Tributyltin Fluoride

Method no.:	ID-223SG
Target concentration:	0.1 mg/m^3
Procedure:	Samples are collected by drawing a known volume of air through a polystyrene cassette containing a PVC filter. Samples are digested with nitric acid and analyzed by atomic absorption.
Recommended sampling time and sampling rate:	200 min at 1 L/min (200 L) (maximum flow is 2 L/min for 200 L)
Reliable quantitation limit:	0.25 mg/m^3
Status of method:	Partially evaluated method. This method has been subjected to established evaluation procedures of the Methods Development Team and is presented for information and trial use.
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Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Similar products from other sources can be substituted.

1. Introduction

1.1 Scope

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

1.2 Physical and Chemical Properties

$(C_4H_9)_3$ SnF
Mol. wt. - 309.04 Crystal
% Sn - 38.41

2. Range and Detection Limit

2.1 The lower analytical limit for TBTF is 0.1 µg/ml.

2.2 This is based on a detection limit of .02 µg/ml for graphite furnace analysis of Sn as TBTF in 1-propanol.

3. Precision and Accuracy

3.1 Precision	S = 0.019
3.2 Coefficient of Variation	CV = 0.019
3.3 Recovery	Average mean recovery = 0.996

The above are based on recovery data for eighteen FWSB-PVC filters, spiked with TBTF in 1-propanol at 1/2, 1, and 2× the PEL based on a 200 liter air volume and 0.1 mg/m^3 PEL. Six samples were spiked at each level. Refer to addendum for data on recovery study.

4. Interferences

Other organotins would interfere if they are insoluble in 1-propanol.

5. Sampling Procedure

The sample is collected on a FWSB-PVC filter (0.8 µm, 37 nm diameter) at a flow rate of 1-2 L/min.

The 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 1-Propanol

6.2.2 Stock tributyltin fluoride

6.3 Safety precautions

6.3.1 Use caution when handling 1-propanol and organotins. Tributyltin fluoride 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 furnace, a fume hood 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 50 mL volumetric flasks 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 The procedure is to analyze the tin in tributyl tin fluoride. Prepare the standards by diluting stock TBTF in 1-propanol assuming a theoretical tin content of 38.41%.

6.5.2 Prepare a stock solution by weighing 0.26035 g TBTF into a 100 ml volumetric flask, diluting to volume with 1-propanol and mixing well. This is equivalent to 1000 ppm Sn.

From this, a 10 ppm Sn stock solution is made by two serial 10-fold dilutions.

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

Prepared std.	Std. soln. used	Aliquot	Dil. vol.
1.0 ppm	10.0 ppm	5 mL	50 mL
0.4 ppm	10.0 ppm	2 mL	50 mL
0.2 ppm	1.0 ppm	10 mL	50 mL
0.1 ppm	1.0 ppm	5 mL	50 mL
0.04 ppm	1.0 ppm	2 mL	50 mL
0.02 ppm	1.0 ppm	1 mL	50 mL

6.6 Sample Preparation

Transfer the FWSB-PVC filter to a clean 50 mL volumetric flask. Add 40 mL 1-propanol to each flask and sonicate for 5 minutes. Dilute to volume with 1-propanol 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 1-propanol are as follows:

Atomic absorption unit:

Sn wavelength	224.6 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	100°C	50 s	40 s	50 mL/min
char	800°C	50 s	20 s	50 mL/min
atomize	2500°C	0 s	8 s	30 mL/min

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

Chart = 5 mv scale, 20 mm/min

6.7.2 Parameters are adjusted so that the 1.0 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/m^3 Sn.

Addendum I

A recovery study of TBTF from FWSB-PVC filters by desorption in 1-propanol was done.

0.27057 TBTF was weighed into a 100 ml volumetric, diluted to volume with 1- propanol, and mixed. Assuming the TBTF is 38.41% Sn, this is 1039 ppm Sn as TBTF.

Six FWSB-PVC filters were spiked at each level = 1/2, 1, and 2× the PEL based on a 200 liter air volume and 0.1 mg/m^3 PEL. The spikes were made as follows:

Std used (ppm Sn)	Spike Vol. (µl)	Sn (µg)	PEL (multiple)
1039	10	10	1/2 ×
1039	20	20	1 ×
1039	40	40	2 ×

The filters were then desorbed in 1-propanol, diluted to 50 mL, and run on the graphite furnace as described in section 6.7. The mean standard deviation and coefficient of variation for the recovery at each level using the OSHA "Precision and Accuracy Data" program =

PEL (multiple)	Mean Recovery	Std. Dev.	CV_1
1/2 ×	1.016	0.025	0.024
1 ×	1.013	0.012	0.012
2 ×	0.960	0.020	0.021

The mean recoveries were then pooled =

Average mean recovery = 0.996
Standard Deviation = 0.019
Coefficient of variation = 0.019

Addendum II*

A recovery study of the loss of TBTF on FWSB-PVC filters due to volatility was done. A 40 µL spike of 1039 ppm Sn as TBTF was placed on six filters and attached to six personal sampling pumps (calibrated at 2 liters per minute). 200 liters of air (100 minutes) were drawn through each. The filters were then placed into 50 mL volumetric flasks, diluted to volume with 1-propanol, and run on the graphite furnace as described in section 6.7. The recoveries are as follows:

Sample	Found	Theor.	Found/Theor.
2× - 1A	41.32	41.56	0.994
2× - 2A	42.47	41.56	1.022
2× - 3A	41.60	41.56	1.001
2× - 4A	43.66	41.56	1.051
2× - 5A	44.59	41.56	1.073
2× - 6A	42.47	41.56	1.022