Table 1 MW: Table 1 CAS: Table 1 RTECS: Table 1

METHOD: 5504, Issue 2 **EVALUATION: FULL** **Issue 1: 15 August 1987**
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OSHA : 0.1 mg/m^3
NIOSH: 0.1 mg/m^3 (skin)
ACGIH: 0.1 mg/m^3 (skin)

PROPERTIES: Table 1

SYNONYMS: Table 1.

SAMPLING

SAMPLER: FILTER + SORBENT (glass fiber + XAD-2, 80 mg/40 mg)

FLOW RATE: 1 to 1.5 L/min

VOL-MIN: 50 L
-MAX: 500 L

SHIPMENT: ship assembled sampler in dry ice

SAMPLE STABILITY: stable 7 days @ 0 °C [1]

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 12 per sample set

ACCURACY

RANGE STUDIED: 0.07 to 0.2 mg/m^3 [1] (300-L samples)

BIAS: see EVALUATION OF METHOD

OVERALL PRECISION ($\hat{S}_{rT}$): 0.07 to 0.10 [1]

ACCURACY: see EVALUATION OF METHOD

MEASUREMENT

TECHNIQUE: HPLC/ATOMIC ABSORPTION, GRAPHITE FURNACE

ANALYTE: tin

DESORPTION: 10 mL 0.1% acetic acid/CH_3CN; ultrasonic, 30 min

SEPARATION: HPLC (cation exchange)

GRAPHITE FURNACE: dry 30 sec @ 80 °C; atomize 5 sec @ 2750 °C (gas interrupt mode)

INJECTION VOLUME: 20 µL

WAVELENGTH: 286.3 nm, with background correction

CALIBRATION: standard solutions of organotin compounds in acetic acid/CH_3CN

RANGE: 5 to 50 µg Sn per sample

ESTIMATED LOD: 1 µg Sn per sample [1]

PRECISION ($\hat{S}_r$): 0.07 to 0.08 [1]

APPLICABILITY: The working range is 0.015 to 1 mg/m^3 (as Sn) for a 300-L air sample. The method was validated using TeBT, TBTC, TCHH, and BuIOMA as surrogates for the most important classes of organotin compounds [1]. If speciation of organot in compounds is not required and if inorganic tin compounds are absent, the HPLC separation may be deleted. Use special car e to avoid losses of TeBT and other volatile tetra-substituted organotin compounds.

INTERFERENCES: Organotin compounds not separated chromatographically will mutually interfere. Other compounds with similar retention times will not interfere unless they contain tin.

OTHER METHODS: This replaces the colorimetric criteria document method [2].

REAGENTS:

1. Zirconium acetate oxide, reagent grade.
2. Ammonium acetate, reagent grade.
3. Diammonium citrate, reagent grade.
4. Acetonitrile, chromatographic grade.
5. Deionized water.
6. Acetic acid, glacial, reagent grade.
7. Methanol, chromatographic grade.
8. Acetic acid, 0.1% (v/v) in acetonitrile.
9. Acetate buffer solution (v/v) 70% methanol, 27% deionized water, 3% aqueous 1 M ammonium acetate.
10. Citrate buffer solution (v/v) 70% methanol, 26.8% deionized water, 3% aqueous 1 M diammonium citrate in 0.2% (v/v) glacial acetic acid.
11. Organotin standard solutions, 1000 µg/mL (as Sn), prepared from pure organotin compounds in 0.1% (v/v) acetic acid in acetonitrile.
12. Calibration stock solution, 10 µg/mL (as Sn). Prepare a standard mixture of the organotin compounds of interest. Pipet 0.1 mL of each organotin standard solution into a 10-mL volumetric flask. Dilute to the mark with 0.1% (v/v) acetic acid in acetonitrile. Prepare fresh daily.

EQUIPMENT:

