratory-defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for a mid-range LCS shall fall within ±15 % of the known concentration.

14.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1025. Contact ASTM Customer Service at service@astm.org.

14.5 *Method Blank:*

14.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of molybdenum found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of molybdenum is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of this test method.

14.6 *Matrix Spike (MS):*

14.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of molybdenum and taking it through the analytical method.

14.6.2 The spike concentration plus the background concentration of molybdenum must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

14.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = [A\ (V_s + V) - BV_s]/CV \quad (4)$$

where:

A = analyte known concentration (µg/L) in spiked sample,
B = analyte known concentration (µg/L) in unspiked sample,
C = known concentration (µg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

14.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of this test method.

NOTE 11—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

14.7 *Duplicate:*

14.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

14.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

14.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of this test method.

14.8 *Independent Reference Material (IRM):*

14.8.1 In order to verify the quantitative value produced by the test method, analyze an independent reference material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

15. Keywords

15.1 atomic absorption; molybdenum; water

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3372 – 12) that may impact the use of this standard. (Approved June 1, 2017.)

(1) Revised 1.4 to update the units of measurement statement.
(2) Revised Section 2 to include D1976 and D5673.
(3) Revised Section 3 to update and add terms.
(4) Added 5.4 to include information on using ICP-AES or ICP-MS.
(5) Added 8.17 to include information on filter paper.
(6) Revised Note 3 to allow for pH of the samples in the laboratory.
(7) Revised 10.3 and 12.1 to allow for direct reading instruments.
(8) Revised Section 11 and Note 6 were modified to include updated information about the use of block digestion systems.
(9) Rewrote and expanded Section 14.