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Techniques of Water-Resources Investigations
of the United States Geological Survey

Chapter A1

METHODS FOR DETERMINATION
OF INORGANIC SUBSTANCES
IN WATER
AND FLUVIAL SEDIMENTS

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First Edition 1970
Second Edition 1979
Third Edition 1989

Book 5
LABORATORY ANALYSIS

Lead, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:
Lead, dissolved, I-1400-85 (μg/L as Pb): 01049
Lead, total recoverable, I-3400-85 (μg/L as Pb): 01051
Lead, suspended recoverable, I-7400-85 (μg/L as Pb): 01050

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 5 to 100 μg/L of lead. Sample solutions containing more than 100 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method.

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

1.3 Total recoverable lead in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

1.4 If the iron concentration of the sample exceeds 25,000 μg/L, determine lead by the atomic absorption spectrometric direct method.

2. Summary of method

Lead is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into an air-acetylene flame of the spectrometer (Fishman and Midgett, 1968).

3. Interferences

Concentrations of iron greater than 25,000 μg/L interfere by suppressing the lead absorption.

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 -------- 283.3 nm
Source (hollow-cathode
   lamp or electrodeless-
   discharge lamp) --- Lead
Oxidant ------------ Air
Fuel ---------------- Acetylene
Type of flame ------- Oxidizing

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

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 1 g/100 mL: Dissolve 1 g APDC in 100 mL demineralized water. Prepare fresh daily.

5.2 *Citric acid-sodium citrate buffer solution*: Dissolve 126 g citric acid monohydrate and 44 g sodium citrate dihydrate in demineralized water and dilute to 1 L with demineralized water. See NOTE 3 before preparation.

5.3 *Lead standard solution I*, 1.00 mL = 200 μg Pb: Dissolve 0.2000 g Pb shot in a minimum of dilute HNO$_3$. Heat to increase rate of dissolution. Add 10 mL concentrated HNO$_3$ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.4 *Lead standard solution II*, 1 mL = 2.00 μg Pb: Dilute 10.0 mL lead standard solution I and 1 mL concentrated HNO$_3$ (sp gr 1.41) to 1,000 mL with demineralized water. This standard is used to prepare working standards at the time of analysis.

5.5 *Methyl isobutyl ketone* (MIBK).

5.6 *Potassium hydroxide*, 10 M: Dissolve 56 g KOH in demineralized water, cool, and dilute to 100 mL.

5.7 *Potassium hydroxide*, 2.5*M*: Dissolve 14 g KOH in demineralized water and dilute to 100 mL (NOTE 1).

NOTE 1.   Alternatively, a 2.5*M* NH$_4$OH solution may be used. Add 167 mL concentrated NH$_4$OH (sp gr 0.90) to 600 mL demineralized water. Cool, and dilute to 1 L.

5.8 *Water, acidified*: Add 1.5 mL concentrated HNO$_3$ (sp gr 1.41) to 1 L of demineralized water.

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 solution containing less than 10.0 μg Pb (100 mL max) into a 200-mL volumetric flask and adjust the volume to approx 100 mL.

6.3   Prepare a blank of acidified water and sufficient standards, and adjust the volume of each to approx 100 mL with acidified water.

6.4   With a pH meter, adjust the pH of each solution to 2.4 with 2.5*M* KOH (NOTES 2 and 3). Shake for 3 min.

NOTE 2.   For water-suspended sediment samples that have been digested, add 1 to 2 mL 10*M* KOH or concentrated NH$_4$OH (sp gr 0.90) before pH adjustment.

NOTE 3.   If an automated titration system is used to adjust the pH, add 2.5 mL citric acid-sodium citrate buffer solution prior to pH adjustment. This will prevent over-shooting the end point in poorly buffered samples.

6.5   Add 2.5 mL APDC solution and mix.

6.6   Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7   Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.8   Aspirate the ketone layer within 1 h. Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of 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 lead in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing lead concentrations that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

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

8. Report

Report lead (Pb), dissolved (01049), total-recoverable (01051), and suspended-recoverable (01050), concentrations as follows: 5 to 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

9.1   Precision for dissolved lead for 23 samples within the range of 3.8 to 73 μg/L may be expressed as follows:

$$S_T = 0.231X + 0.458$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of lead, micrograms per liter.

The correlation coefficient is 0.8702.

9.2   Precision for dissolved lead for five of the 23 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
6	3.83	76
7	4.00	38
14	13.9	30
14	26.5	29
17	72.9	28

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

Reference

Fishman, M. J., and Midgett, M. R., 1968, Extraction techniques for the determination of cobalt, nickel, and lead in fresh water by atomic absorption, *in* Trace inorganics in water: American Chemical Society, Advances in Chemistry Series, no. 73, p. 230–5.

Lead, atomic absorption spectrometric, direct

Parameters and Codes:

Lead, dissolved, I-1399-85 (μg/L as Pb): 01049
Lead, total recoverable, I-3399-85 (μg/L as Pb): 01051
Lead, suspended recoverable, I-7399-85 (μg/L as Pb): 01050
Lead, recoverable-from-bottom-material, dry wt, I-5399-85 (μg/g as Pb): 01052

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 100 μg/L of lead. Sample solutions containing more than 4,000 μg/L need either to be diluted or to be read on a less expanded scale. Sample solutions containing less than 100 μg/L need to be analyzed by the atomic absorption spectrometric chelation-extraction method, providing that the interference limits discussed in that method are not exceeded.

