

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

METHOD: 5526, Issue 2

EVALUATION: FULL

Issue 1: 15 March 2003

Issue 2: 13 January 2016

OSHA: See Table 1

PROPERTIES: See Table 1

NIOSH: See Table 1

SYNONYMS: Methyltin trichloride: monomethyltin trichloride, trichloromethylstannane
 Dimethyltin dichloride: dichlorodimethylstannane, dichlorodimethyltin
 Trimethyltin chloride: chlorotrimethylstannane, chlorotrimethyltin, trimethylstannyl chloride

SAMPLING	MEASUREMENT
<p>SAMPLER: FILTER + SORBENT TUBE (OVS-2 tube: 13 mm glass fiber filter; XAD-2, 270 mg/140 mg)</p> <p>FLOW RATE: 0.25 L/min to 1 L/min</p> <p>VOL-MIN: 15 L -MAX: 75 L</p> <p>SHIPMENT: Ship assembled sampler cold</p> <p>SAMPLE STABILITY: 14 d @ 4 °C</p> <p>FIELD BLANKS: 2 to 10 field blanks per set</p>	<p>TECHNIQUE: GAS CHROMATOGRAPHY, FPD (tin-specific filter)</p> <p>ANALYTE: Sodium tetraethylborate derivatives of the analytes</p> <p>DESORPTION: 2 mL 0.17 mol/L acetic acid in acetonitrile</p> <p>INJECTION: 1 µL</p> <p>TEMPERATURE-INJECTOR: Cool on-column -DETECTOR: 250 °C -COLUMN: 50 °C (3 min), 12 °C/min to 200 °C (1 min)</p> <p>CARRIER GAS: Helium, 6 mL/min</p>
ACCURACY	<p>COLUMN: Capillary, fused silica, 30 m × 0.53 mm ID, 1.5 µm film, (5% phenyl)-methylpolysiloxane; US Pharmacopeia (USP) G27</p> <p>CALIBRATION: Analytes in hexane</p> <p>RANGE: 0.01 µg to 15 µg per sample (as tin) [2]</p> <p>ESTIMATED LOD: 0.01 µg [2]</p> <p>PRECISION (\bar{S}): 0.065 [2]</p>
<p>RANGE STUDIED: Table 2</p> <p>BIAS: Table 2</p> <p>OVERALL PRECISION (\hat{S}_{rr}): Table 2</p> <p>ACCURACY: Table 2</p>	

APPLICABILITY: This method was developed for air monitoring of methyltin chlorides [2].

INTERFERENCES: None were identified.

OTHER METHODS: NIOSH method 5504 is another method for the measurement of organotin compounds using a filter with a sorbent tube for collection and HPLC/AA for analysis [3].

REAGENTS:

