TRIPHENYL TIN CHLORIDE (as Sn) 5527

$C_{18}H_{15}ClSn$ MW: 385.46 CAS: 639-58-7 RTECS: WH6860000

METHOD: 5527, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 15 March 2003**

OSHA : 0.1 mg / m^3 as Sn
NIOSH: 0.1 mg / m^3 as Sn (skin)
ACGIH: 0.1 mg / m^3 as Sn

PROPERTIES: solid; MP 108 °C; BP 240 °C

SYNONYMS: Chlorotriphenylstannane, Chlorotriphenyltin, Fentin Chloride, Triphenylchlorostannane, Triphenylchlorotin

SAMPLING

SAMPLER: FILTER (37-mm, 5-µm polyvinyl chloride)

FLOW RATE: 1 to 4 L / min

VOL-MIN: 100 L
-MAX: 2000 L

SHIPMENT: Routine

SAMPLE STABILITY: Stable at ambient temperature for 28 days

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: Not studied

BIAS: Not determined

OVERALL PRECISION ($\hat{S}_{r,T}$): Not determined

ACCURACY: Not determined

MEASUREMENT

TECHNIQUE: HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) / INDUCTIVELY COUPLED ARGON PLASMA ATOMIC EMISSION SPECTROSCOPY (ICP-AES)

ANALYTE: Tin

FILTER DESORPTION: 5 mL tropolone/water/methanol (0.02:22:78)

SEPARATION: HPLC, reverse phase; C_{18}, 250 x 4.60-mm, 5-µm, Kingsorb 5 or equivalent

ICP: Operating under conditions for organic compounds.

DETECTOR WAVELENGTH: 189.9 nm

INJECTION VOLUME: 50 µL

CALIBRATION: Standard solutions of triphenyl tin chloride in methanol

RANGE: 10 µg to 225 µg per sample [1]

ESTIMATED LOD: 3 µg per sample (instrumental) [1]

PRECISION ($\bar{S}_r$): 0.034 [1]

APPLICABILITY: The working range of this method is 0.01 to 0.2 mg/m^3 as tin in a 1000 L air sample.

INTERFERENCES: Other organotin compounds with the same retention time as triphenyl tin chloride would interfere.

OTHER METHODS: There are no other NIOSH methods specifically for triphenyl tin chloride. Other organotin compounds have been determined by NIOSH Method 5504 [2] which uses the analytical technique of HPLC-atomic absorption spectroscopy.

REAGENTS:

1. Tropolone (2-Hydroxy-2,4,6-cycloheptatrienone) min. 99% pure.
2. Glacial Acetic Acid, Trace Metal Grade.*
3. Methanol, HPLC Grade.*
4. Triphenyl tin chloride*, 95% pure.
5. Deionized, distilled water.
6. Mobile Phase: 0.020%(w/v)tropolone, 22%(v/v) water, 6.0% (v/v) acetic acid, 72% (v/v) methanol [3].
7. Desorbing solution: 0.020%(w/v)tropolone, 22%(v/v) water, 78% (v/v) methanol.
8. Triphenyl tin chloride standard solution, 200 µg/mL (as tin) with methanol as solvent.
9. Calibration curve solutions: Pipet appropriate amounts of triphenyl tin chloride standard solution into 10-mL volumetric flasks to prepare solutions that are 1, 5, 15, 25, 35, and 45 µg/mL (as tin). Add desorbing solution to the mark.
10. Argon.
11. Oxygen.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: polyvinyl chloride filter with support pads (3-µm, 5-µm obtainable from SKC, Inc., Eighty Four, PA 15330, Cat. No. 225-8-01-1) in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. High performance liquid chromatograph (HPLC) with reverse phase column (Kingsorb 5 C_{18}, 250 x 4.60-mm, 5-micron, or equivalent), guard column (Alltima 10 mm X 4.60-mm C_{18}, 5-micron) and 50-µL sample loop injector.
4. Inductively coupled argon plasma-atomic emission spectrometer equipped for analysis of organic compounds (See APPENDIX).
5. Regulators for argon and for oxygen.
6. Beakers: Griffin, 50-mL. **
7. Volumetric flasks: 10-, 100- and 1000-mL.**
8. Syringe, 100-µL.
9. Ultrasonic bath.
10. Pipets, various sizes for standard preparation.
11. Polystyrene (8-mL) round bottom tubes with caps.
12. Plastic film.
13. Forceps.

