TETRAETHYL LEAD (as Pb)

$Pb(C_2H_5)_4$ MW: 323.44 CAS: 78-00-2 RTECS: TP4550000

METHOD: 2533, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
Issue 2: 15 August 1994

OSHA : 0.075 mg/m^3 (as Pb; skin)
NIOSH: 0.075 mg/m^3 (as Pb; skin)
ACGIH: 0.1 mg/m^3 (as Pb; skin)

PROPERTIES: liquid; d = 1.653 g/mL @ 20 °C; BP 200 °C (dec.); MP -130 to -138 °C; VP 27 Pa (0.2 mm Hg; 2.2 g/m^3) @ 20 °C

SYNONYMS: TEL; lead tetraethyl

SAMPLING

SAMPLER: SOLID SORBENT TUBE (XAD-2 resin, 100 mg/50 mg)

FLOW RATE: 0.01 to 1.0 L/min

VOL-MIN: 30 L
-MAX: 200 L

SHIPMENT: routine

SAMPLE STABILITY: at least 1 week @ 25 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 0.045 to 0.20 mg/m^3 (as Pb) (120-L samples) [1]

BIAS: 5.6%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.087 [1]

ACCURACY: ± 20.9%

MEASUREMENT

TECHNIQUE: GAS CHROMATOGRAPHY, PHOTOIONIZATION DETECTOR

ANALYTE: tetraethyl lead

DESORPTION: 1 mL pentane; stand 30 min

INJECTION VOLUME: 5 µL

TEMPERATURE-INJECTOR: 185 °C
-MANIFOLD: 200 °C
-PID: 210 °C
-COLUMN: 75 °C

CARRIER GAS: N_2, 20 mL/min

COLUMN: 3 m x 3-mm OD stainless steel packed with 5% Carbowax 20M on 80/100 mesh Chromosorb WHP

CALIBRATION: standard solutions of tetraethyl lead in pentane

RANGE: 2 to 30 µg (as Pb) per sample

ESTIMATED LOD: 0.1 µg (as Pb) per sample [1]

PRECISION ($\hat{S}_r$): 0.067 @ 4.3 to 17 µg (as Pb) per sample

APPLICABILITY: The working range is 0.017 tp 0.23 mg/m^3 (as Pb) for a 120-L air sample.

INTERFERENCES: None identified. The chromatographic column or separation conditions may be changed to circumvent interference problems.

OTHER METHODS: This revises Method S383 [2].

REAGENTS:

1. Pentane (reagent grade).
2. Tetraethyl lead.*
3. XAD-2 resin (Rohm & Haas Co.)(optional, if commercial tubes are used). Extract, in order, for 24 h each in Soxhlet or Giant extractor with: water, methanol, diethylether, and n-pentane. Dry 24 h under vacuum (0.1 to 1 kPa) at low heat.
4. Calibration stock solution, 2 mg/mL (as Pb). Dissolve 31.2 mg tetraethyl lead (ca. 19 µL) in pentane to make 10 mL solution. Prepare in duplicate.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: glass tubes, 10-cm long, 6-mm OD, and 4-mm ID with plastic caps, containing two sections of 20/50 mesh XAD-2 resin (front = 100 mg, back = 50 mg), separated and contained by silylated glass wool plugs. Tubes are commercially available.
2. Personal sampling pump, 0.01 to 1.0 L/min, with flexible connecting tubing.
3. Gas chromatograph, with photoionization detector, integrator, and column.
4. Vials, 2-mL, glass, with PTFE-lined caps.
5. Volumetric flasks, 10-mL.
6. Syringe, 10-µL, readable to 0.1 µL.
7. Pipet, 1 mL, with bulb.

SPECIAL PRECAUTIONS: Tetraethyl lead is extremely poisonous. Acute or chronic poisoning may occur if inhaled or absorbed through skin [3].

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break ends of the sampler immediately before sampling. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.01 and 1 L/min for a total sample size of 30 to 200 L.
4. Cap the samplers. Pack securely for shipment.

SAMPLE PREPARATION:

5. Place the front and back sorbent sections of the sampler tube in separate vials. Discard the glass wool plugs.
6. Add 1.0 mL pentane to each vial. Cap each vial.
   NOTE: A suitable internal standard, such as 0.1% (v/v) dodecane, may be added to samples, blanks, and working standards at this step [2].
7. Allow to stand 30 min with occasional agitation.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to pentane in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain tetraethyl lead (as Pb) concentrations in the range 0.1 to 30 µg/mL.
   b. Analyze with samples and blanks (steps 11 and 12).
   c. Prepare calibration graph [peak area vs. µg tetraethyl lead (as Pb)].

9. Determine desorption efficiency (DE) at least once for each lot of sorbent used for sampling in the range of interest. Prepare three tubes at each of five concentrations plus three media blanks.
   a. Remove and discard back sorbent section of a media blank sampler.
   b. Inject a known amount (2 to 20 µL) of calibration stock solution directly onto front sorbent section with a microliter syringe.
   c. Cap the tube. Allow to stand overnight.
   d. Desorb (steps 5 through 7) and analyze with working standards (steps 11 and 12).
   e. Prepare a graph of DE vs. µg tetraethyl lead (as Pb) recovered.
10. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graph are in control.

MEASUREMENT:

11. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 2533-1. Inject sample aliquot manually using solvent flush technique or with autosampler.
    NOTE 1: Under these conditions, t_r = 4.5 min for tetraethyl lead; dodecane elutes later.
    NOTE 2: If peak area is above the linear range of the working standards, dilute an aliquot of the desorbed liquid with pentane, reanalyze and apply the appropriate dilution factor in calculations.
12. Measure peak area.

CALCULATIONS:

13. Determine the mass, µg (corrected for DE) of tetraethyl lead (as Pb) found in the sample front (W_f) and back (W_b) sorbent sections, and in the average media blank front (B_f) and back (B_b) sorbent sections.
    NOTE: If $W_b > W_f/10$, report breakthrough and possible sample loss.
14. Calculate concentration, C, of tetraethyl lead (as Pb) in the air volume sampled, V (L):

$$C = \frac{(W_f + W_b - B_f - B_b)}{V}, \text{ mg/m}^3.$$

EVALUATION OF METHOD:

Method S383 was issued on March 18, 1977 [2], and validated with generated atmospheres in the range 0.045 to 0.2 mg/m^3 for eighteen 120-L samples [1,4]. Partial breakthrough (effluent = 2.5% of test concentration) occurred after sampling for 240 min at 1.0 L/min from an atmosphere containing 0.156 mg/m^3 tetraethyl lead (as Pb) at 90% RH. Desorption efficiency for eighteen spiked samples in the range 4.3 to 17 µg tetraethyl lead (as Pb) averaged 1.05 with S_r = 0.04.

REFERENCES:

[1] A.D. Little, Inc. Backup Data Report S383 prepared under NIOSH Contract 210-76-0123 (unpublished, 1976), available as "Ten NIOSH Analytical Methods, Set 3," Order No. PB-275-834 from NTIS, Springfield, VA 22161.
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, S383, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 78-175 (1978).
[3] NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards, U.S. Department of Health and Human Services, Publ. (NIOSH) 81-123 (1981), available as Stock #PB83-154609 from NTIS, Springfield, VA 22161.

[4] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

G. David Foley, NIOSH/DPSE.