LEAD by GFAAS 7105

Pb MW: 207.19 (Pb); 223.19 (PbO) CAS: 7439-92-1 (Pb); 1317-36-8 (PbO) RTECS: OF7525000 (Pb) OG1750000 (PbO)

METHOD: 7105, Issue 2 **EVALUATION: PARTIAL** **Issue 1: 15 August 1990**
Issue 2: 15 August 1994

OSHA : 0.05 mg/m^3
NIOSH: <0.1 mg/m^3; blood Pb ≤60 µg/100 g
ACGIH: 0.05 mg/m^3

PROPERTIES: soft metal; d 11.3 g/cm^3; MP 327.5 °C
valences +2, +4 in salts

SYNONYMS: elemental lead and lead compounds except alkyl lead

SAMPLING

SAMPLER: FILTER
(0.8-µm cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 1 L @ 0.05 mg/m^3
-MAX: 1500 L

SHIPMENT: routine

SAMPLE STABILITY: stable

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: not studied

BIAS: not determined

OVERALL PRECISION ($\hat{S}_{rT}$): not determined

ACCURACY: not determined

MEASUREMENT

TECHNIQUE: ATOMIC ABSORPTION SPECTROPHOTOMETER, GRAPHITE FURNACE

ANALYTE: lead

ASHING: conc. HNO_3, 3 mL; 30% H_2O_2; 1 mL; 140 °C

FINAL SOLUTION: 10 mL 5% HNO_3

WAVELENGTH: 283.3 nm

GRAPHITE TUBE: pyrolytic coated

INJETION: 20 µL + 10 µL matrix modifier,
DRY: 110 °C, 70 sec;
CHAR: 800 °C, 30 sec;
ATOMIZE: 1800 °C, 5 sec.

BACKGROUND CORRECTION: D_2, H_2, or Zeeman

CALIBRATION: Pb^{2+} in 5% HNO_3

RANGE 0.05 to 100 µg per sample [1]

ESTIMATED LOD: 0.02 µg per sample [1]

PRECISION ($\hat{S}_r$): 0.049 [1]

APPLICABILITY: The working range is 0.002 to >1 mg/m^3 for a 200-L air sample. If high concentrations are expected, the samples should be analyzed by flame AAS. The method is applicable to elemental lead, including Pb fume, and all other aerosols containing lead. This is an elemental analysis, not compound specific. Aliquots of the sample may be analyzed separately for additional elements.

INTERFERENCES: Use D_2 or H_2 continuum or Zeeman background correction to control molecular absorption. High concentrations of calcium, sulfate, carbonate, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be offset by an additional sample treatment step.

OTHER METHODS: This revises and replaces P&CAM 214 (2). Method 7300 (ICP-AES) is an alternate analytical method. Method 7505 is specific for lead sulfide by X-ray diffraction. Method 7082 is a flame AAS method, with a higher working range.

REAGENTS:

1. Nitric acid, conc.*
2. Nitric acid, 5% (v/v). Add 50 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% H_2O (w/w), reagent grade.*
4. Calibration stock solution, 1000 µg/mL Pb. Commercial standard or dissolve 1.00 g Pb metal in minimum volume of HNO_3 and dilute to 1 L with 1% (v/v) HNO_3. Store in a polyethylene bottle.
5. Matrix Modifier. Place 0.2 g $NH_4H_2PO_4$ and 0.3 g $Mg(NO_3)_2$ in a 100-mL volumetric flask. Add 2 mL conc. HNO_3 and bring to volume with distilled or deionized water.
6. Argon, prepurified.
7. Distilled or deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Cellulose ester membrane filter, 0.8-µm, 37-mm, in 2-piece cassette.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with graphite furnace atomizer and background correction.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for Argon.
6. Beakers, Phillips, 125-mL, or Griffin, 50-mL with watchglass covers.**
7. Volumetric flasks, 10- and 100-mL.**
8. Assorted volumetric pipets as needed.**
9. Hotplate, surface temperature 140°C.
10. Bottles, polyethylene, 100-mL.