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

1.3 This method may be used to analyze bottom material containing at least 10 μg/g of lead. Prepared sample solutions containing more than 4,000 μg/L need either to be diluted or to be read on a less expanded scale.

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

2. Summary of method

Lead is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame.

3. Interferences

Individual concentrations of sodium (9,000 mg/L), potassium (9,000 mg/L), calcium (4,000 mg/L), magnesium (4,000 mg/L), nitrate (900 mg/L), iron (4 $\times$ 10^6 μg/L), and cadmium, nickel, copper, zinc, cobalt, and chromium (10,000 μg/L) do not interfere. Higher concentrations of each constituent were not investigated.

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 -------- 283.3 nm
Source (hollow-cathode
   or electrodeless-dis-
   charge lamp) ----- Lead
Oxidant ------------ Air
Fuel ---------------- Acetylene
Type of flame ------- Slightly oxidizing

4.3 The 100-mm (4-in.), flathead, single-slot burner allows a working range of 100 to 4,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Lead standard solution I*, 1.00 mL = 200 μg Pb: Dissolve 0.2000 g Pb shot in a minimum of dilute HNO$_3$. Heat to increase rate of dissolution. Add 10 mL concentrated HNO$_3$ (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Lead standard solution II*, 1.00 mL = 20 μg Pb: Dilute 100.0 mL lead standard solution I and 1 mL concentrated HNO$_3$ (sp gr 1.41) to 1,000 mL with demineralized water.

5.3 *Lead working standards*: Prepare a series of at least six working standards containing

from 100 to 4,000 $\mu g/L$ of lead by appropriate dilution of lead standard solution II with acidified water. Prepare fresh daily.

5.4 *Water, acidified*: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of 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 lead in each sample solution from the digital display or printer while aspirating each sample. Dilute those samples containing lead concentrations that exceed the working range of the method and multiply by the proper dilution factors.

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

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

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

8. Report

8.1 Report lead, dissolved (01049), total-recoverable (01051), and suspended-recoverable (01050), concentrations to the nearest 100 $\mu g/L$.

8.2 Report lead, recoverable-from-bottom-material (01052), concentrations as follows: less

than 100 $\mu g/g$, nearest 10 $\mu g/g$; 100 $\mu g/g$ and above, two significant figures.

9. Precision

9.1 Precision for dissolved lead for 15 samples within the range of 6.70 to 80.3 $\mu g/L$ (NOTE 1) may be expressed as follows:

$$S_T = 0.498X - 0.509$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of lead, micrograms per liter.

The correlation coefficient is 0.9118.

NOTE 1. Precision data are given for lead concentrations below the reporting level of 100 $\mu g/L$. Samples were not available that contained greater lead concentrations; however, precision should improve at greater concentrations.

9.2 Precision for dissolved lead for four of the 15 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean ($\mu g/L$)	Relative standard deviation (percent)
7	6.70	75
8	25.5	56
13	46.4	51
18	80.3	55

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

9.4 Precision for total recoverable lead expressed in terms of percent relative standard deviation for two water-suspended sediments is as follows:

Number of laboratories	Mean ($\mu g/L$)	Relative standard deviation (percent)
9	44.1	54
7	51.9	38

Lead, atomic absorption spectrometric, graphite furnace

Parameter and Code:
Lead, dissolved, I-1401-85 (μg/L as Pb): 01049

1. Application

1.1 This method may be used to determine lead in low ionic-strength water and precipitation. With deuterium background correction and a 20-μL sample, the method is applicable in the range from 0.3 to 20 μg/L. With Zeeman background correction and a 20-μL sample, the method is applicable in the range from 0.5 to 50 μg/L. Sample solutions that contain lead concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method, or by the atomic emission spectrometric ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Lead is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite plat-form reduces the effects of many interferences. Calcium (25 mg/L), magnesium (8 mg/L), sodium (20 mg/L), sulfate (34 mg/L), and chloride (25 mg/L) do not interfere. Higher concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of lead. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contribution from contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 283.3 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-μL sample with 5 μL of matrix modifier (NOTE 1).

NOTE 1. A 20-μL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms.* Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware.* Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this,

fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Lead standard solution I*, 1.00 mL = 1,000 μg Pb: Dissolve 1.0000 g Pb shot in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41) Ultrex or equivalent and dilute to 1,000 mL with Type 1 water.

