Lead, atomic absorption spectrophotometry, graphite furnace

Parameters and Codes:
Lead, dissolved, I-2403-89 (µg/L as Pb): (01049)
Lead, whole water recoverable, I-4403-89 (µg/L as Pb): (01051)

1. Application

1.1 This method is used to determine lead in samples of water and water-suspended sediment with a specific conductance not greater than 10,000 µS/cm. With Zeeman background correction and a 20-µL sample, the method is applicable in the range from 1 to 25 µg/L. Sample solutions that contain lead concentrations greater than 25 µg/L must be diluted or be analyzed by an alternate method. This method was implemented in the National Water Quality Laboratory in May 1989.

1.2 The analytical range and detection limit can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings.

1.3 Whole water recoverable lead in samples of water-suspended sediment must undergo preliminary digestion by method I-3485 before being determined.

2. Summary of method

Lead is determined by atomic absorption spectrophotometry 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 then is evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal produced during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences for samples with specific conductances less than 10,000 µS/cm normally are small. In addition, the use of the graphite platform reduces the effects of many interferences.

3.2 Special precautionary measures to prevent contamination need to be used during sample collection and laboratory determination.

4. Apparatus

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

4.1.1 Refer to the manufacturer's manual to optimize operations and instrumental performance. A 20-µL sample with a 25-µg/L concentration of lead should yield a signal of approximately 0.18 absorbance-second. This absorbance signal is based on lead's characteristic mass of 12.0 pg for a signal of 0.0044 absorbance-second. A 20-µL sample generally requires 30 seconds at 130°C to dry. Samples that have a complex matrix might require a longer drying or charring time. Peak shapes may be used to detect insufficient drying, charring, or atomization times or temperatures.

4.1.2 *Graphite furnace,* capable of reaching a temperature of 1,800°C sufficient to atomize the lead. **Warning**: dial settings frequently are inaccurate, and newly conditioned furnaces need to be temperature-calibrated.

4.1.3 *Graphite tubes and platforms,* pyrolytically coated graphite tubes and platforms are suggested.

4.2 *Labware.* Many trace metals at small concentrations adsorb rapidly to glassware. To preclude this problem, fluorinated ethylene propylene (FEP) or Teflon labware is used. Alternatively, glassware, particularly flasks and pipets, can be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co.) according to the manufacturer's instructions. Check autosampler cups for contamination. Lancer polystyrene disposable cups are satisfactory after acid rinsing. Alternatively, reusable Teflon or FEP cups can be purchased.

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

5. Reagents

5.1 *Lead standard solution I*, 1.00 mL = 1,000 µg Pb: A commercially prepared and certified lead standard is used. An alternate method is to dissolve 1.0000 g lead wire in a minimum of dilute HNO_3. Heat to increase rate of dissolution. Add 4.0 mL ultrapure concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with 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 1).

NOTE 1. Use acidified water (paragraph 5.7) to make dilutions. Store all standards in sealed Teflon or FEP containers. Rinse each container twice with a small volume of standard before filling the storage container. Standards stored for 6 months in FEP containers yielded values equal to freshly prepared standards.

5.3 *Lead standard solution III,* 1.00 mL = 1.00 µg Pb: Dilute 100 mL lead standard solution II to 1,000 mL with acidified water. Prepare fresh monthly.

5.4 *Lead working solution IV*, 1.00 mL = 0.025 µg Pb: Dilute 25.0 mL lead standard solution III to 1,000 mL with acidifed water. Prepare fresh monthly.

5.5 *Lead working solution V*, 1.00 mL = 0.010 µg Pb: Dilute 10.0 mL lead standard solution III to 1,000 mL with acidifed water. Prepare fresh monthly.

5.6 *Nitric acid, concentrated,* ultrapure (sp gr 1.41): J.T. Baker Ultrex brand HNO_3 is adequately pure; however, check each lot for contamination. Analyze acidified water (paragraph 5.7) for lead. Add 1.5 mL of concentrated HNO_3 per liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-second.

