Molybdenum, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Molybdenum, dissolved, I-1490-85 (μg/L as Mo): 01060
Molybdenum, total recoverable, I-3490-85 (μg/L as Mo): 01062
Molybdenum, suspended recoverable, I-7490-85 (μg/L as Mo): 01061
Molybdenum, recoverable-from-bottom-material, dry wt, I-5490-85 (μg/g as Mo): 01063

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 1 to 50 μg/L of molybdenum. Samples containing more than 50 μg/L need to be diluted prior to chelation-extraction.

1.2 Suspended recoverable molybdenum is calculated by subtracting dissolved molybdenum from total recoverable molybdenum.

1.3 This method may be used to analyze bottom material containing at least 0.05 μg/g of molybdenum. Prepared sample solutions containing more than 50 μg/L of molybdenum need to be diluted.

1.4 Total recoverable molybdenum in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable molybdenum in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

Molybdenum is determined by atomic absorption spectrometry following chelation with 8-hydroxyquinoline and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into a nitrous oxide-acetylene flame of the spectrometer (Chau and Lum-Shue- Chan, 1969).

3. Interferences

The method is free from interference from most elements commonly found in fresh water. Vanadium(V) and iron(III) enhance the absorption, and chromium(VI) and tungsten(VI) suppress it. With the addition of ascorbic acid, up to 50,000 μg/L of iron(III), 1,000 μg/L of vanadium(V), and 10,000 μg/L of chromium(VI) or tungsten(VI) can be tolerated (Chau and Lum-Shue-Chan, 1969).

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

4.2 Refer to the manufacturer's manual to optimize instrument for the following:

Grating ------------ Ultraviolet
Wavelength -------- 313.3 nm
Source (hollow-cathode
  lamp) ------------ Molybdenum
Oxidant ------------ Nitrous oxide
Fuel --------------- Acetylene
Type of flame ------- Fuel-rich

4.3 Different nitrous oxide burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ascorbic acid solution*, 1 g/100 mL: Dissolve 1 g ascorbic acid in 100 mL demineralized water.

5.2 *Bromophenol blue indicator solution*, 0.1 g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Hydrochloric acid*, 0.3M: Mix 25 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.4 *8-Hydroxyquinoline-methyl isobutyl ketone solution*, 1 g/100 mL: Dissolve 1 g 8-hydroxyquinoline in 100 mL MIBK. Prepare fresh daily.

5.5 *Methyl isobutyl ketone (MIBK)*.

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5.6 *Molybdenum standard solution I*, 1.00 mL = 100 μg Mo: Dissolve 0.1500 g reagent-grade MoO_3 in 10 mL 0.1M NaOH (warm if necessary). Make just acidic with 0.1M HCl and dilute to 1,000 mL with demineralized water.

5.7 *Molybdenum standard solution II*, 1.00 mL = 1.0 μg Mo: Dilute 10.0 mL molybdenum standard solution I to 1,000 mL with demineralized water.

5.8 *Molybdenum standard solution III*, 1.0 mL = 0.10 μg Mo: Immediately before use, dilute 10.0 mL molybdenum standard solution II to 100 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.9 *Sodium hydroxide solution*, 2.5M: Dissolve 100 g NaOH in demineralized water and dilute to 1 L.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9), and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample or prepared sample solution containing less than 5.0 μg Mo (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.3 Prepare a demineralized-water blank with 1.5 mL concentrated. HNO_3 per liter of demineralized water and at least six standards, and adjust the volume of each to approx 100 mL with demineralized water.

6.4 Add 5 mL ascorbic acid solution and mix.

6.5 Add 2 drops bromophenol blue indicator solution and mix.

6.6 Adjust the pH by addition of 2.5M NaOH until a blue color persists. Add 0.3M HCl by drops until the blue color just disappears; then add 2.0 mL 0.3M HCl in excess. The pH at this point should be 2.3 (NOTE 1).

NOTE 1. The pH adjustment in paragraphs 6.5 and 6.6 may be made using a pH meter instead of using indicator. Add 2.5M NaOH to the solution until the pH is 2.3.

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

6.8 Allow the layers to separate; then add demineralized water until the ketone layer is completely in the neck of the flask.

6.9 While aspirating the ketone layer of the blank, use the automatic zero control to set the digital display to read zero concentration. While aspirating standards, use the automatic concentration control to set the digital display to read the concentration of the standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable molybdenum in each sample from the digital display or printer. Dilute those samples containing molybdenum concentrations that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

7.2 To determine micrograms per liter of suspended recoverable molybdenum, subtract dissolved-molybdenum concentration from total-recoverable-molybdenum concentration.

7.3 To determine micrograms per gram of molybdenum in bottom-material samples, first determine the micrograms per liter of molybdenum as in paragraph 7.1; then

$$Mo \ (\mu g/g) = \frac{\mu g/L \ Mo \times \dfrac{mL \ of \ original \ digest}{1,000}}{wt \ of \ sample \ (g)}$$

8. Report

8.1 Report molybdenum, dissolved (01060), total recoverable (01062), and suspended recoverable (01061), concentrations as follows: less than 100 μg/L, nearest microgram per liter; 100 μg/L and above, two significant figures.

8.2 Report molybdenum, recoverable-from-bottom-material (01063), concentrations as follows: less than 10 μg/g, nearest 0.1 μg/g; 10 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved molybdenum for seven samples within the range of 1.3 to 56.7 μg/L may be expressed as follows:

$$S_T = 0.068X + 1.320$$

where

S_T = overall precision, micrograms per liter, and,

X = concentration of molybdenum, micrograms per liter.

The correlation coefficient is 0.8718.

9.2 Precision for dissolved molybdenum for four of the seven samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
3	1.3	115
5	2.0	35
4	25.2	17
3	56.7	8

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable molybdenum and for recoverable molybdenum in bottom material will be greater than that reported for dissolved molybdenum.

Reference

Chau, Y. K., and Lum-Shue-Chan, K., 1969, Atomic absorption determination of microgram quantities of molybdenum in lake waters: Analytical Chimica Acta, v. 48, p. 205.