5.2 *Lead standard solution II*, 1.00 mL = 10.0 μg Pb: Dilute 10.0 mL lead standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.7) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Lead standard solution III*, 1.00 mL = 1.00 μg Pb: Dilute 100.0 mL lead standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Lead standard solution IV*, 1.00 mL = 0.010 μg Pb: Dilute 10.0 mL lead standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Matrix modifier solution*, 40 g $NH_4H_2PO_4$/L: Add 40.0 g $NH_4H_2PO_4$ to 950 mL Type 1 water, mix, and dilute to 1,000 mL. Analyze 20 μL of matrix modifier for lead contamination. If the lead reading is more than 0.005 absorbance-seconds, purify the solution by

chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK) (NOTE 3). Analyze 20 μL of the purified solution. Repeat extractions until the lead level is reduced to the acceptable level. DO NOT ADD ACID TO THE PURIFIED MATRIX MODIFIER SOLUTION.

NOTE 3. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. Add 0.25g APDC for each liter of solution. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Transfer portions of the solution to a separatory funnel, add 100 mL MIBK/liter of solution, and shake vigorously for at least 5 min. Frequently, vent the funnel in a hood. Collect the extracted solution in the FEP container. Repeat the extraction with 50 mL MIBK/liter of solution. Because MIBK can dissolve some plastic autosampler cups, boil the solution for at least 10 min in a silicone-treated or acid-rinsed container covered with a watchglass to remove MIBK.

5.6 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for lead. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. The integrated signal should not increase by more than 0.003 absorbance-seconds.

5.7 *Water, acidified*, Type 1: Add 1.5 mL high-purity, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water, Type 1.*

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1+1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards plus 5 μL of modifier each and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and (or) platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of lead in each sample from the digital display or printer output. Dilute those samples containing concentrations of lead that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report lead, dissolved (01049), concentrations as follows: less than 10.0 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of six samples six times each by a single operator using deuterium background correction is as follows:

Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
1.13	0.13	12
2.06	.12	5.7
3.95	.16	4.1
6.02	.22	3.6
10.41	.32	3.1
20.21	.35	1.7

9.2 Analysis of five samples by a single operator using Zeeman background correction is as follows:

Number of replicates	Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
4	0.62	0.17	27
4	1.80	.27	15
4	5.68	.05	.9
10	24.00	.77	3.2
14	48.31	.79	1.6

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of lead was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
11	10.63	0.48	4.5	97
13.5	13.30	.78	5.9	98
15	15.27	.96	6.3	102
22	21.40	.58	2.7	97
30	29.37	.54	1.8	98
Tap water (NOTE 4)				
11	10.15	1.19	10	92
13.5	15.37	2.40	15	114
15	15.18	.92	5.6	101
22	20.88	.83	3.7	95
30	30.81	1.70	5.3	103

NOTE 4. The tap water contained 1.3 μg/L of lead, and the standard deviation and percent relative standard deviation were calculated prior to subtraction of lead originally present.

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of lead was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
11	10.70	0.81	7.6	97
13.5	12.63	1.18	9.3	94
15	13.82	.76	5.5	92
22	21.18	.86	4.1	96
30	30.60	1.72	5.6	102
Tap water (NOTE 4)				
11	10.64	.63	5.3	97
13.5	15.37	1.59	9.9	114
15	17.78	3.70	19.4	119
22	21.49	1.97	8.6	98
30	29.68	1.13	3.7	99

9.5 Interlaboratory precision for dissolved lead for 16 samples within the range of 3.4 to 37.4 μg/L, without regard to type of background correction and use of matrix modifiers, if any, may be expressed as follows:

$$S_T = 0.448X + 1.478$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of lead, micrograms per liter.

The correlation coefficient is 0.8247.

References

American Society for Testing and Materials, 1984, Annual book of American Society for Testing and Materials standards, section 11, water: Philadelphia, v. 11.01, p. 39-41.

Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101-5.

Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16-21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1-11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1-11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89-92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621-4.

Lead, atomic emission spectrometric, ICP

Parameter and Code:
Lead, dissolved, I-1472-85 (μg/L as Pb): 01049

2. Summary of method

Lead is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

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Lead, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:
Lead, total, I-5474-85 (mg/kg as Pb): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Lead is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

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Lithium, atomic absorption spectrometric, direct

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 μg/L of lithium. Sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale.

1.2 Brines need to be diluted to eliminate interference from other elements. (See section 3, "Interferences.") If the lithium concentrations in the diluted samples are below detection, the undiluted samples need to be analyzed by the standard-addition method.

1.3 Suspended recoverable lithium is calculated by subtracting dissolved lithium from total recoverable lithium.

1.4 This method may be used to analyze bottom material containing at least 1 μg/g of lithium. Prepared sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale.

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

2. Summary of method

2.1 Lithium is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer or both.

3. Interferences

The following elements interfere when the indicated concentrations are exceeded: sodium, 1,000 mg/L; potassium, 100 mg/L; magnesium, 200 mg/L; calcium, 200 mg/L; chloride, 1,000 mg/L; sulfate, 2,000 mg/L; nitrate, 100 mg/L; and strontium, 5,000 μg/L.

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 ------------	Visible
Wavelength --------	670.8 nm
Source (hollow-cathode lamp) ------------	Lithium
Oxidant ------------	Air
Fuel ---------------	Acetylene
Type of flame -------	Oxidizing

4.3 The 50-mm (2-in.), flathead, single-slot burner allows a working range of 10 to 1,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Lithium standard solution I*, 1.00 mL = 1,000 μg Li: Dissolve 9.936 g LiNO$_3$ in demineralized water and dilute to 1,000 mL.