5.7 *Water, acidified:* Add 4.0 mL ultrapure concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water:* All references to water shall be understood to mean ASTM Type I reagent water (American Society for Testing and Materials, 1991).

5.9 *Matrix modifier solution,* 6.9 g/L $NH_4H_2PO_4$ and 1.005 g/L $Mg(NO_3)_2 \cdot 6H_2O$: Add 13.8 g $NH_4H_2PO_4$ to 950 mL water, mix, and dilute to 1,000 mL. Add 2.01 g $Mg(NO_3)_2 \cdot 6H_2O$ to 950 mL water, mix, and dilute to 1,000 mL. Mix the two solutions together 1 + 1. Analyze 20 µL of matrix modifier to determine if lead contamination is present. If the lead reading is more than 0.005 absorbance-second, purify the solution by chelation with ammonium pyrrolidine dithiocarbamate (APDC) followed by extraction with methyl isobutyl ketone (MIBK) (NOTE 2). 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 2. To purify matrix modifier solution, pour the solution into a Teflon or FEP container. While stirring, adjust the solution to pH 2.9 by dropwise addition of concentrated HNO_3 (sp gr 1.41). Add 10.0 g APDC to 1 L of water and mix well. Add 5.0 mL, of the APDC solution to each 100.0 mL of matrix modifier. Shake vigorously for 10 minutes. Add 10 mL MIBK/100 mL of solution and shake vigorously for at least 10 minutes. Separate MIBK by draining through separatory funnel. Repeat process. Since some MIBK will remain in the solution, boil for 10 minutes in a silicone-treated or acid-rinsed container covered with a watch glass.

6. Procedure

6.1 The autosampler and the graphite furnace need to be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1*N* HNO_3 solution.

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 a minimum of two standards (NOTE 3) in duplicate. Construct the analytical curve from the integrated peak areas (absorbance-seconds).

NOTE 3. The automatic sampler is programmed to inject 5.0 µL of matrix modifier along with blank, standards, and samples.

6.5 Similarly, inject and analyze the samples in duplicate. Every tenth sample cup needs to contain either a standard, blank, or a reference material.

6.6 Restandardize as required, although with the use of L'vov platforms, restandardization generally is not necessary. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, 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 factor.

8. Report

Report concentrations of lead, dissolved (01049), and whole water recoverable (01051), as follows: less than 10 µg/L, the nearest 1 µg/L; 10 µg/L and greater, two significant figures.

9. Precision

9.1 Analysis of five samples for dissolved lead by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
7	1.7	0.03	1.8
108	11.8	0.79	6.7
111	15.2	1.04	6.8
41	24.0	0.94	3.9

9.2 Analysis of three samples for whole water recoverable lead by a single operator is as follows:

Number of replicates	Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
7	0.6	0.47	78.3
11	11.3	1.51	13.4
10	16.6	0.66	4.0

9.3 The precision and bias for dissolved lead was tested on several standard reference water samples. A known amount of lead was added to each sample, and single-operator precision and bias for the samples are as follows:

Amount present	Number of replicates	Amount added (µg/L)	Found (µg/L) (NOTE 4)	Standard deviation (percent)	Relative standard deviation (percent)	Percent recovery
11.2	6	44.9	40.8	2.1	5.1	90.9
11.4	6	21.5	21.4	4.3	19.9	99.5
11.7	6	9.3	8.9	0.6	6.6	95.7
17.5	6	15.8	18.3	1.1	6.1	115.8
23.0	6	4.9	5.4	1.6	29.6	110.2
23.7	6	13.8	12.9	0.8	6.2	93.5
23.9	6	10.0	10.8	1.0	9.7	108.0

NOTE 4. The amount originally present has been subtracted.

References

American Society for Testing and Materials, 1991, Annual book of ASTM standards, Section 11, Water: Philadelphia, American Society for Testing and Materials, v. 11.01, p. 45-47.

Hinderberger, E.J., Kasser, 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.