LEAD by Flame AAS 7082

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

METHOD: 7082, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984 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		MEASUREMENT	
SAMPLER:	FILTER (0.8-µm cellulose ester membrane)	**TECHNIQUE:**	ATOMIC ABSORPTION SPECTROPHOTOMETER, FLAME
FLOW RATE:	1 to 4 L/min	**ANALYTE:**	lead
VOL-MIN:	200 L @ 0.05 mg/m^3	**ASHING:**	conc. HNO_3, 6 mL + 30% H_2O_2, 1 mL; 140 °C
-MAX:	1500 L	**FINAL SOLUTION:**	10% HNO_3, 10 mL
SHIPMENT:	routine	**FLAME:**	air-acetylene, oxidizing
SAMPLE STABILITY:	stable	**WAVELENGTH:**	283.3 nm
BLANKS:	2 to 10 field blanks per set	**BACKGROUND CORRECTION:**	D_2 or H_2 lamp, or Zeeman
ACCURACY		**CALIBRATION:**	Pb^{2+} in 10% HNO_3
RANGE STUDIED:	0.13 to 0.4 mg/m^3 [1]; 0.15 to 1.7 mg/m^3 (fume) [2]	**RANGE**	10 to 200 µg per sample [2,3]
BIAS:	− 3.1%	**ESTIMATED LOD:**	2.6 µg per sample [4]
OVERALL PRECISION($\hat{S}_{rT}$):	0.072 [1]; 0.068 (fume) [2]	**PRECISION ($\bar{S}_r$):**	0.03 [1]
ACCURACY:	± 17.6%		

APPLICABILITY: The working range is 0.05 to >1 mg/m^3 for a 200-L air sample. 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 samples can be analyzed separately for additional elements.

INTERFERENCES: Use D_2 or H_2 continuum or Zeeman background correction to control flame or molecular absorption. High concentrations of calcium, sulfate, carbonate, phosphate, iodide, fluoride, or acetate can be corrected.

OTHER METHODS: This method combines and replaces P&CAM 173 [3] and S341 [4,5] for lead. Method 7300 (ICP-AES) and 7105 (AAS/GF) are alternate analytical methods. Method 7505 is specific for lead sulfide. The following have not been revised: the dithizone method, which appears in P&CAM 102 [5] and the lead criteria document [6]; and P&CAM 191 (ASV) [7].

REAGENTS:

1. Nitric acid, conc.*
2. Nitric acid, 10% (v/v). Add 100 mL conc. HNO_3 to 500 mL water; dilute to 1 L.
3. Hydrogen peroxide, 30% H_2O_2 (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 (1+1) HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable ≥ one year.
5. Air, compressed, filtered.
6. Acetylene
7. Distilled or deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Cellulose ester filter, 0.8-µm pore size, 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic Absorption Spectrophotometer with an air-acetylene burner head and background correction.
4. Lead hollow cathode lamp or electrode dischargeless lamp.
5. Regulators, two-stage, for air and acetylene.
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 200 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 2 mg total dust.

SAMPLE PREPARATION:

NOTE 1: The following sample preparation gave quantitative recovery (see EVALUATION OF METHOD) [4]. Steps 4 through 9 of Method 7300 or other quantitative ashing techniques may be substituted, especially if several metals are to be determined on a single filter.

NOTE 2: The Appendix gives a microwave digestion procedure which may be necessary for complete recovery of lead from some matrices, especially epoxy-based paint.

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.
   NOTE: If PbO_2 is not present in the sample, the 30% H_2O_2 need not be added [2,4].
5. Heat on 140 °C hotplate until volume is reduced to about 0.5 mL.
6. Repeat two more times using 2 mL conc. HNO_3 and 1 mL 30% H_2O_2 each time.
7. Heat on 140 °C hotplate until ca. 0.5 mL liquid remains.
8. When sample is dry, rinse the watchglass and walls of the beaker with 3 to 5 mL 10% HNO_3. Allow the solution to evaporate to dryness.
9. Cool each beaker and dissolve the residues in 1 mL conc. HNO_3.
10. Transfer the solution quantitatively to a 10-mL volumetric flask and dilute to volume with distilled water.