5.2 *Lithium standard solution II*, 1.00 = 10.0 μg Li: Dilute 10.0 mL lithium standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.3 *Lithium working standards*: Prepare a series of at least six working standards containing from 10 to 1,000 μg/L of lithium by appropriate dilution of lithium standard solution II. Prepare fresh daily.

6. Procedure

Aspirate the blank (demineralized water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of 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 lithium in each sample solution from the digital display or printer while aspirating each sample. Dilute those samples containing lithium concentrations that exceed working range of the method and multiply by the proper dilution factors.

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

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

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

8. Report

8.1 Report lithium, dissolved (01130), total-recoverable (01132), and suspended-recoverable (01131), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

8.2 Report lithium, recoverable-from-bottom-material (01133), concentrations as follows: less than 10 μg/g, nearest microgram

per gram; 10 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved lithium for 19 samples within the range of 32 to 632 μg/L may be expressed as follows:

$$S_T = 0.080X + 1.13$$

where
S_T = overall precision, micrograms per liter, and
X = concentration of lithium, micrograms per liter.

The correlation coefficient is 0.8270.

9.2 Precision for dissolved lithium for five of the 19 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
13	32	12
10	113	9
12	215	7
10	395	4
12	632	7

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

9.4 Precision for total recoverable lithium expressed in terms of percent relative standard deviation for one water-suspended sediment is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
7	116	17
6	222	9

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 30-5.

Lithium, atomic emission spectrometric, ICP

Parameter and Code:
Lithium, dissolved, I-1472-85 (μg/L as Li): 01130

2. Summary of method

Lithium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

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Lithium, total-in-sediment, atomic absorption spectrometric, direct

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Lithium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

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Magnesium, atomic absorption spectrometric, direct

Parameters and Codes:
Magnesium, dissolved, I-1447-85 (mg/L as Mg): 00925
Magnesium, total recoverable, I-3447-85 (mg/L as Mg): none assigned
Magnesium, suspended recoverable, I-7447-85 (mg/L as Mg): 00926
Magnesium, recoverable-from-bottom-material, dry wt, I-5447-85 (mg/kg as Mg): 00924

1. Application

1.1 This method may be used to analyze atmospheric precipitation, water, brines, and water-suspended sediment.

1.2 Two analytical ranges for magnesium are included: from 0.01 to 5.0 mg/L and from 2.5 to 50 mg/L. Sample solutions containing magnesium concentrations greater than 50 mg/L need to be diluted.

1.3 Suspended recoverable magnesium is calculated by subtracting dissolved magnesium from total recoverable magnesium.

1.4 This method may be used to analyze bottom material containing at least 10 mg/kg of magnesium. Prepared sample solutions containing more than 50 mg/L to be diluted.

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

2. Summary of method

2.1 Magnesium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 This procedure may be automated by the addition of a sampler, a proportioning pump, and either a strip-chart recorder or a printer or both (fig. 28).

3. Interferences

3.1 The interference caused by aluminum concentrations greater than 2,000 μg/L is masked by addition of lanthanum. Because low magnesium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field with use of nitric acid solution.

3.2 Nitrate, sulfate, and silica interfere, but in the presence of lanthanum chloride-hydrochloric acid solution at least 2,000 mg/L, 1,000 mg/L, and 200 mg/L, respectively, can be tolerated. The addition of nitric acid at the time of collection to preserve the samples causes no problem in the following procedure.

3.3 Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

4. Apparatus

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

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

Grating ------------- Ultraviolet
Wavelength -------- 285.2 nm
Source (hollow-cathode
  lamp) ------------ Magnesium
Oxidant ------------ Air
Fuel --------------- Acetylene
Type of flame ------- Slightly
                       reducing

4.3 The 50-mm (2-in.), flathead, single-slot burner allows a working range of 0.01 to 5.0 mg/L. This burner, rotated 90°, allows a working range of 2.5 to 50 mg/L. Different burners may be used according to manufacturers' instructions.
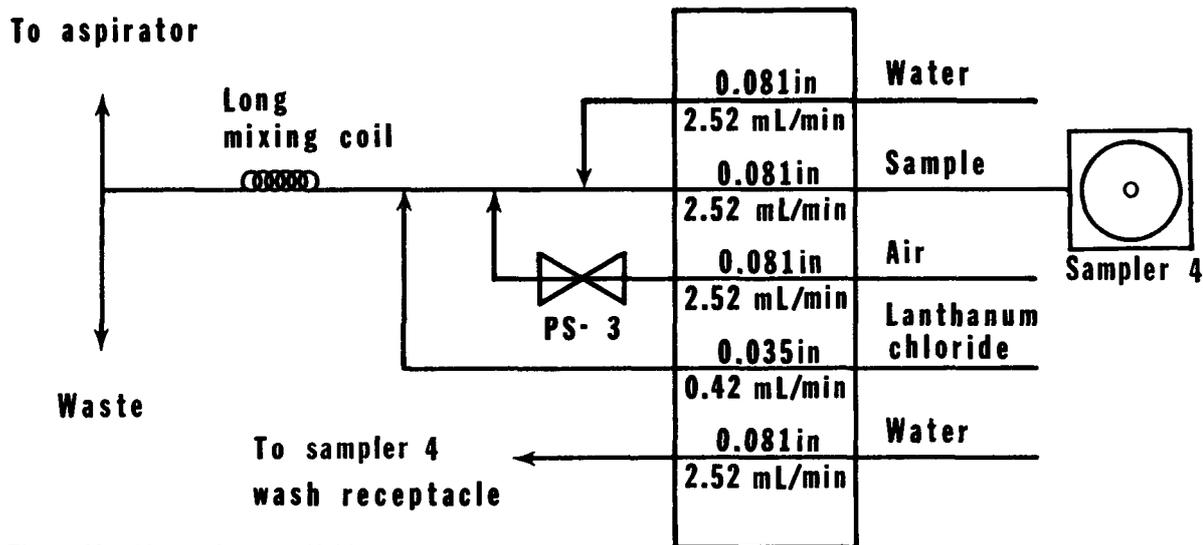
To aspirator

