LEAD BY PORTABLE ULTRASONIC EXTRACTION/ASV

7701

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

METHOD: 7701, Issue 3 **EVALUATION:** FULL **Issue 1:** 15 January 1998 **Issue 3:** 17 February 2016

OSHA: 0.05 mg/m³
NIOSH: 0.05 mg/m³

PROPERTIES: soft gray metal; d 11.3 g/cm³ @ 20 °C; MP 327.5 °C, BP 1749 °C; valences 2+, 4+ in salts

SYNONYMS: elemental lead, lead compounds (except alkyl lead)

SAMPLING

SAMPLER: FILTER (37-mm, 0.8-µm pore, mixed cellulose ester membrane)

FLOW RATE: 1 to 4 L/min

VOL-MIN: 20 L @ 0.05 mg/m³
-MAX: 1500 L

SHIPMENT: Routine

SAMPLE STABILITY: Stable

BLANKS: Minimum of 2 field blanks per set

ACCURACY

RANGE STUDIED: 0.025 to 0.150 mg/m³ (as Pb) (based on Pb mass loadings) [4]

BIAS: None identified in laboratory studies [3-5] <10% in field study [6]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.087 (screen-printed electrodes); 0.094 (Hg film on glassy carbon electrodes) [4]

ACCURACY: ± 17.2%
± 19.3%

MEASUREMENT

TECHNIQUE: PORTABLE ANODIC STRIPPING VOLTAMMETRY

ANALYTE: Lead

EXTRACTION: 10% HNO_3 10 mL; ultrasonication

ANALYSIS ALIQUOT VOL: 0.1 to 5 mL

DEPOSITION POTENTIAL: -0.8 V to -1.0 V vs. Ag/AgCl

ANODIC SWEEP: Deposition potential to 0.0 V vs. Ag/AgCl sweep rate variable [1,2]

REFERENCE ELECTRODE: Ag/AgCl or calomel

WORKING ELECTRODE: Mercury film on glassy carbon or screen printed

SUPPORTING ELECTROLYTE: Mixture of NaCl/NaOH or KCl/KOH, L-ascorbic acid

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

RANGE: 0.31 to >1000 µg Pb per sample [3,4]

ESTIMATED LOD: 0.05 µg/sample [1]

PRECISION ($\bar{S}_r$): 0.068 @ 60 µg (as Pb) per sample [3]

APPLICABILITY: The working range is (at least) 0.20 to 5.00 mg/m³ (as Pb) for a 120-L air sample. Lead determination by ultrasonic extraction/ASV method is applicable to the on-site, field-based determination of lead in air filter samples, and also may be used for laboratory-based air filter sample preparation and analysis.

INTERFERENCES: Thallium is a known interference, but its presence is unlikely in the vast majority of samples. Extremely high concentrations of copper may cause a positive bias. Surfactants can poison electrode surfaces, so if the presence of surfactants is suspected they must be eliminated during sample preparation [7,8].

OTHER METHODS: Laboratory-based methods include atomic spectrometric methods following concentrated acid hotplate digestion: NIOSH methods 7082 (flame AAS), 7105 (graphite furnace AAS), and 7300-series methods (ICP-AES) [9]. ASTM standards based on NIOSH methods for sample collection, preparation and analysis have been published [10].

REAGENTS:

1. Nitric acid,* 10% (v/v) (Prepared from concentrated nitric acid, reagent grade; spectroscopic grade if trace analysis).
2. Distilled or deionized water (ASTM Type I or better [11]).
3. Calibration stock solution, 1000 µg/mL Pb. Commercial standard, or dissolve 1.00 g Pb metal in minimum of 10 mL of 50% HCl and dilute to 1 L with 1% (v/v) HCl. Store in a polyethylene bottle. Stable for at least one year.
4. Supporting electrolyte: Aqueous inert salt mixture such as 2.5 M NaCl and 0.25 M NaOH * (reagent grade or equivalent) [3,4].
5. Dissolved oxygen scavenger such as 0.25 M L-ascorbic acid (tissue culture grade or equivalent) [3,4].
6. Mercuric nitrate (reagent grade), if required (for Hg film electrodes).
7. Certified Reference Materials (CRMs) for lead.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Mixed cellulose ester filter, 0.8 µm pore size, 37-mm diameter, in cassette filter holder or cellulosic internal capsule.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Field-portable anodic stripping voltammeter.
4. Disposable or renewable voltammetry electrodes.
5. Ultrasonic bath, 50 watts minimum power.
6. Power source for ultrasonic bath.
7. Plastic centrifuge tubes, 50-mL, with screw caps.
8. Test tube rack (size to fit in ultrasonic bath).
9. Plastic sample cell container.
10. Mechanical pipets (class A equivalent), 0.1-mL to 10-mL, as needed.
11. Pipet tips for mechanical pipets.
12. Forceps.
13. Bottles, polyethylene, 100- to 1000-mL.
14. Volumetric flasks, 100-mL (for preparatory lab work).
15. Plastic rods.
16. Wipes (ASTM E1792 [12])
    NOTE: Clean all glassware and reusable plasticware with diluted nitric acid and rinse thoroughly with distilled or deionized water before use.