1. Sampler: glass fiber filter, 37-mm (Gelman Type AE or equivalent) in cassette filter holder followed by XAD-2 sorbent tube, 80 mg front section/40 mg back section separated and retained by silanized glass wool (SKC, Inc., Eighty-Four, PA 15330, Cat. No. 226-30).
2. Personal sampling pump, 1 to 1.5 L/min, with flexible connecting tubing.
3. Shipping container, refrigerated, with dry ice.
4. High performance liquid chromatograph (HPLC), interfaced with autoinjection system (Fig. 1), with binary solvent capability, solvent gradient capability and columns:
   a. non-tetraorganotin species: cation exchange column (Whatman, Inc., Partisil-10 Strong Cation Exchange Column and Solvecon Pre-Column Kit).
   b. tetraorganotin compounds: C_{18} column, (Whatman, Inc., Lichrosorb).
5. Atomic absorption spectrophotometer (AAS) having recorder output proportional to absorbance units, graphite furnace accessory (pyrolytic with Zr coating, coated L'vov platform may be required; see APPENDIX), sample autoinjection system with moving sample tube rack or carrousel (Fig. 1), automatic micropipettor for accurately injecting 20-µL sample aliquots into graphite furnace, background correction (e.g., D_2 or H_2 lamp) capability, and tin electrodeless discharge lamp or hollow cathode lamp.
6. Bath, ultrasonic.
7. Volumetric flasks, 10-mL.
8. Syringe, 20-µL, readable to 0.5 µL.
9. Beakers, Phillips, 125-mL.
10. Pipets, 5- and 10-mL; 10- and 100-µL.
11. Oven or muffle furnace, 200 °C.
12. Plastic film.

SPECIAL PRECAUTIONS: None.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Break the ends of the sorbent tube immediately before sampling and connect to the filter with a short piece of tubing. Attach sampler to personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 1 and 1.5 L/min for a total sample size of 50 to 500 L.
4. Cap the samplers. Pack securely for shipment in dry ice.
   NOTE: The cassette and sorbent tube should remain connected for storage. Store samples at less than 0 °C. Analyze within seven days after collection.

SAMPLE PREPARATION:

5. Open the cassette filter holder. With tweezers, carefully transfer the filter to a 125-mL beaker.
6. Place the front sorbent section and front glass wool plug into a second beaker. Place the back sorbent section and remaining glass wool plugs into a third beaker.
7. Pipet 10.0 mL acetonitrile and 10 µL acetic acid into each beaker. Cover with plastic film.
8. Agitate beakers in ultrasonic bath for 30 min.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards.
   a. Add known amounts of calibration stock solution to 0.1% (v/v) acetic acid in acetonitrile in 10-mL volumetric flasks and dilute to the mark. Use serial dilutions as needed to obtain concentrations of each organotin compound in the range 0.1 to 5 µg/mL (as Sn).
   b. Analyze with samples and blanks (steps 12 through 15), alternating samples and standards with similar responses.
   c. Prepare calibration graphs (peak height vs. µg Sn) for each organotin compound.
10. Determine recovery (R) in the range of interest. Prepare three samplers at each of three levels 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 organotin standard solution directly onto front sorbent section and a separate aliquot onto the filter, with a microliter syringe.
   c. Cap the sampler. Allow to stand overnight.
   d. Desorb (steps 5 through 8) and analyze with working standards (steps 12 through 15).
   e. Prepare a graph of R vs. µg Sn recovered for each organotin compound.
11. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graphs and recovery graphs are in control.

MEASUREMENT:

12. Set the AAS and graphite furnace according to manufacturer's recommendations and to conditions on page 5504-1. Adjust the sample injection/dry/atomize cycle so that it occurs exactly once every 60 sec.
13. Operate the HPLC according to manufacturer's recommendations and the following conditions:
   a. For non-tetraorganotin compounds:
      (1) Column: strong cation exchange (EQUIPMENT, 4.a).
      (2) Flush column with 50 to 60 mL acetate buffer prior to sample injection.
      (3) Eluent: flowrate = 2 mL/min
      (4) Eluent Gradient:

Time (min)	% Acetate Buffer	% Citrate Buffer
0 - 15	100	0
15 - 18	100 - 0	0 - 100
18 - 40	0	100

      (5) After the chromatogram is complete, re-equilibrate the HPLC system to initial conditions by pumping acetate buffer through the column for 15 min.
      (6) Inject 100-µL sample aliquot.
   b. For tetraorganotin compounds:
      (1) Column: C_{18}.
      (2) Flush column with 50 to 60 mL of 100% acetonitrile prior to sample injection.
      (3) Eluent: flowrate = 2 mL/min, isocratic, 100% acetonitrile.
      (4) Inject a 100-µL aliquot of sample solution.

14. Collect HPLC eluent at the rate of 1 fraction (2 mL) per minute in AAS autosampler (Fig. 1).
    NOTE: In this example system, the column effluent is fed directly into one of the sample cups. After 1 min, the sample holder rotates and the eluted sample is in a position to be sampled for AA measurement. The furnace injection device withdraws a portion of the sample and places it in the furnace while the next sample is being eluted and collected.
15. Measure total AAS peak area for each organotin compound.
    NOTE 1: The recorder output will consist of AA peaks which form a chromatographic peak for each organotin compound if a line is drawn connecting the highest points of the AA peaks. Determine total absorbance for a species by the sum of the absorbencies of the corresponding AA peaks.
    NOTE 2: The characteristics of the graphite tube can influence the results drastically. Pay careful attention to the response of the standards and replace the graphite tube if erratic results and non-reproducible peak areas occur.