Long mixing coil

Waste

To sampler 4 wash receptacle

0.081 in	Water	
2.52 mL/min		
0.081 in	Sample	
2.52 mL/min		
0.081 in	Air	
2.52 mL/min		
0.035 in	Lanthanum chloride	
0.42 mL/min		
0.081 in	Water	
2.52 mL/min		

PS-3

Sampler 4

Figure 28.—Magnesium manifold

5. Reagents

5.1 *Lanthanum chloride solution*, 87 g/L: Mix 29 g La_2O_3 with a few milliliters of demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

5.2 *Magnesium standard solution I*, 1.00 mL = 0.50 mg Mg: Dissolve 0.500 g pure metallic Mg in a minimum amount of dilute HCl, and dilute to 1,000 mL with demineralized water.

5.3 *Magnesium working standards*: Prepare a series of at least six working standards containing either from 0.01 to 5.0 mg/L or from 2.5 to 50 mg/L magnesium by appropriate dilution of magnesium standard solution I. Add 1.0 mL $LaCl_3$ solution for each 10 mL of working standard. Similarly, prepare a demineralized water blank.

6. Procedure

6.1 Add 1.0 mL lanthanum chloride solution to 10.0 mL of sample solution.

6.2 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of 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 milligrams per liter of dissolved or total recoverable magnesium in each sample solution from the digital display or printer while aspirating each sample. Dilute those samples containing magnesium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per liter suspended recoverable magnesium, subtract dissolved-magnesium concentration from total-recoverable-magnesium concentration.

7.3 To determine milligrams per kilogram of magnesium in bottom-material samples, first determine the milligrams per liter of magnesium in each sample as in paragraph 7.1; then

$$Mg \ (mg/kg) = \frac{mg/L \ Mg \times \dfrac{mL \ of \ original \ digest}{1000}}{wt \ of \ sample \ (kg)}$$

8. Report

8.1 Report magnesium, dissolved (00925), total-recoverable (none assigned), and suspended-recoverable (00926), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

8.2 Report magnesium, recoverable-from-bottom-material (00924), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved magnesium for 35 samples within the range of 0.1 to 120 mg/L may be expressed as follows:

$$S_T = 0.062X + 0.003$$

where

S_T = overall precision, milligrams per liter, and

X = concentration magnesium, milligrams per liter.

The correlation coefficient is 0.9823.

9.2 Precision for dissolved magnesium for five of the 35 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
20	0.10	50
23	1.98	9
38	11.1	7
40	54.7	7
39	120	7

9.3 Precision for dissolved magnesium within the range of 0.03 to 5.2 mg/L in terms of the percent relative standard deviation by a single operator is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
8	0.033	21.2
8	.315	1.6
7	.993	2.6
6	5.18	4.2

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

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 30-5.

Magnesium, atomic absorption spectrometric, direct-EPA

Parameter and Code:
Magnesium, total recoverable, I-3448-85 (mg/L as Mg): 00927

1. Application

1.1 This method may be used to analyze water-suspended sediment.

1.2 For ambient water, analysis may be made on a measured portion of the acidified water-suspended sediment sample.

1.3 For all other waters, including domestic and industrial effluent, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain about the type of sample, the digestion-solubilization procedure must be used.

1.4 Two analytical ranges are provided: from 0.1 to 10 mg/L of Mg and from 2.5 to 50 mg/L. Samples containing magnesium at concentrations greater than 50 mg/L need to be diluted.

2. Summary of method

2.1 Magnesium is determined by atomic absorption spectrometry (Fishman and Downs, 1966). Lanthanum chloride is added to mask interferences.

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

3. Interferences

3.1 The interference caused by aluminum at concentrations greater than 2,000 μg/L is masked by addition of lanthanum. Because low magnesium values result if the pH of the sample is above 7, standards are prepared in hydrochloric acid solution and samples are preserved in the field using a nitric acid solution.