1. Acetic acid, 99+%.*
2. Acetonitrile, HPLC grade.*
3. Diethyl ether, 99+%.*
4. Hexane, HPLC grade*.
5. Methyltin trichloride, 97%.
6. Dimethyltin dichloride, 97%.
7. Trimethyltin chloride.
8. Acetic acid, 0.17 mol/L in acetonitrile. Dilute 1.00 mL of glacial acetic acid to 100 mL with acetonitrile.
9. Sodium tetraethylborate.*
NOTE: Purity of sodium tetraethylborate is critical. It should appear as a fine white powder. Clumping or yellowing indicates that the compound must be replaced.
10. Sodium acetate-acetic acid buffer, pH 4.0 ± 0.2 .
11. Derivatizing solution: Prepare a solution containing 10 g/L of sodium tetraethylborate in diethyl ether. Prepare the solution fresh daily, preferably immediately before use.
12. Calibration stock solution: Prepare a stock calibration solution by accurately weighing (to ± 0.1 mg) about 0.1 g each of methyltin trichloride, dimethyltin dichloride, and trimethyltin chloride into a 50 mL volumetric flask. Dilute to volume with 0.17 mol/L acetic acid in acetonitrile. The stock solution contains about 1000 $\mu\text{g/mL}$ (as tin) of each component. Stored in a freezer, this solution remains stable for several weeks.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: OSHA versatile sampler (OVS-2 tube), 13 mm OD inlet, 6 mm OD outlet. Front section contains 270 mg 20/60 mesh XAD-2 sorbent held in place by an 11 mm diameter glass fiber filter and PTFE ring, separated from the back section of 140 mg XAD-2 sorbent by a short plug of polyurethane foam. The back section is held in place with a long plug of polyurethane foam. The tube is available commercially.
2. Personal sampling pump: 0.1 L/min to 1 L/min with flexible and inert connecting tubing.
3. Gas chromatograph equipped with a cool on-column injection port, automated injector, capillary column, flame-photometric detector (FPD) with a tin-specific filter (610 nm), and data collection system (page 5526-1).
4. Balance capable of weighing to ± 0.1 mg.
5. Mechanical shaker.
6. Vials, 10 mL, with PTFE-lined screwcaps.
7. Transfer pipettes or eyedroppers.
8. GC autosampler vials with PTFE-lined caps.
9. Volumetric flasks, 5 mL, 10 mL, and 50 mL.
10. Pipettes capable of accurately delivering 10 μL , 1.0 mL, and 2.0 mL.
11. Refrigerant packs for shipping.

SPECIAL PRECAUTIONS: Concentrated acetic acid is corrosive and an irritant. Sodium tetraethylborate is sensitive to air and moisture. This chemical should be stored and handled under a nitrogen atmosphere. Acetonitrile, diethyl ether, and hexane are all flammable. Wear appropriate protective clothing and work with these compounds in a well-ventilated hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Uncap the sorbent tube immediately before sampling and connect to a personal sampling pump with flexible tubing.
3. Sample at an accurately known flow rate between 0.25 L/min for full shift sampling and 1 L/min for 15 min samples (STEL) for a maximum of 75 L.
4. Cap the samplers. Pack securely for shipment with cold refrigerant packs.
NOTE: After receipt at the laboratory, samples should be stored at 4 °C and analyzed within 14 d of collection.

SAMPLE PREPARATION:

5. Remove the retaining ring from the sorbent tube and discard. Transfer the glass fiber filter and the main resin bed to a 10 mL sample vial.
6. Remove and discard the foam plug that separates the two resin sections in the sorbent tube. Transfer the backup resin bed to a second 10 mL sample vial.
7. Into each vial, add 2 mL of 0.17 mol/L acetic acid in acetonitrile to desorb the methyltin chlorides. Put the vials on a mechanical shaker for 30 min.
8. Into each vial, add 2 mL of pH 4 buffer and 1 mL of derivatizing solution. Place the vials on the mechanical shaker for 15 min.
9. Extract the solution with three 1 mL portions of hexane. Combine the hexane fractions in a 5 mL volumetric flask and dilute to volume with hexane.

CALIBRATION AND QUALITY CONTROL:

10. Calibrate daily with at least six working standards over the range of interest.
 - a. Accurately pipette 10 μL of the calibration stock solution into a vial that contains 5 mL of 0.17 mol/L acetic acid in acetonitrile. Derivatize like a sample following steps 7, 8, and 9.
 - b. Serially dilute this standard derivatized solution with hexane to produce solutions over the range of 0.2 $\mu\text{g}/\text{mL}$ to 0.02 $\mu\text{g}/\text{mL}$ (as tin) of each methyltin chloride.
 - c. Transfer to autosampler vials with PTFE-lined caps.
 - d. Analyze together with samples and blanks (steps 13, 14, and 15).
 - e. Prepare calibration graph (peak areas vs. μg tin for each methyltin chloride).
11. Determine desorption efficiency (DE) at least once for each lot of OVS tubes used for sampling in the calibration range (step 10). Prepare three samplers at each of six levels plus three media blanks.
 - a. Transfer the front sorbent section of the OVS sampler to a 4 mL vial.
 - b. Inject a known volume of calibration stock solution, or serial dilution, directly onto the front sorbent bed of each OVS tube.
 - c. Cap vial and allow spiked sorbent bed to stand overnight.
 - d. Desorb (steps 7, 8, and 9) and analyze together with standards and blanks (steps 13, 14, and 15).
 - e. Prepare a graph of DE vs. μg for each methyltin chloride recovered.
12. Analyze three quality control blind spikes and three analyst spikes to ensure that the calibration graph and DE graphs are in control.