** Clean all glassware with conc. nitric acid and rinse thoroughly with distilled water.

SPECIAL PRECAUTIONS: Triphenyl tin chloride is highly toxic and readily absorbed through skin. Avoid breathing dust and wear gloves when working with it and its solutions. Concentrated acetic acid is corrive, and a skin and eye irritant. Methanol is flammable and toxic.

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 a total sample size of 100 to 1000 L.

SAMPLE PREPARATION:

3. Open the cassette filter holders and, with tweezers, transfer the samples and blanks to clean beakers.
4. Add 5 mL of desorbing solution. Cover with plastic film.
5. Agitate beakers in an ultrasonic bath for 5 min.
6. Transfer the solutions to polystyrene tubes. Cap.

CALIBRATION AND QUALITY CONTROL:

7. Calibrate with six working standards in the range of 5 to 225 µg as tin per sample.
   a. Pipet known amounts of triphenyl tin chloride stock solution into 10-mL volumetric flasks. Dilute

with desorbing solution.
   b. Analyze samples and blanks (steps 10 and 11).
   c. Prepare a calibration graph (peak area vs µg Sn).
8. One day before analyzing samples, prepare three spiked media blanks. Desorb (steps 3 through 6) and analyze with standards and blanks.
9. Analyze three quality control blind spikes and three analyst spikes to check calibration graph.

MEASUREMENT:

10. Set ICP for analysis of organic compounds according to manufacturer's specifications.
11. Operate HPLC under the following conditions:
    a. C_{18} column
    b. Flush column with approximately 30 mL of mobile phase before connecting to ICP
    c. Mobile phase flow rate: 1 mL/min
    d. After ICP is ready for analysis, connect effluent from HPLC to ICP spray chamber.
12. Inject standards, samples, and blanks onto HPLC column and record chromatograms.

CALCULATIONS:

13. Analyze chromatograms using a convenient HPLC software program.
14. Construct a calibration graph (peak area versus µg of tin).
15. From calibration graph determine the mass in µg of tin for each sample (W) and for the average media blank (B). Calculate the concentration, C, of tin in the volume of air sampled, V (L):

$$C = \frac{(W - B)}{V}, mg / m^3$$

NOTE: µg/L ≅ mg/m^3

EVALUATION OF METHOD:

This method was developed in response to an increased use of organotin compounds in the workplace and to test the applicability of the hyphenated technique of HPLC-ICP-AES for their analysis. Triphenyl tin chloride, the compound of this method, is a pesticide and an antifouling agent for paints.

ICP instruments are typically set up for the analysis of inorganic metal compounds. When one is used as a detector for organo-metal compounds in the effluent of an HPLC instrument, certain modifications of the operating conditions of the ICP must be considered. Its torch and spray chamber must be suited to the analysis of organic compounds and gas flow rates are different for analysis of solutions containing organic compounds. Such information can be obtained from the manufacturer of a specific ICP instrument. In addition, oxygen gas is introduced into the plasma to prevent the formation of carbon deposits.

This method was evaluated for limit of detection (LOD), linear range, and sample stability [1]. An instrumental LOD of 3 µg as tin per sample was determined. This corresponds to a Limit of Quantitation that is approximately 0.1 x the Permissible Exposure Limit (PEL). Calibration standards showed the method to be linear to an upper limit of approximately 240 µg per sample which is equivalent to 2.4 times the PEL. Samples with higher concentrations were not tested.

