Method no.:	ID-197SG
Analyte Code:	2431
Matrix:	Air
OSHA Standard:	0.1 mg/m³ as Sn
Validation Level:	0.05 to 0.1 mg/m³
Collection Procedure:	Samples are collected on glass fiber filters with XAD-2 backup tubes. Include bulk sample if material is available.
Recommended Air Volume:	100 - 250 liters
Recommended Sampling Rate:	1 - 2 liters
Analytical Procedure:	Samples are desorbed with 10% acetic acid in toluene and analyzed using and atomic absorption spectrometer with a L'vov platform.
Detection Limit:	0.005 mg/m³ for a 100 L air volume
Reliable Quantitation Limit:	0.012 mg/m³
Precision:	For six samples at the PEL level, the standard deviation was 0.083 µg and the coefficient of variation was 0.086.
Method Classification:	Partially Validated

1. Introduction

   1.1. Scope

   This method describes the collection and analysis of airborne dibutyltin oxide (DBTO). It is applicable for time-weighted average exposure evaluations. The analysis is based on the technique of L'vov platform graphite furnace atomic absorption.

   1.2. History

   1.3. Uses

   Dibutyltin oxide is used as an intermediate for preparation of other organotins and as a condensation catalyst.

   1.4. Physical and chemical proprieties:

   $(C_4H_9)_2SnO$ White Powder
   Molecular Weight   248.92   Density   1.58 g/mL
   % Sn   47.68 %   M.P.   > 300 °C

2. Range and Detection Limit

   2.1. The lower limit for DBTO is 1-2 µg.

   2.2. This is based on a detection limit of 0.05 µg/mL for graphite furnace analysis of DBTO as Sn in 10% acetic acid in toluene.

3. Precision and Accuracy Data

   Six glass fiber filters were spiked with dibutyltin oxide in 10% acetic acid toluene at two levels: 12 µg and 25 µg, or about 1/2 and one times the PEL, respectively, based on a 250 L air volume and 0.1 mg/m³ PEL. For the six samples at 1/2 times the PEL level, the standard deviation was 0.046 µg and the coefficient of variation was 0.046. For the six samples at the PEL level, the standard deviation was 0.083µg and the coefficient of variation was 0.086. Additional data on recovery studies is found in Addendum I.

4. Interferences

   Other organotins will interfere if they are soluble in 10% acetic acid in toluene.

5. Sampling Procedure

   5.1. The samples are collected on a glass fiber filter with a backup pad and an XAD-2 tube in series at a flow rate of 1-2 L/min, using an MSA Model G sampling pump, or equivalent.

   5.2. The recommended air volume is 100-250 L.

   5.3. The sample cassettes and tubes are plugged, sealed with OSHA Form 21, and then sent to the laboratory for analysis as soon as possible.

6. Analytical Procedure

   6.1. Apparatus

      6.1.1. Sample Collection

      Personal sampling pumps, glass fiber filters with backup pads, and sampling cassettes.

6.1.2. Sample analysis laboratory glassware including volumetric flasks, 125-mL Erlenmeyer flasks, and assorted pipettes. An atomic absorption spectrophotometer with graphite furnace and a Sn electrodeless discharge lamp (EDL). In this study, a L'vov platform was used in the graphite tube.

6.2. Reagents: ACS analyzed reagent grade or better

6.2.1. Acetic acid, Glacial; Baker Analyzed Reagent, or equivalent.

6.2.2. Stock Dibutyltin Oxide, 98%; Aldrich, or equivalent.

6.3. Safety Precautions

6.3.1. Use caution when handling acids, solvents, and organotins. Dibutyltin oxide is a toxic material. Always wear rubber gloves and work in a fume hood. Waste organics should be collected in a suitable, marked container and be properly disposed of as a hazardous waste.

6.3.2. Never pipette by mouth; an assortment of pipetting bulbs is available. Avoid using glassware with chips or sharp edges.

6.3.3. Before using the graphite furnace, the analyst should read the operator's manual and be familiar with the equipment. Ensure that the furnace tube is properly seated and aligned, the contact rings are cleaned, that cooling water is circulating, and the argon cylinder has been turned on. Do not exceed an atomization temperature of 2650 degrees.