MEASUREMENT:

13. Set gas chromatograph according to manufacturer's recommendations and to conditions given on page 5526-1.
14. Inject a 1 μL sample aliquot manually using solvent flush technique or with an autosampler.
NOTE: If peak area is above the linear range of the working standards, dilute with hexane, reanalyze, and apply the appropriate dilution factor in the calculations.
15. Measure the areas of the peaks of the methyltin chlorides. A sample chromatogram is shown in Figure 1.

CALCULATIONS:

16. Determine the mass, μg (corrected for DE), for each methyltin chloride 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 $W_f > W_b / 10$, report breakthrough and possible sample loss.
17. Calculate concentration, C , of each methyltin chloride in the air volume sampled, V (L):

$$C = \frac{W_f + W_b - B_f - B_b}{V}, \mu\text{g/L or mg/m}^3.$$

EVALUATION OF METHOD:

This method, developed to collect air samples and analyze the methyltin chlorides, was adapted from existing methodology for measuring organotin compounds in air [3,4]. Reference 2 details the validation of this method for sampling and quantifying of trimethyltin chloride, dimethyltin dichloride, and methyltin trichloride in air. The validated method was needed to provide air monitoring capabilities during methyltin chloride and stabilizer production. Table 2 lists the results of the validation experiments, which followed the guidelines established by NIOSH [5]. However, fewer replicates and concentration levels were used than recommended. This method met the NIOSH criteria for accuracy, bias, and sample stability. The recommended sampling conditions are 250 mL/min for 5.5 h maximum for time-weighted average (TWA) sampling and 1000 mL/min for 20 min maximum for short-term exposure limit (STEL) sampling.

REFERENCES:

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- [3] NIOSH [1994]. Organotin compounds (as): Method 5504 (supplement issued 3/15/2003). In: Schlecht PC, O'Connor PF, eds. NIOSH manual of analytical methods. 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113 [www.cdc.gov/niosh/nmam/].
- [4] Shangwei H [1997]. Development of a method for the sampling and analysis of dimethyltin dichloride and trimethyltin chloride. New Orleans, LA: Tulane University, Department of Environmental Sciences, School of Public Health and Tropical Medicine. Unpublished.
- [5] NIOSH [1995]. Guidelines for air sampling and analytical method development and evaluation. By Kennedy ER, Fischbach TJ, Song R, Eller PM, Shulman SA. Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95-117 [www.cdc.gov/niosh/docs/95-117/pdfs/95-117.pdf].

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Table 1. General information [1]

Analyte	Formula	MW	CAS No.	RTECS No.	Properties	OSHA PEL* (mg/m ³)	NIOSH REL* (mg/m ³)
Methyltin trichloride	CH ₃ Cl ₃ Sn	240.08	993-16-8	WH8585500	Colorless crystals; MP 43 °C; BP 171 °C	0.1	0.1
Dimethyltin dichloride	(CH ₃) ₂ Cl ₂ Sn	219.67	753-73-1	WH7245000	Colorless crystals; MP 90 °C (107 °C); BP 185 °C to 190 °C	0.1	0.1
Trimethyltin chloride	(CH ₃) ₃ ClSn	199.26	1066-45-1	WH6850000	Colorless crystals; MP 37.5 °C; BP 154 °C to 156 °C	0.1	0.1

*Measured as the amount of tin for organotin compounds in air.

