Dibutyltin Maleate as Sn

Method no.:	ID-224SG
Target concentration:	Samples are collected by drawing a known volume of air through mixed cellulose ester filters. Samples are digested and analyzed by atomic absorption/graphite furnace.
Recommended sampling time and sampling rate:	1-2 L/min for a total air volume of 200 L
Reliable quantitation limit:	13 µg/m³
Status of method:	Partially evaluated method. This method ahs been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.

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1. Introduction

1.1 Scope

This method describes the collection and analysis of airborne dibutyltin maleate (DBTM). It is applicable for time-weighted average exposure evaluations. The analysis is based on the technique of graphite furnace atomic absorption.

1.2 History

This method is developed as a 'stop-gap' for sample analysis.

1.3 Uses

Stabilizer for polyvinyl chloride resins; condensation catalyst.

1.4 Physical and Chemical Properties

$(C_4H_9)_2Sn(OOCCH)_2$

Mol. wt.	-	346.98	White amorphous powder
% Sn	-	34.20	m.p. - 110 °C
flash pt.	-	204 °C	combustible

2. Range and Detection Limit

2.1 The analytical limit for DBTM is 2.5 µg as Sn. This is based on an analytical detection, limit of 0.05 µg/mL for graphite furnace analysis of DBTM as Sn using the standards and- parameters listed within.

3. Precision and Accuracy

Not determined. See recovery study data in Addendum 1.

4. Interferences

If present, other tin compounds would interfere if they are soluble in a concentrated sulfuric acid, hydrogen peroxide, and 10% hydrochloric acid matrix.

5. Sampling Procedure

The sample is collected on a 0.8 micron MCEF filter at a flow rate of 1-2 L/min.

The minimum recommended air volume is 200 L.

The sample cassettes are plugged, sealed with OSHA tape, labeled, and sent to the laboratory for analysis as soon as possible.

6. Analytical Procedure

6.1 Apparatus

6.1.1 Sample collection

Personal sampling pumps
AA sampling cassettes as needed

6.1.2 Sample analysis

Atomic absorption spectrophotometer
HGA graphite furnace
Electrodeless discharge lamp for Sn
Laboratory glassware

6.2 Reagents

All reagents should be ACS analyzed reagent grade or better.

6.2.1 Sulfuric acid

6.2.2 Hydrogen perozide, 30%

6.2.3 Hydrochloric acid

6.2.4 Stock dibutyltin maleate or 1000 µg/mL Sn standard.

6.3 Safety precautions

6.3.1 Use caution when handling concentrated acids and organotins. Dibutyltin Maleate is a toxic compound. Always wear rubber gloves and work under a fume hood. Waste organics should be collected in a suitable marked container and properly disposed of in the organic laboratory.

6.3.2 Avoid using glassware with chips or sharp edges. Never pipette by mouth.

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, the contact rings are clean, and that cooling water is circulating. Do not exceed an atomization temperature of 2750 degrees. Heating or cooling problems could cause the tube to explode on atomization.

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

Be aware of the high current supplied to the furnace through the copper cables; check that the insulating cover is in place over the terminals.

Since toxic substances are vented by the furnaces a fume blood must be in operation over the furnace.

6.3.4 Observe care with respect to harming the equipment. Do not operate an EDL below its recommended wattage. Be certain that the purge air is circulating when using the background corrector. Do not operate any equipment without first reading its instruction manual.

6.4 Glassware Preparation

6.4.1 Clean the laboratory glassware used by refluxing with 1:1 nitric acid. Thoroughly rinse all glassware with D.I. water, invert, and allow to dry.

6.5 Standard Preparation

6.5.1 Using standard stock 1000 µg/mL Sn (Fisher, S.P., or equivalent), prepare a 10 ppm Sn stock solution by making two serial 10-fold dilutions with 10% HCl.