3.2 Nitrate, sulfate, and silica interfere, but in the presence of lanthanum chloride-acid solution at least 2,000 mg/L, 1,000 mg/L, and 200 mg/L, respectively, can be tolerated. The addition of nitric acid to the sample as a preservative at the time of collection causes no problem in the following procedure. Samples should be evaporated just to dryness following HNO_3 digestion to avoid any possible nitrate interference.

3.3 Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

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 -------- 285.2 nm
Source (hollow-cathode
    lamp) ------------ Magnesium
Oxidant ------------ Air
Fuel ---------------- Acetylene
Type of flame ------- Slightly
              reducing

4.3 The 50-mm (2-in.), flathead, single-slot burner allows a working range of 0.1 to 10 mg/L. This burner, rotated 90°, allows a range of 2.5 to 50 mg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Hydrochloric acid, 6M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.2 *Hydrochloric acid, 0.3M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.3 *Lanthanum chloride solution, 87 g/L*: Mix 29 g La_2O_3 with a few milliliters of

demineralized water to form a slurry. Slowly add 250 mL concentrated HCl (sp gr 1.19) while stirring (reaction may be violent) to dissolve the La_2O_3. Dilute to 500 mL with demineralized water.

5.4 *Magnesium standard solution I*, 1.00 mL = 0.50 mg Mg: Dissolve 0.500 g pure metallic Mg in a minimum amount of dilute HCl, and dilute to 1,000 mL with demineralized water.

5.5 *Magnesium working standards*: Prepare a series of at least six working standards containing from 0.1 to 50 mg/L magnesium by diluting magnesium standard solution I. Add 1.0 mL $LaCl_3$ solution for each 10 mL of working standard.

5.6 *Nitric acid*, concentrated (sp gr 1.41).

6. Procedure

6.1 Transfer the entire sample to a beaker.

6.2 Rinse the sample bottle with 3 mL concentrated HNO_3 for each 100 mL of sample and add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL of demineralized water.

6.3 Evaporate samples and blank to dryness on a hotplate, making sure the samples do not boil.

6.4 Cool and add an additional 3 mL concentrated HNO_3 to the beaker. Cover with a watchglass, return to the hotplate, and gently reflux the sample.

6.5 Continue heating, adding additional acid as necessary, until digestion is complete (indicated by a light-colored residue). Evaporate just to dryness.

6.6 Add 6 mL 6M HCl solution per 100 mL of original sample and warm the beaker to dissolve the residue.

6.7 Wash the watchglass and beaker with demineralized water and filter the sample

(Whatman No. 41 or equivalent), rinsing the filter with hot, dilute 0.3M HCl. Dilute to the original volume with demineralized water.

6.8 Add 1.0 mL lanthanum chloride solution per 10.0 mL of sample.

6.9 Aspirate the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of 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

Determine the milligrams per liter of magnesium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing magnesium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report magnesium, total-recoverable (00927), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for total recoverable magnesium over the range of the method will be greater than 9 percent.

References

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 30-5.
U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 215.1-1.

Magnesium, atomic emission spectrometric, ICP

Parameter and Code:
Magnesium, dissolved, I-1472-85 (mg/L as Mg): 00925

2. Summary of method

Magnesium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

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Magnesium, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:
Magnesium, total, I-5473-85 (mg/kg as Mg): none assigned
Magnesium, total, I-5474-85 (mg/kg as Mg): none assigned

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000 °C. The resulting bead is dissolved in acidified, boiling, demineralized water and magnesium determined by atomic absorption spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Magnesium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Manganese, atomic absorption spectrometric, chelation-extraction

Parameter and Code:
Manganese, dissolved, I-1456-85 (μg/L as Mn): 01056

1. Application

This method may be used to analyze water and brines containing from 1 to 100 μg/L of manganese. Brines containing more than 100 μg/L need either to be diluted or to be read on a less expanded scale. Samples containing more than 100 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method, providing that the interference limits discussed in that method are not exceeded.

2. Summary of method

Manganese is determined by atomic absorption spectrometry following chelation with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with chloroform. The extract is evaporated to dryness, treated with hot nitric acid to destroy organic matter, dissolved in hydrochloric acid, and diluted to a specified volume with demineralized water. The resulting solution is aspirated into the air-acetylene flame of the spectrometer.

3. Interferences

Concentrations of iron to 4×10^6 μg/L do not interfere; higher concentrations were not tested.

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 --------	279.5 nm
Source (hollow-cathode lamp) ------------	Manganese
Oxidant ------------	Air
Fuel ---------------	Acetylene
Type of flame -------	Oxidizing

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 4 g/100 mL: Dissolve 4 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 *Bromocresol green indicator solution*, 0.1 g/100 mL: Dissolve 0.1 g bromocresol green in 100 mL 20-percent ethanol.

5.3 *Chloroform.*

5.4 *Hydrochloric acid*, 4M: Mix 333 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 1 L.

5.5 *Manganese standard solution I*, 1.00 mL = 100 μg Mn: Dissolve 0.1000 g manganese flakes in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.6 *Manganese standard solution II*, 1.00 mL = 1.00 μg Mn: Immediately before use, dilute 10.0 manganese standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.7 *Sodium hydroxide*, 0.25M: Dissolve 10 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 containing less than 5 μg Mn (50 mL max) into a 125-mL separatory funnel. Adjust the volume to approx 50 mL.