** Clean all glassware with conc. nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Concentrated nitric acid is an irritant and may burn skin. Perform all acid digestions in a fume hood. Hydrogen peroxide is a strong oxidizing agent, a strong irritant, and corrosive to the skin. Wear gloves and eye protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for up to 8 h for a total sample size of 1 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE: Some matrices, especially bulk samples containing epoxy-based paint, may require a different digestion procedure for complete recovery of lead. See the Appendix of Method 7082 (Lead by Flame AAS) for a microwave digestion procedure which can be used for this purpose.

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 3 mL conc. HNO_3, and 1 mL 30% H_2O_2 and cover with a watchglass. Start reagent blanks at this step.
5. Heat on 140 °C hotplate until volume is reduced to about 0.5 mL.
6. Rinse the watchglass and walls of the beaker with 3 to 5 mL 5% HNO_3. Allow the solution to evaporate to 0.5 mL.
7. Cool each beaker.
8. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.

CALIBRATION AND QUALITY CONTROL:

9. Prepare a series of six working standards covering the range 0.002 to 0.1 µg/mL Pb (0.02 to 1.0 µg Pb per sample).
   a. Add aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 5% HNO_3. Store the working standards in polyethylene bottles and prepare fresh weekly.
   b. Analyze the working standards together with the blanks and samples (steps 12 through 14).
   c. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
10. Analyze a standard for every 10 samples to check for instrument drift.

11. Check recoveries with at least one spiked media blank per 10 samples.
    NOTE: Perform a matrix spike of a sample occasionally to check for matrix interferences. If an adequate recovery is not obtained (85 to 115%), an alternate method of analysis should be used, such as flame AAS or ICP.

MEASUREMENT:

12. Set spectrophotometer as specified by the manufacturer and to conditions on page 7105-1.
    NOTE: An alternate wavelength is 217.0 nm [3]. Analyses at 217.0 nm have slightly greater sensitivity, but poorer signal-to-noise ratio compared to 283.3 nm. Also, non-atomic absorption is significantly greater at 217.0 nm, making the use of D_2 or H_2 continuum, or Zeeman background correction mandatory at that wavelength.
13. Add matrix modifier to samples and standards in proper ratio of 2 to 1 (sample or standard to matrix modifier).
14. Analyze standards, samples, and blanks. Record absorbance readings.
    NOTE: If the absorbance value for the sample is above the linear range of the standards, dilute with 5% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

15. Using the measured absorbances, calculate the corresponding concentrations (µg/mL) of lead in the sample, C_s, and average media blank, C_b, from the calibration graph.
16. Using the solution volumes (mL) of the sample, V_s, and media blanks, V_b, calculate the concentration, C (mg/m^3), of lead in the air volume sampled, V (L):

$$\mathbf{C = \frac{C_s V_s - C_b V_b}{V}, \ mg/m^3.}$$

EVALUATION OF METHOD:

Method P&CAM 214 [2], issued on 1/29/76, was based on a method for metal pollutants in water [4]. Air sampling and digestion procedures follow those in Method 7082. The analytical procedure was evaluated by DataChem Laboratories in 1990 [1]. The LOD was determined at 0.02 µg per sample, with a LOQ of 0.05 µg per sample. The precision of the measurement procedure was 0.049. The overall precision, bias, and accuracy of the method were not determined. The reagents for digesting various lead species are given below:

Species	Digestion Method
Pb metal	HNO_3 only
Pb metal	$HNO_3 + H_2O_2$
Pb	HNO_3 only
PbS	HNO_3 only
PbO_2	HNO_3 only
PbO_2	$HNO_3 + H_2O_2$
Pb in paint*	HNO_3 only
Pb in paint*	$HNO_3 + H_2O_2$

* Standard Reference Material #1579, U.S. National Institute of Standards and Technology.

REFERENCES:

[1] Backup Data Report for Method 7105 submitted to NIOSH by DataChem Laboratories, NIOSH (Unpublished, September, 1990).
[2] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 214, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).
[3] Analytical Methods for Atomic Absorption Spectrophotometry, Perkin-Elmer Corporation (1976).
[4] Fernandez, F.J. and D.C. Manning. Atomic Absorbtion Analyses of Metal Pollutants in Water Using a Heated Graphite Atomizer, Atomic Absorption Newsletter 10, 65 (1971).

METHOD REVISED BY:

James B. Perkins, Brent E. Stephens, and Michael P. Beesley, DataChem Laboratories, Salt Lake City, UT.