NOTE: If the concentration (M) of any of the following is expected to exceed the lead concentration (M) by 10-fold or more, add 1 mL 1 M Na_2EDTA to each flask before dilution to volume: CO_3^{2-}, PO_4^{3-}, I^-, F^-, CH_3COO^-. If Ca^{2+} or SO_4^{2-} are present in 10-fold or greater excess, make all standards and samples 1% (w/w) in La^{3+}[3].

CALIBRATION AND QUALITY CONTROL:

11. Prepare a series of working standards covering the range 0.25 to 20 µg/mL Pb (2.5 to 200 µg Pb per sample).
    a. Add aliquots of calibration stock solution to 100-mL volumetric flasks. Dilute to volume with 10% 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 14 and 15).
    c. Prepare a calibration graph of absorbance vs. solution concentration (µg/mL).
12. Aspirate a standard for every 10 samples to check for instrument drift.
13. Check recoveries with at least one spiked media blank per 10 samples. Use method of standard additions occasionally to check for interferences.

MEASUREMENT:

14. Set spectrophotometer as specified by the manufacturer and to conditions on page 7082-1.
    NOTE: An alternate wavelength is 217.0 nm [8]. 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.
15. Aspirate standards, samples, and blanks. Record absorbance readings.
    NOTE: If the absorbance values for the samples are above the linear range of the standards, dilute with 10% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

16. 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.
17. 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):

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

NOTE: µg/mL = mg/m

EVALUATION OF METHOD:

Method S341 [9] was issued on October 24, 1975, and validated over the range 0.13 to 0.4 mg/m^3 for a 180-L air sample, using generated atmospheres of lead nitrate [1]. Recovery in the range 18 to 72 µg Pb per sample was 98%, and collection efficiency of 0.8-µm mixed cellulose ester filters (Millipore Type AA) was 100% for the aerosols. Subsequent studies on analytical recovery of 200 µg Pb per sample gave the following results [2,4]:

Species	Digestion Method	Analytical Recovery, %
Pb metal	HNO_3 only	92 ± 4
Pb metal	$HNO_3 + H_2O_2$	103 ± 3
PbO	HNO_3 only	93 ± 4
PbS	HNO_3 only	93 ± 5
PbO_2	HNO_3 only	82 ± 3
PbO_2	$HNO_3 + H_2O_2$	100 ± 1
Pb in paint*	HNO_3 only	95 ± 6
Pb in paint*	$HNO_3 + H_2O_2$	95 ± 6

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

Additional collection efficiency studies were also done using Gelman GN-4 filters for the collection of Pb fume, which had geometric mean diameter of 0.1 µm [2]. Mean collection efficiency for 24 sampling runs at flow rates between 0.15 and 4.0 L/min was > 97 ± 2%. Overall precision, $\hat{S}_{rT}$, was 0.072 for lead nitrate aerosol [1,9] and 0.068 for Pb fume [2,4].

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).

[2] Heavy Metal Aerosols: Collection and Dissolution Efficiencies, Final Report of NIOSH Contract 210-79-0058, W. F. Gutknecht, M. H. Ranade, P. M. Grohse, A. Damle, and D. O'Neal, Research Triangle Institute; available as Order No. PB 83-106740 from NTIS, Springfield, VA 22161 (1981).

[3] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 173, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1979).

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[5] NIOSH Manual of Analytical Methods, 2nd. ed., V. 1, P&CAM 102, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A (1977).

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[10] DataChem Laboratories in-house procedure for microwave sample digestion.

[11] Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd Ed; U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, SW-846 (1986).

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METHOD REVISED BY:

Mark Millson, NIOSH/DPSE and R. DeLon Hull, Ph.D., NIOSH/DBBS; S341 originally validated under NIOSH Contract CDC-94-74-45; additional studies under NIOSH Contract 210-79-0058.

James B. Perkins, David L. Wheeler, and Keith Nicholson, Ph.D., DataChem Laboratories, Salt Lake City, UT, prepared the microwave digestion procedure in the Appendix.

APPENDIX - MICROWAVE DIGESTION FOR LEAD IN PAINT CHIPS (AND OTHER MATRICES)

This procedure is an alternative to the procedure presented in the Sample Preparation section of this method. It provides a rapid, complete acid digestion prior to analysis by flame atomic absorption (FAA), heated graphite furnace atomic absorption (HGFAA), and inductively coupled plasma spectroscopy (ICP) [10].