6.3.4. Always wear safety glasses and never look at the furnace tube during atomization. Even during normal firing, the intense light may be harmful to the eyes.

6.3.5. Be careful to not damage the equipment. Do not operate an EDL below its recommended wattage. Be certain that the purge air is circulating when using the background corrector. Don't operate any equipment without first reading its instruction manual.

6.4. Glassware Preparation

6.4.1. Volumetric flasks should be rinsed with either acetic acid toluene or 10% nitric acid and deionized water.

6.4.2. Clean the conical beakers with 1:1 nitric acid. Then thoroughly rinse with deionized water, invert, and allow to dry.

6.5. Standard Preparation

6.5.1. Prepare a 1000 µg/mL stock standard of DBTO (as Sn) by weighing 0.20978 g DBTO into a 100 mL volumetric flask and diluting to volume with 10% acetic acid in toluene. DBTO is 47.68% Sn.

6.5.2. Prepare a 100 ppm stock Sn standard by volumetrically pipetting 5 mL of the 1000 ppm stock standard into a 50 mL volumetric flask and diluting to volume with 10% acetic acid in toluene.

6.5.3. Prepare a 10 ppm stock Sn standard by volumetrically pipetting 5 mL of the 100 ppm stock standard into a 50 mL volumetric flask and diluting to volume with solvent.

6.5.4. Working standards are prepared from the 10 ppm Sn stock standard as follows:

Prepared Std	Std Soln Used	Aloquot	Dil Vol
1.0 ppm	10.0 ppm	5 mL	50 mL
0.5 ppm	1.0 ppm	25 mL	50 mL
0.2 ppm	1.0 ppm	10 mL	50 mL
0.1 ppm	1.0 ppm	5 mL	50 mL
0.05 ppm	0.5 ppm	5 mL	50 mL
0.02 ppm	0.2 ppm	5 mL	50 mL
0.01 ppm	0.1 ppm	5 mL	50 mL

6.6. Sample Preparation

6.6.1. Transfer the glass fiber filter to a clean 125-mL conical beaker. Add 10 mL 10% acetic acid toluene to each beaker and swirl for 5 minutes.

6.6.2. Repeat step 6.6.1 with a second 10 mL aliquot.

6.6.3. In a 25 mL volumetric flask, dilute to volume with 10% acetic acid in toluene and invert several times to ensure thorough mixing.

6.6.4. Transfer the A and B portions of the XAD-2 tubes to two separate 125-mL conical beakers, add 10 mL 10% acetic acid in toluene to each beaker and swirl or sonicate for 5 minutes. Dilute to volume in a 25 mL volumetric flask with 10% acetic acid in toluene and invert several times to ensure complete mixing.

6.6.5. If subsequent dilutions are necessary, make them in the 10% acetic acid toluene. Include aliquots for reagent blank and filter blank.

6.7. Analysis

6.7.1. This analysis is done by graphite furnace atomic absorption with a L'vov platform. It is very important that a pyrocoated tube is used. The instrument parameters for determining this organotin are as follows:

Sn Wavelength:	286.3 nm
Injection Volumes(s):	10 µL for the sample
	5 µL for the matrix modifier
Slit Width:	0.7 Low

Graphite furnace:

Step	Dry	Char	Atomize	Burnout	Cooldown
Temp	110	800	2500	2650	20
Ramp	40	30	0	1	1
Hold	10	10	8	5	10
Int. Flow	300	300	0	300	300

6.7.2. The entire series of standards is run at the beginning and end of the analysis; a standard is also run after every fifth or sixth sample during the analysis.

6.8. Calculations

    6.8.1. Blank corrected peak area and the standard concentrations are used for the calculations.

    6.8.2. Results are reported as mg/m³ Sn based on the total micrograms of DBTO (as Sn) and the air volume in liters.

7. References

7.1. Condensed Chemical Dictionary, G.G. Hawley, 10th Edition, 1981.

7.2. "Determination of Butyl Organotin Compounds in Air Samples by AAS-Graphite Furnace," Standard Test Methods, Method Number AA-62 M&T Chemicals, Inc. June 6, 1984.

ADDENDUM I

A recovery study of DBTO from glass fiber filters by desorption in 10% acetic acid toluene was done.

