



Tetramethyltin

Method number: PV2057

Target concentration: 0.1 mg/m³ The OSHA PEL for tin (organic compounds)

Procedure: Samples are collected by drawing a known volume of air through a charcoal tube. Samples are desorbed with carbon disulfide and analyzed by gas chromatography with a flame ionization detector (GC-FID).

Air volume and sampling rate studied: 100 minutes at 0.2 Lpm (20 L)

Status of method: Partially Validated method. This method has been only partially evaluated and is presented for information and trial use.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

The OSHA Laboratory received samples collected on charcoal tubes lot 120 requesting analysis for tetramethyltin (TMT). A write-up describing a charcoal tube procedure was submitted with the air samples. There was no information on desorption or retention efficiencies so a further evaluation was undertaken. The most common solvent for desorbing charcoal tubes is carbon disulfide. This solvent was tried and the desorption efficiency was 100%. Retention studies showed breakthrough at 30 liters humid air (91% RH), so a recommended air volume of 20 liters is used in this study.

1.1.2 Potential workplace exposure (Ref 5.1)

Tetramethyltin is used as an intermediate in manufacturing.

1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Ref 5.2)

Tetramethyltin exposure has the following effects at low concentrations: headaches, visual defects, depression, cerebral swelling, reversible paralysis, unconsciousness, and hypoglycemia.

1.1.4 Physical properties (Ref 5.1 and 5.3):

CAS:	594-27-4
IMIS:	2431 (organic tin compounds)
RTECS:	78608 (WH8630000)
Molecular weight:	178.83
Density:	1.297
Freezing point:	- 54 °C
Boiling point:	74 °C
Flash point:	-12 °C (9 °F)
Color:	colorless liquid
Gravimetric factor:	0.6637
Compound:	(CH ₃) ₄ Sn

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 0.05188 µg tetramethyltin (0.03443 ug tin). This is the smallest amount that could be detected under the operating conditions used in this study.

1.2.2 The overall detection limit of Sn is 0.00172 mg/m³ based on a 20-liter air volume. All air concentrations in this study will be based on a 20-liter air volume.

1.3 Advantages

1.3.1 The sampling procedure is convenient.

1.3.2 The analytical method is reproducible and sensitive.

1.3.3 Reanalysis of samples is possible.

1.3.4 It may be possible to analyze other compounds at the same time.

1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

For lower air concentrations, a larger air sample should be taken, with two tubes in series, or with a larger sampling tube.

2 Sampling procedure

2.1 Apparatus

2.1.1 A calibrated personal sampling pump, the flow of which can be determined within $\pm 5\%$ at the recommended flow.

2.1.2 Charcoal tubes, lot 120, containing 100-mg adsorbing section with a 50-mg backup section separated by a 2-mm portion of urethane foam, with a silanized glass wool plug before the adsorbing section and a 3-mm plug of urethane foam at the back of the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 7-cm x 6-mm o.d. and 4-mm i.d., SKC tubes or equivalent.

2.2 Sampling technique

2.2.1 The ends of the charcoal tube are opened immediately before sampling.

2.2.2 Connect the charcoal tube to the sampling pump with flexible tubing.

2.2.3 Tubes should be placed in a vertical position to minimize channeling, with the smaller section towards the pump.

2.2.4 Air being sampled should not pass through any hose or tubing before entering the charcoal tube.

2.2.5 Seal the charcoal tube with plastic caps immediately after sampling. Seal each sample lengthwise with Form OSHA-21 seal.

2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.

2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.

2.2.8 Bulks submitted for analysis must be shipped in a separate container from the samples.

2.3 Desorption efficiency

Six tubes were liquid spiked at each loading of tetramethyltin of 0.3113 μg (0.2066 μg tin or 0.01033 mg/m^3 tin), 1.297 μg (0.8608 μg tin or 0.04304 mg/m^3 tin), 3.113 μg (2.066 μg tin or 0.133 mg/m^3 tin), 6.395 μg (4.304 μg tin or 0.2152 mg/m^3 tin), and 12.97 μg (8.608 μg tin or 0.4304 mg/m^3 tin). They were allowed to equilibrate overnight at room temperature. They were then opened; each section placed into a separate 2-mL vial, desorbed with 1 mL of the desorbing solution for 30 minutes with occasional shaking, and analyzed by GC-FID. The overall average was 100 %. (Table 1)