CALCULATIONS:

16. Read the mass, µg Sn (corrected for R), for each organotin compound found on the filter (W) and front sorbent (W_f) and back sorbent (W_b) sections, and on the average media blanks [filter (B) and front sorbent (B_f) and back sorbent (B_b) sections] from the calibration graphs.
17. Calculate concentration, C (mg/m^3), for each organotin compound as Sn in air as the sum of the particulate concentration and the vapor concentration in the air volume sampled, V (L):

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

NOTE: W_f and W_b will include any analyte originally collected on the filter as particulate, then volatilized during sampling or storage.

EVALUATION OF METHOD:

The method was validated with tetrabutyltin (TeBT), tributyltin chloride (TBTC), tricyclohexyltin hydroxide (TCHH), and dibutyltin bis(isooctylmercaptoacetate) (BuIOMA) [1]. The working ranges, validation ranges, and estimated linear working ranges (as tin) for 300-L air samples of these organotin species at an atmospheric temperature and pressure of 20 °C and 756 mm Hg, respectively, appear below:

Species	Validation Range (mg/m^3)	Estimated Linear Working Range (mg/m^3)	(µg/mL)	($\%\ \hat{S}_r$)	Measurement Precision (%)	Bias ($\%\ \hat{S}_{rT}$)	Overall Precision (± %)	Accuracy
TeBT	0.027-0.112	0.02-0.17	0.05-5.0		8.1	+1.8	10.0	21.4
TBTC	0.042-0.191	0.01-0.34	0.3-10		5.9	-6.7	9.9	26.1
TCHH	0.071-0.218	0.01-0.34	0.3-10		6.9	-2.3	7.1	16.2
BuIOMA	0.070-0.220	0.01-0.34	0.3-10		7.7	-1.2	7.4	15.7

REFERENCES:

[1] Gutknecht, W.F., P.M. Grohse, C.A. Homzak, C. Tronzo, M.H. Ranade, and A. Damle. Development of a Method for the Sampling and Analysis of Organotin Compounds, NIOSH Contract 210-80-0066, Research Triangle Institute, Research Triangle Park, NC 27709, available through NTIS, Springfield, VA 22161, as PB83-180737 (May, 1982).

[2] Criteria for a Recommended Standard...Occupational Exposure to Organotin Compounds, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157 (1976).

METHOD REVISED BY:

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APPENDIX:

PREPARATION OF Zr-COATED GRAPHITE FURNACE TUBE AND PLATFORM

1. Zirconium coating: soak pyrolytic graphite tubes and platforms overnight in 4.5% (w/v) zirconium acetate oxide solution; then dry in a muffle furnace for 2 h at 200 °C.
2. Pyrolytic zirconium-coated graphite furnace tubes are acceptable for measurements of all organotin compounds. However, a pyrolytic zirconium-coated graphite platform (e.g., L'vov platform) is recommended for better precision at low levels and improved atomization response for volatile species such as TeBT. Platforms may be purchased commercially or prepared from pyrolytic graphite tubes, as shown in Fig. 2. Special care must be exercised during placement of the platform in the tube (Fig. 3) and in optical alignment.

Table 1. Formulae and physical properties [3].

Compound RTECS	Formula	M.W.	% Sn	Synonyms
Dibutyltin bis(isooctyl mercaptoacetate) WH6719000	$C_{28}H_{56}O_4S_2Sn$	639.57	18.6	BuIOMA; CAS #25168-24-5
Tetrabutyltin WH8605000	$C_{16}H_{36}Sn$	347.16	34.2	Stannane, tetrabutyl-; TEBT; CAS# 1461-25-2
Tributyltin chloride WH6820000	$C_{12}H_{27}ClSn$	325.49	36.5	Stannane, chlorotributyl-; TBTC; CAS #1461-22-9
Tricyclohexyltin hydroxide WH8750000	$C_{18}H_{34}OSn$	385.16	30.8	Stannane, tricyclohexylhydroxy-; TCHH; Plictran; Dowco-213; CAS #13121-70-5

Figure 1. HPLC/AAS interface system.

Figure 2. Construction of a laboratory-made platform.

Figure 3. Placement of commercial and "laboratory-made" graphite L'vov platforms in furnace tubes.