The method was further evaluated by a recovery study using spiked lab samples on polyvinyl chloride filters that contained triphenyl tin chloride at four levels in the range of 9.5 to 190 µg as tin per sample. This range is from approximately 0.1 to 2 x the PEL. At each level six filters were analyzed. Recoveries ranged from 97% to 100% with an average RSD of 0.034. Filters were also spiked at 95 µg/sample and stored at room temperature for 7, 14, and 28 days. Recoveries ranged from 96% to103% with an average RSD of 0.032.

REFERENCES:

[1] Hopkins BM [2002] Backup data report for Triphenyl Tin Chloride, August 15, 2002, (unpublished report). NIOSH/DART.
[2] NIOSH [1994]. NIOSH Manual of Analytical Methods, 4th ed., Method 5504, DHHS(NIOSH) Publication 94-113 (August 1994)
[3] Dauchy X, Cottier R, Batel A, Jeannot R, Borsier M, Astruc A, Astruc M [1993]. Mobile phase composition based on speciation of butyltin compounds by high-performance liquid chromatography with inductively coupled plasma mass spectrometry detection. J Chromatogr Sci *31*: 416-421.

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APPENDIX: **Operation of ICP-HPLC Instrument:**
ICP conditions refer specifically to the Spectroflame EOP.

1. Install torch and spray chamber for analysis of organic compounds into ICP instrument.
2. Connect inlet tubing for organic analysis to spray chamber and direct ICP waste into a suitable waste container.
3. Once argon is flowing through instrument adjust gas pressures so that nebulizer pressure is 2.2 bar and auxiliary gas flow rate is 23 SKT.
4. Set valve for switching between pumping aqueous solutions and organic solvents to position for aqueous. Allow water to pump through system while following typical procedures for lighting the torch. Light torch and allow system to warm up for 30 minutes.
5. Start mobile phase pumping through HPLC instrument at a flow rate of 1 ml/min. Check for correct flow rate.
6. After warm-up period, profile the optics on the ICP using an aqueous solution that is 10 ppm Cd^{+2}, 10 ppm Li^{+1}, and 50 ppm Zn^{+2}.
7. Following successful profiling, open the valve on the oxygen tank and then change certain settings on the ICP under INSTRUMENT PARAMETERS (a subset of OPERATIONS) so that the following are applied:

GENERATOR PARAMETERS	
Plasma Power (W)	1500
Pump Step	2
Coolant Step	5
Auxiliary Step	1
Nebulizer Step	1
Heating	0
SPECIAL VALVE	
Flush Step	2

8. Change the position of the valve for switching between pumping aqueous solutions and organic solvents to the position for organic and connect the tubing from the ICP to the end of the HPLC column. Check the valve on the inside of the ICP side panel for leaks.
9. Allow mobile phase to run through ICP for about 10 min before injecting.
10. Plug in sample loop position controller being sure that it is in Position A.
11. In order to obtain a transient scan, select SCAN MANAGER, SCAN, TRANSIENT SCAN on ICP computer. Type in the name of the sample, the measure time (100), the interval time (600), and the number of points (999). Select the Sn line (189.9 nm).
12. Inject a sample of methanol (about 70 µL) into the 50 µL sample loop. Simultaneously push the button on the sample injector and the START button on the computer.
13. After the sample loop controller has moved from Position B back to Position A, remove the syringe.
14. Upon completion of the scan, save the scan on a floppy disc.
15. Inject standards and unknowns in triplicate following procedures 11-14.

16. After the last injection, disconnect HPLC column from ICP instrument, and allow water to run through the ICP for 15 min.
17. Flush HPLC column with a mixture of 70% methanol and 30% water and cap.
18. Close oxygen valve and change Flush Step setting on ICP to 1.
19. Turn off ICP following typical shut-down procedures.