Table 2. Method evaluation [2]

Compound	Range Studied (µg tin per sample)	Bias (%)	Precision (\hat{S}_{rt}) (%)	Accuracy (%)
Trimethyltin chloride	0.46 to 9.29	0.3	5.2	±11
Dimethyltin dichloride	0.42 to 9.17	-2.5	5.8	±12
Methyltin trichloride	0.07 to 10.48	-5.2	7.6	±16

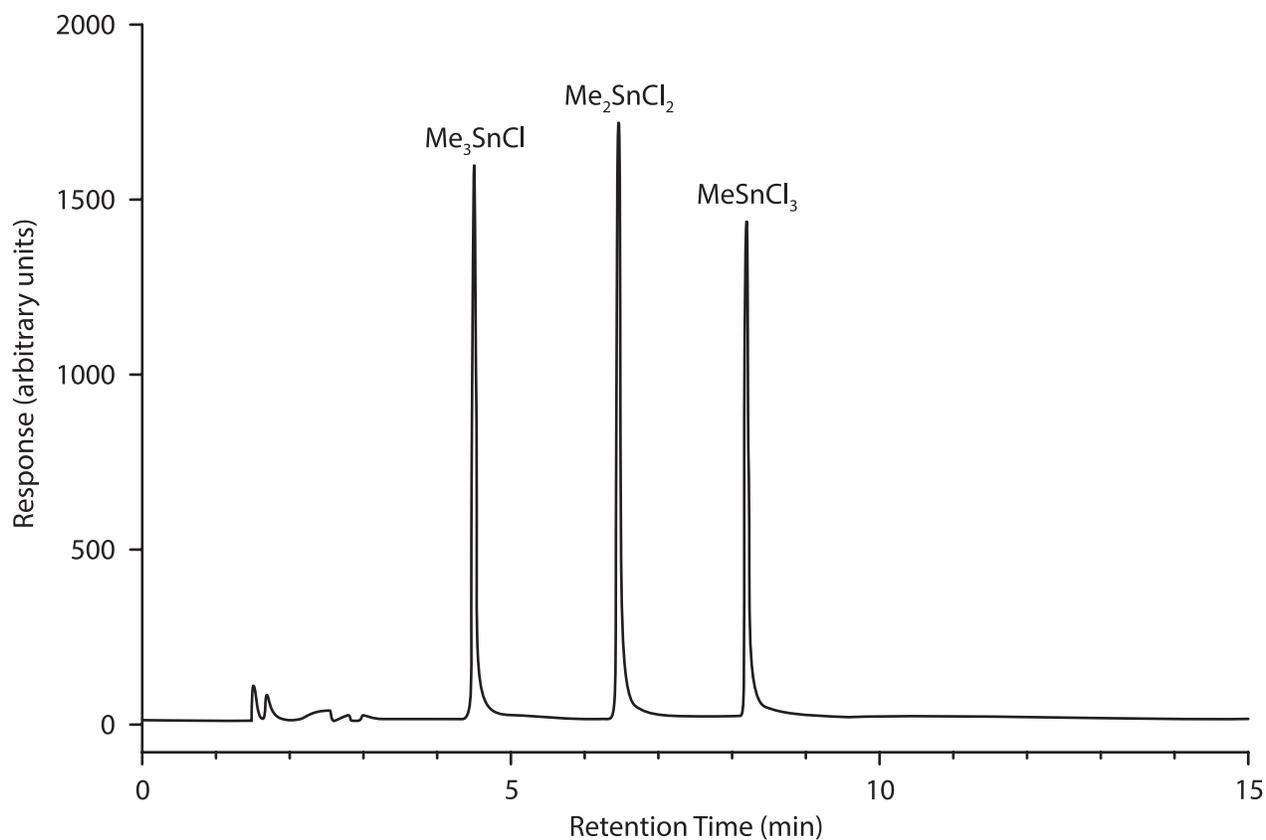


Figure 1. Sample chromatogram.