An amount of DBTO equal to 0.20978 g. was weighed into a 100 mL volumetric flask, dissolved and diluted with 10% acetic acid in toluene, and mixed. Assuming that the DBTO is 48.68% Sn, this is 1000 ppm Sn.

Six glass fiber filters were spiked at each of two levels: 10 µg and 25 µg, which correspond to 1/2 and one times the FEL, respectively, based on a 250 liter air volume and 0.1 mg/mL PEL. The spikes were made as follows:

Std used (ppm Sn)	Spike Vol (µL)	Sn (µg)	PEL (multiple)
100	100	10	1/2
1000	25	25	1

The spiked filters were placed in cassettes and attached to personal sampling pumps which had been calibrated to 2 Lpm. Air was drawn through the filters and cassettes for 50-75 minutes, after which the filters were removed, placed in 125 mL Philips beakers and desorbed with 10 mL of 10% acetic acid toluene. The solvent was decanted into 25 mL volumetric flasks and desorbed with a second aliquot of solvent, then diluted to volume. The samples were then analyzed on the graphite furnace as described in Section 6.7. Statistical data were calculated on the results as follows:

	½ PEL (10 µg)	1 PEL (25 µg)
(1)	9.4362	21.3523
(2)	9.9335	25.4787
(3)	10.3416	26.5187
(4)	10.3854	22.5149
(5)	9.8639	22.7419
(6)	9.2725	25.4787
mean =	0.987	0.961
SD =	0.046	0.083
CV =	0.046	0.086

ADDENDUM II

DETECTION LIMIT STUDIES

Qualitative Detection Limit
Rank Sum Method

Rank	0.01 ppm Sample	Corr. Peak Area	0.02 ppm Sample	Corr. Peak Area	0.05 ppm Sample	Corr. Peak Area
1	RBL	-0.012	RBL	-0.012	RBL	-0.012
2	RBL	0.000	RBL	0.000	RBL	0.000
3	RBL	0.001	RBL	0.001	RBL	0.001
4	RBL	0.002	RBL	0.002	RBL	0.002
5	0.01 ppm	0.003	RBL	0.007	RBL	0.007
6	0.01 ppm	0.005	RBL	0.008	RBL	0.008
7	RBL	0.007	0.02 ppm	0.017	0.05 ppm	0.046
8	RBL	0.008	0.02 ppm	0.018	0.05 ppm	0.050
9	0.01 ppm	0.008	0.02 ppm	0.019	0.05 ppm	0.050
10	0.01 ppm	0.009	0.02 ppm	0.020	0.05 ppm	0.051
11	0.01 ppm	0.009	0.02 ppm	0.023	0.05 ppm	0.051
12	0.01 ppm	0.011	0.02 ppm	0.029	0.05 ppm	0.052

	0.01 ppm	0.02 ppm	0.05 ppm
	$S_1 = 25$	$S_1 = 21$	$S_1 = 21$
	$S_2 = 53$	$S_2 = 57$	$S_2 = 57$
	$n_1 = n_2 = 6$	$n_1 = n_2 = 6$	$n_1 = n_2 = 6$
	$T_1 = S_1 - n(n_1+1)/2$	$T_1 = 0$	$T_1 = 0$
	$= 4$		
	$T_2 = 32$	$T_2 = 36$	$T_2 = 29$
	Reject Null Hypoth	Reject Null Hypoth	Reject Null Hypoth

Quantitative Detection Limit
IUPAC Method

Sample Number	0.01 µg/m LPA	0.02 µg/m LPA	0.05 µg/m LPA
1	0.008	0.029	0.052
2	0.009	0.018	0.051
3	0.009	0.019	0.051
4	0.011	0.023	0.046
5	0.003	0.017	0.050
6	0.005	0.020	0.050
n =	6	6	6
Mean =	0.0075	0.021	0.050
Std. Dev. =	0.0029	0.0044	0.0021
C.V. =	0.39	0.21	0.042

From the IUPAC Method: $C_{1d} = k(sd)/m$ for $k = 10$, sd = standard deviation, and m = slope
Then:

$$C_{1d} = \frac{10(0.0044)}{0.998} = 0.04 \; ug/mL$$