6.5.2 Working standards are prepared from the 10 ppm Sn stock as follows:

Prepared std.	Std. soln. used	Aliquot	Dil. Vol.
2.0 ppm	10.0 ppm	20 mL	100mL
1.0 ppm	10.0 ppm	10 mL	100 mL
0.5 ppm	10.0 ppm	5 mL	100 mL
0.2 ppm	1.0 ppm	20 mL	100 mL
0.1 ppm	1.0 ppm	10 mL	100 mL
0.05 ppm	1.0 ppm	5 mL	100 mL

6.6 Sample Preparation

6.6.1 Prepare several 'carry-through' samples for a recovery check by weighing known amounts of DBTM onto AA filters and ashing them with the samples. A theoretical tin content of 34.2% is expected based on the molecular weight of tin in DBTM.

6.6.2 Transfer the AA filter to a clean 125 mL Phillips beaker. Add 2 mL concentrated sulfuric acid and heat. When solution darkens, add (dropwise) 30% hydrogen peroxide until clear. Cool and dilute to volume (50 mL) with 10% HCl and invert several times to ensure thorough mixing.

6.7 Analysis

The analysis is done by graphite furnace/AA. The instrumental parameters for determining Sn in DBTM are as follows:

Atomic absorption unit:

Sn wavelength	286.4 nm
integ. time	10 sec.
slit width	0.7 low
signal	Pk. Ht.
mode	Abs.
BGC	on

Furnace parameters:

step	temperature	ramp time	hold time	internal flow
dry	120 °C	50 s	40 s	300 mL/min
char	800 °C	50 s	20 s	300 mL/min
atomize	2500 °C	0 s	8 s	100 mL/min

(with HGA 500, program -10 chart and 0 read in atomization step)

Chart = 5 mv scale, 20 mm/min

Injection = 20 μL

6.7.2 Parameters are adjusted so that the 2.0 ppm standard gives a near full-scale deflection on the chart. The entire series of standards is run at the beginning and end of the analysis; a standard is also run after every fourth or fifth sample during the analysis.

6.8 Calculations

6.8.1 The OSHA Auto Colorimetric program is used for the calculations.

6.8.2 Results are reported as mg/m³ Sn.

Addendum I

A recovery study of DBTM on 0.8 micron MCEF filters by ashing with H_2SO_4, H_2S_2 and HCl was done.

0.070, 0.400, and 6.00 mg of DBTM were weighed onto 0.8 micron MCEF filters and placed into 125 mL Phillips flasks.

The following ashing procedure was used:

a. 2 mL concentrated H_2SO_4
b. When solution darkens, add (dropwise) 30% H_20_2 until clear.
c. Cool and dilute to volume (100 mL) with 10% HCl.

Assuming DBTM is 34.2% Sn, the samples are theoretically 23.9, 136.8. and 2052 micrograms Sn respectively. They were then compared to known standards prepared from serial dilutions of a 1000 µg/mL stock solution (Fisher-- Lot 712319).

The recoveries were as follows:

	DBTM weighed	theor. Sn	found Sn	% recovery
Recovery Study 1 -	70	23.90	25.30	1.059
Recovery Study 2 -	400	136.8	135.5	0.990
Recovery Study 3 -	6000	2052	2007	0.978
			average =	1.009

Addendum II

The following is a list of various solvents and/or acids used at varied concentrations with little or no success in ashing DBTM.

Organic:

1. Ethyl Acetate
2. Methyl Ethyl Ketone
3. Methyl Isobutyl Ketone
4. Acetone
5. Ethyl Alcohol
6. Isopropyl Alcohol
7. Ethyl Acetate + 10%

Inorganic

1. Nitric acid
2. Hydrochloric acid
3. Nitric + Hydrochloric Acid (Aqua Regia)
4. Hydrochloric Acid + Hydrogen Peroxide (30%)
5. Ammonium Hydroxide

These solvents, acids, or combinations thereof, would either give little recovery or no recovery at all. Some of these would appear to ash DBTM, but would either fall out of solution when diluted or form an organic "scum" that floated on the surface.