SPECIAL PRECAUTIONS: Nitric acid and sodium hydroxide are irritants and may burn skin. Perform extractions in a well-ventilated area. Wear gloves and eye protection.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in the 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 20 to 1500 L for TWA measurements. Do not exceed a filter loading of ca. 5 mg total dust.
   NOTE: Filter overloading can be assessed by periodic visual checks. See NMAM guidance chapters for additional discussion on filter capacity.

SAMPLE PREPARATION:

3. Open the cassette filter holders and, with forceps, transfer the samples and blanks to separate 50-mL centrifuge tubes. Use internal cellulosic capsules or wipe the internal cassette surfaces with a 37 mm MCE filter or cellulosic wipe wetted with deionized water and add to the centrifuge tube to transfer non-filter aerosol deposits into the tube. See [13] for additional information. Push the filters to the bottom of the tubes with plastic rods.
   NOTE: An alternative means to include non-filter aerosol deposits is to carry out extraction directly within the cassette.
4. Add 10 mL of 10% HNO_3 and cap the centrifuge tubes.

5. Place centrifuge tubes in ultrasonic bath, and agitate at room temperature for at least 30 min.
   NOTE 1: The water level in the bath should be above the level of liquid within the centrifuge tubes.
   NOTE 2: Proper performance of the ultrasonic bath should be demonstrated before use. This can be accomplished by checking recoveries of lead from performance evaluation materials.
6. Shake tubes for 5 to 10 sec, and allow to settle.

CALIBRATION AND QUALITY CONTROL:

7. Prior to field work, prepare a series of working standards covering the range 0.25 to 20 µg/mL Pb.
   a. Add aliquots of calibration stock solution to 100-mL volumetric flasks, and dilute to volume with 10% HNO_3. Store and transport the working standards in polyethylene bottles, and prepare fresh weekly.
   b. Analyze the working standards together with the blanks and samples (steps 11 through 14).
   c. Prepare a calibration graph of instrumental response vs. lead concentration (µg/mL Pb).
      NOTE: Some portable instruments read concentration directly. Calibrate according to manufacturer's directions.
8. Analyze at least one standard for every 20 samples to check for instrument drift (steps 11 through 14).
9. Check recoveries with at least one spiked media blank per 20 samples (one per batch minimum). Use certified reference materials to substantiate recoveries. Use method of standard additions to check for matrix effects or interferences.
10. Check for lead contamination by analyzing at least one reagent and one media blank per 20 samples (minimum of one per batch) (steps 11 through 14).

MEASUREMENT:

11. Set instrument parameters as specified by the manufacturer, or use conditions specified on page 7701-1.
    NOTE: If renewable electrodes are used, clean the glassy carbon electrode and deposit a fresh mercury film prior to conducting analyses.
12. Transfer sample aliquot (1 to 5 mL) to analytical cell, and dilute with 10% HNO_3, if necessary.
    NOTE: High concentrations of lead may require analysis of diluted analyte solutions.
13. Add supporting electrolyte and oxygen scavenger to sample cell. Ensure final volume of the cell is 5 mL (disposable electrodes) or 10 mL (renewable electrodes) by diluting with distilled or deionized water.
14. Measure lead content of the sample aliquot (µg/sample or µg/mL), and record the result.
    NOTE 1: For renewable electrodes, rinse and drain electrochemical sample cell at least three times with distilled or deionized water between sample runs. For disposable electrodes, use a fresh plastic sample cell container for each sample analyzed.
    NOTE 2: If the measured value is above the linear range of the standards, dilute with 10% HNO_3, reanalyze, and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

15. Using measured lead contents, calculate the corresponding concentrations (µg/mL) of lead in the original extracted sample, C_s, and average media blank, C_b, from the calibration graph.
    NOTE: Be sure to account for dilution factors.
16. Using solution volumes (mL) of the samples, 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/L ≅ mg/m^3

EVALUATION OF METHOD:

This method was evaluated with lead aerosol samples generated in the laboratory (40 to 80 µg Pb per filter) [3], and with air particulate samples collected from workplaces where abrasive blasting of leaded paint on highway bridges was being conducted [4]. For the latter, lead loadings cover the range from below the detection limit of 0.09 µg Pb per filter to loadings in excess of 1500 µg Pb per filter [4]. The method also has been evaluated with performance evaluation materials and by interlaboratory testing [3-5]. Lead recoveries from Certified Reference Materials (CRMs) were found to be quantitative (≥90%) and equivalent to recoveries obtained using confirmatory analytical methods (NIOSH 7082, 7105, and 7300 [9]).

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