Apparatus and Material [11-16]

1. Microwave apparatus requirements
   a. The microwave unit provides programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.
   b. The microwave unit cavity is corrosion resistant as well as ventilated. All electronics are protected against corrosion for safe operation.
   c. The system requires Teflon PFA digestion vessels (120-mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).
   d. A rotating turntable is employed to ensure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.
   e. A safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained [12].
   f. Polymeric volumetric ware in plastic (Teflon or polyethylene), 50- or 100-mL capacity.
   g. Disposable polypropylene filter funnel.
   h. Analytical balance, 300-g capacity, and minimum ± 0.001 g.

Reagents

1. Nitric acid, concentrated, spectroscopy grade.
2. Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water that meets the ASTM Type 2 standard.

Procedure

1. Calibration of Microwave Equipment
   Calibrate microwave equipment in accordance with manufacturer's instructions. If calibration instructions are not available, see EPA Method 3051 [11].
2. All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. All digestion vessels should be cleaned by leaching with hot (1:1) nitric acid for a minimum of fifteen minutes, rinsed with reagent water, and dried in a clean environment.
3. Sample Digestion
   a. Tare the Teflon PFA digestion vessel.
   b. Weigh out 0.1 g paint chip sample to the nearest 0.001 g into the tared Teflon PFA sample vessel. With large paint chip samples, measure out a 2 cm^2 piece, weigh to the nearest 0.001 g, and quantitatively transfer it to the vessel.
   c. Add 5.0 ± 0.1 mL concentrated nitric acid to the sample vessel in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lb (16 N-m) according to the manufacturer's directions. The sample vessel may be connected to an overflow vessel using Teflon PFA connecting tubes. Place the vessels in the microwave carrousel. Connect the overflow vessels to the center well of the unit.
   d. Place the vessels evenly distributed in the turntable of the microwave unit using groups of two, six,

or 12 sample vessels. Any vessels containing 5 mL of nitric acid for reagent blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, i.e., three samples plus one blank, the remaining vessels should be filled with 5 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity [14]. Irradiate each group of samples to achieve a temperature of 180 °C in five minutes at a pressure of 50 psi. Continue to irradiate to achieve a temperature of 180 °C at 100 psi after 25 minutes. Continue digestion for five minutes. A sample digestion program for 12 samples is presented in the following table.

PROGRAM VARIABLES FOR PAINT CHIPS SAMPLE DIGESTION WITH NITRIC ACID

Stage	(1)	(2)	(3)
Power	90%	90%	0%
Pressure, psi	50	100	0
Run Time, min	10:00	20:00	05:00
Time @ P, min	05:00	15:00	00:00
Temperature	180°C	180°C	0°C
Fan Speed	100%	100%	100%

Number of Vessels:	12
Liquid Volume per Vessel:	5 mL
Sample Weight:	0.1 g

If the analyst wishes to digest other than two, six, or 12 samples at a time, use different values of power as long as they result in the same time and temperature conditions.

e. At the end of the microwave program, allow the vessels to cool for a minimum of five minutes before removing them from the microwave unit. If a loss of sample is detected (e.g., material in overflow collection vessel, liquid outside liner), determine the reason for the loss (e.g., loss of vessel seal integrity, use of a digestion time longer than 30 minutes, too large a sample, or improper heating conditions). Once the source of the loss has been corrected, prepare a new sample beginning at Section 2. If insufficient material is available for reanalysis, dilute remaining digestate and note that some sample loss may have occurred.

f. Uncap and vent each vessel in a fume hood. Add 20 mL reagent water, then reseal vessels and shake to mix thoroughly. Transfer the sample to an acid-cleaned polyethylene bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, allow the sample to settle or filter it:

Settling: Allow the sample to stand until the supernatant is clear (usually, overnight is sufficient). If it does not clear, filter the sample.

Filtering: The filtering apparatus must be thoroughly precleaned and rinsed with dilute nitric acid. Filter the sample through quantitative filter paper into a second acid-cleaned container.

The digestate is now ready for analysis for elements of interest using the appropriate method.

4. Calculations: Report the concentrations based on the actual weight of the original sample.