6.3 Prepare a blank and at least six standards, and adjust the volume of each to approx 50 mL with demineralized water.

6.4   Add 2 drops bromocresol green indicator solution and adjust the pH of each sample, standard, and blank to 4.0 (light olive-green color) with the addition of 0.25M NaOH.

6.5   Add 5.0 mL APDC solution and mix.

6.6   Add 10 mL chloroform and shake for 2 min.

6.7   Allow the phases to separate and drain the chloroform phase into a 100-mL beaker.

6.8   Repeat the extraction with an additional 10 mL chloroform and drain the chloroform phase into the same beaker.

6.9   Place the beaker on a steam bath and evaporate just to dryness.

6.10 Hold the beaker at a 45° angle, and slowly add 2 mL concentrated HNO_3 (sp gr 1.41), rotating the beaker to effect thorough contact of the acid with the residue (CAUTION—NOTE 1).

NOTE 1.   If acid is added to the beaker in a vertical position, a violent reaction may occur accompanied by high heat and spattering.

6.11 Place the beaker on a hotplate at low heat and evaporate just to dryness.

6.12 Add 2 mL 4M HCl and heat, while swirling, for 1 min.

6.13 Cool and transfer the solution to a 10-mL volumetric flask and dilute to volume with demineralized water.

6.14 While aspirating 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 concentrations of 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

Determine the micrograms per liter of dissolved manganese in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing concentrations of manganese that exceed the working range of the method. Repeat those analyses and multiply by the proper dilution factors.

8.   Report

Report manganese, dissolved (01056), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9.   Precision

Precision for dissolved manganese for three samples expressed in terms of percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
6	22.2	16
6	121	7
6	291	5

Manganese, atomic absorption spectrometric, direct

Parameters and Codes:

Manganese, dissolved, I-1454-85 (μg/L as Mn): 01056
Manganese, total recoverable, I-3454-85 (μg/L as Mn): 01055
Manganese, suspended recoverable, I-7454-85 (μg/L as Mn): 01054
Manganese, recoverable-from-bottom-material, dry wt, I-5454-85 (μg/g as Mn): 01053

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 μg/L of manganese. Sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale. Brines need to be analyzed by the atomic absorption spectrometric, chelation-extraction method, providing that the interferences discussed in that method are not exceeded.

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

1.3 This method may be used to analyze bottom material containing at least 1 μg/g of manganese. Prepared sample solutions containing more than 1,000 μg/L need either to be diluted or to be read on a less expanded scale.

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

2. Summary of method

2.1 Manganese is determined by atomic absorption spectrometry by direct aspiration of the sample into an air-acetylene flame without preconcentration or pretreatment.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer or both.

3. Interferences

Magnesium (100 mg/L) and silica (100 mg/L) do not interfere. Magnesium in excess of 100 mg/L may present some interference, especially when the manganese concentration exceeds 500 μg/L. Silica interferes above 100 mg/L. Iron concentration to 4×106 μg/L does not interfere.

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 -------- 279.5 nm
Source (hollow-cathode
  lamp) ------------ Manganese
Oxidant ------------ Air
Fuel ---------------- Acetylene
Type of flame ------- Oxidizing

4.3 The 100-mm (4-in.), flathead, single-slot burner allows a working range from 10 to 1,000 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Manganese standard solution I*, 1.00 mL = 100 μg Mn: Dissolve 0.1000 g manganese flakes in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL with demineralized water.

5.2 *Manganese standard solution II*, 1.00 mL = 10.0 μg Mn: Immediately before use,

dilute 10.0 mL manganese standard solution I to 100 mL with demineralized water.

5.3 *Manganese working standards*: Prepare at least six working standards containing from 10 to 1,000 μg/L manganese by appropriate dilution of manganese standard solution II with acidified water. Prepare fresh daily.

5.4 *Water*, acidified: Add 1.5 mL concentrated HNO_3 (sp gr 1.41) to 1 L of demineralized water.

6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of 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 manganese in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing manganese concentrations that exceed the working range of the method and multiply by the proper dilution factors.

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

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

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

8. Report

8.1 Report manganese, dissolved (01056), total-recoverable (01055), and suspended-recoverable (01054), concentrations as follows: less than 100 μg/L, nearest 10 μg/L; 100 μg/L and above, two significant figures.

8.2 Report manganese, recoverable-from-bottom-material (01053), concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 μg/g and above, two significant figures.

9. Precision

9.1 Precision for dissolved manganese for 30 samples within the range of 3.0 to 568 μg/L may be expressed as follows:

$$S_T = 0.056X + 8.28$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of manganese, micrograms per liter.

The correlation coefficient is 0.9003.