Table 1
Desorption Efficiency

tube #	% recovered ($\mu\text{g TMT}$)/($\mu\text{g tin}$)				
	0.3113 (0.2066)	1.297 (0.8608)	3.113 (2.066)	6.395 (4.244)	12.97 (8.608)
1	102	99.5	100	101	93.6
2	103	99.0	96.0	102	101
3	104	99.6	96.6	101	101
4	97.0	99.5	102	102	101
5	102	99.5	101	102	101
6	100	100	lost	101	101
average	101	99.5	99.1	102	99.8

overall average = 100%
standard deviation = ± 2.22

2.4 Retention efficiency

Twelve tubes were liquid spiked with 12.97 μg tetramethyltin (0.4304 mg/m^3 tin), allowed to equilibrate overnight, and then had 10, 20, 30, or 40 liters humid air (91% RH) pulled through them. They were opened, desorbed, and analyzed by GC-FID. There was tetramethyltin found on the backup portions of the 30, and 40-liter samples, so a recommended air volume of 20 liters was chosen (Table 2.4). The retention efficiency averaged 99.8%.

Table 2.4
Retention Efficiency

liters drawn	% recovered		
	'A'	'B'	total
10	101	0	101
10	101	0	101
10	101	0	101
20	101	0	101
20	99.2	0	99.2
20	99.5	0	99.5
30	92.9	5.8	98.7
30	91.8	6.0	97.8
30	94.1	4.0	98.1
40	90.9	10.1	101
40	92.6	8.2	101
40	89.3	9.5	98.8

average = 99.8%

2.5 Storage

Charcoal tubes were spiked with 3.113 μg tetramethyltin (2.066 $\mu\text{g tin}$ or 0.1033 mg/m^3) and 12.97- μg tetramethyltin (8.608 $\mu\text{g tin}$ or 0.4304 mg/m^3) and stored at room temperature until opened and analyzed. The recoveries averaged 99.2% for the 12 days stored. (Table 2.5)

Table 2.5
Storage Study

day	% recovered	
	3.113 µg TMT (2.066 µg tin)	12.97 µg TMT (8.608 µg tin)
5	102	99.6
5	102	101
5	102	102
12	99.2	98.8
12	92.9	97.1
12	97.3	96.6
average	99.2	99.2

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 0.3113 µg/mL TMT (0.2066 µg/mL tin), 1.557 µg/mL TMT (1.033 µg/mL tin), 3.113 µg/mL TMT (2.066 µg/mL tin), and 6.226 µg/mL TMT (4.132 µg/mL tin) (Table 2.6).

Table 2.6
Precision Study

injection number	tetramethyltin (µg/mL)/(tin µg/mL)			
	0.3113 (0.2066)	1.557 (1.033)	3.113 (2.066)	6.226 (4.132)
1	781	2539	4770	9192
2	783	2516	4761	9130
3	755	2521	4769	9229
4	764	2545	4768	9141
5	765	2564	4768	9177
6	797	2546	4768	9161
average	744	2539	4756	9172
standard deviation –	±15.5	±17.7	±28.8	±36.1
CV -	0.02083	0.006971	0.006056	0.003936

pooled CV = 0.01155

Where:

$$CV \text{ (Coefficient of Variation)} = \frac{\text{(standard deviation)}}{\text{(average)}}$$

$$\text{Pooled CV} = \sqrt{\frac{A1(CV1)^2 + A2(CV2)^2 + A3(CV3)^2 + A4(CV4)^2}{A1 + A2 + A3 + A4}}$$

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = Coefficient of variation at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied is 20 liters

2.7.2 The sampling rate studied is 0.2 liters per minute.

2.8 Interferences

Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame ionization detector, an HP 5840 was used in this study.

3.1.2 GC column capable of separating the analyte and an internal standard from any interference. The column used in this study was a stainless steel 10-ft, 20% SP2100, 0.1% Carbowax 1500 on 100/120 mesh Supelcoport.

3.1.3 An electronic integrator or some other suitable method of measuring peak areas.

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 A 10-uL syringe or other convenient size for sample injection.