9.2 Precision for dissolved manganese for six of the 30 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
6	3.0	267
6	12	83
27	60	17
25	106	12
34	256	9
36	568	7

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

9.4 Precision for total recoverable manganese expressed in terms of percent relative standard deviation for two water-suspended sediment samples is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
21	52	44
22	317	6

Manganese, atomic absorption spectrometric, graphite furnace

Parameter and Code:
Manganese, dissolved, I-1455-85 (µg/L as Mn): 01056

1. Application

1.1 This method may be used to determine manganese in low ionic-strength water and precipitation. With deuterium background correction and a 20-µL sample, the method is applicable in the range from 0.2 to 12 µg/L. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 0.2 to 20 µg/L. Sample solutions that contain manganese concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method, or by the atomic emission spectrometric ICP method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Manganese is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (60 mg/L), magnesium (14 mg/L), sodium (56 mg/L), sulfate (110 mg/L), and chloride (45 mg/L) do not interfere. Higher concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of manganese. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 279.5 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-µL sample with 5 µL of matrix modifier (NOTE 1).

NOTE 1. A 20-µL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms.* Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware.* Many trace metals at very low concentrations have been found to sorb very

rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Matrix modifier solution*, 10 g $Mg(NO_3)_2$/L, Suprapur MCB reagent or equivalent: Add 16.8 g $Mg(NO_3)_2 \cdot 6H_2O$ to 950 mL Type 1 water, mix, and dilute to 1,000 mL. **DO NOT ADD ACID TO THE MATRIX MODIFIER SOLUTION.**

5.2 *Manganese standard solution I*, 1.00 mL = 1,000 μg Mn: Dissolve 1.0000 g Mn flakes in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with Type 1 water.

5.3 *Manganese standard solution II*, 1.00 mL = 10.0 μg Mn: Dilute 10.0 mL manganese standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.7) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.4 *Manganese standard solution III*, 1.00 mL = 1.00 μg Mn: Dilute 100.0 mL manganese standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.5 *Manganese standard solution IV*, 1.00 mL = 0.01 μg Mn: Dilute 10.0 mL manganese standard solution III to 1,000 mL. This

standard also is used to prepare working standards serially at time of analysis.

5.6 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for manganese. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. The integrated signal should not increase by more than 0.001 absorbance-seconds.

5.7 *Water*, acidified, Type 1: Add 1.5 mL high-purity, concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water*, Type 1.

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1+1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards plus 5 μL of modifier each and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and/or platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of manganese in each sample from the digital

display or printer output. Dilute those samples containing concentrations of manganese that exceed the working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report manganese, dissolved (01056), concentrations as follows: less than 10.0 μg/L, nearest 0.1 μg/L; 10 μg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of four rainwater samples six times each by a single operator using deuterium background correction is as follows:

Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
0.53	0.07	13.7
1.14	.05	4.8
1.53	.04	2.8
1.79	.05	3.0

9.2 Analysis of four samples by a single operator using Zeeman background correction is as follows:

Number of replicates	Mean (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)
7	3.94	0.38	9.6
11	9.92	.60	6.0
4	15.48	.25	1.6
12	19.06	.51	2.7

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of manganese was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
3.95	4.38	0.35	8.0	111
7.9	8.13	.77	9.5	103
13	13.43	.64	4.8	103
15.5	16.03	.77	4.8	103
26	25.45	1.29	5.1	98
Tap water (NOTE 3)				
3.95	3.11	1.11	6.4	79
7.9	6.63	.66	3.2	84
13	9.67	1.48	6.2	74
15.5	14.83	1.59	7.2	96
26	24.94	2.11	5.4	96

NOTE 3. The tap water contained approx 14.4 μg/L of manganese, and the standard deviation and percent relative standard deviation were calculated prior to subtraction of manganese originally present.

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 μS/cm). A known amount of manganese was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (μg/L)	Amount found (μg/L)	Standard deviation (μg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
3.95	3.89	0.23	5.9	98
7.9	8.12	.57	7.0	103
13	13.32	.58	4.4	102
15.5	14.76	1.17	7.9	95
26	26.12	.72	2.8	100
Tap water (NOTE 3)				
3.95	6.61	2.19	10.3	167
7.9	9.07	1.43	6.1	115
13	12.16	1.99	7.4	94
15.5	17.53	1.34	5.4	113
26	23.85	3.07	8.0	92

9.5 Interlaboratory precision for dissolved manganese for 9 samples within the range of 40 to 547 μg/L, without regard to type of background correction and use of matrix modifiers, if any, may be expressed as follows:

$$S_T = 0.144X + 5.023$$

where

S_T = overall precision, micrograms per liter, and

X = concentration of manganese, micrograms per liter.

The correlation coefficient is 0.8074.

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Manganese, atomic emission spectrometric, ICP

Parameter and Code:
Manganese, dissolved, I-1472-85 (μg/L as Mn): 01056

2. Summary of method

Manganese is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

Manganese, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:
Manganese, total, I-5473-85 (mg/kg as Mn): none assigned
Manganese, total, I-5474-85 (mg/kg as Mn): none assigned

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000 °C. The resulting bead is dissolved in acidified, boiling, demineralized water; manganese is then determined by atomic absorption spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Manganese is determined on the resulting solution by atomic absorption spectrometry. See method I- 5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

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