3.1.6 Pipettes for dispensing the desorbing solution. The Glenco 1-mL dispenser was used in this method.

3.1.7 Volumetric flasks, 10-mL, and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

3.2.2 Tetramethyltin, Reagent grade

3.2.3 Carbon disulfide, Reagent grade. In the carbon disulfide used in this study, there was a small amount of benzene as a contaminant, and this benzene was used as an internal standard.

3.3 Sample preparation

3.3.1 Sample tubes were opened and the front and back section of each tube placed in separate 2-mL vials.

- 3.3.2 Each section is desorbed with 1 mL of carbon disulfide.
- 3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

- 3.4.1 Standards are prepared by diluting a known quantity of tetramethyltin with carbon disulfide. An analytical standard of 1 µL TMT/25 mL carbon disulfide is 51.88 µg TMT/mL (34.43 µg tin/mL). A 1 to 10 mL dilution of this standard is 5.188 µg/mL TMT (3.443 µg tin or 0.1722 mg/m³).
- 3.4.2 At least two separate stock standards should be made, and dilutions made from both. A low and a high standard should be run to check the calibration.

3.5 Analysis

3.5.1 Gas chromatograph conditions.

<u>Flow rates</u>	<u>(mL/min)</u>	<u>Temperature</u>	<u>(°C)</u>
Nitrogen:	27	Injector:	150
Hydrogen:	30	Detector:	200
Air:	240	Column:	70
 <u>Injection size:</u>	 2 µL		
 <u>Elution time:</u>	 4.67 min		
 Chromatogram:	 (See Figure 1)		

- 3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

- 3.6.1 Any compound having the general retention time as the analyte or the internal standard used is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted, if necessary, so these interferences will pose no problems.
- 3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

- 3.7.1 To convert mass of tetramethyl tin to mass of tin multiply by the gravimetric factor 0.6637.
- 3.7.2 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\text{mass of analyte, } \mu\text{g} = \frac{(\mu\text{g} / \text{mL})(\text{desorption volume, mL})}{(\text{desorption efficiency, decimal})}$$

$$\text{moles of analyte} = \frac{(\text{mass of analyte, } \mu\text{g})(1\text{ g})}{(\text{molecular weight})(10^6 \mu\text{g})}$$

$$\text{volume of analyte} = (\text{moles of analyte})(\text{molar volume})$$

$$\text{ppm} = \frac{(\text{volume of analyte})(10^6)^*}{(\text{air volume, L})}$$

* All units must cancel.

3.7.3 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 10-liter air sample

$$\text{ppm} = \frac{(\mu\text{g / mL})(DV)(24.46)}{(L)(DE)(MW)}$$

Where:

$\mu\text{g/mL}$ = concentration of analyte in sample

24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg

MW = Molecular weight (g/mole)

DV = Desorption volume, mL

20 L = Air volume, L

DE = Desorption efficiency, decimal

3.7.4 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendations for further study

Collection studies need to be performed. A better detection limit may be obtained by using a capillary column for analysis.

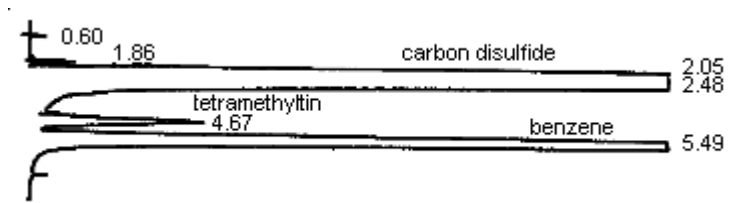


Figure 1. A standard of 12.97 μg tetramethyltin/mL carbon disulfide.

5 References

5.1 Grayson, M., "Kirk Othmer Encyclopedia of Chemical Technology," Third Edition, John Wiley & Son, N.Y., 1981, Vol. 16, p. 574.

- 5.2 Grayson, M., "Kirk Othmer Encyclopedia of Chemical Technology," Third Edition, John Wiley & Son, N.Y., 1981, Vol. 16, p. 578.
- 5.3 Sweet, D., "Registry of Toxic Effects of Chemical Substances," 1985-86 Edition, U.S. Department of Health and Human Services, Public Health Service, Center for Disease Control, NIOSH, 1987, Vol. 2, p. 1205.