Organo Tin Analysis by Capillary Gas Chromatography

Application Note 12530898

Keywords
Bioaccumulation
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The analysis of tributyl tin is important because of the potential adverse health effects of this compound. Until the 1980s tributyl tin was commonly used as an antifouling agent in marine paint and as a pesticide and fungicide. As awareness of its danger as an endocrine disrupter grows, environmental laboratories receive more requests for the analysis of tributyl tin and its breakdown products. As a result, laboratories need the ability to perform this analysis at low cost using common glassware and instrumentation.

This paper discusses the performance of the OI Analytical Model 5380 Pulsed Flame Photometric Detector (PFPD) in the analysis of tributyl tin. The Model 5380 PFPD is highly selective and sensitive, making it an excellent detector for analyzing tributyl tin with increased sensitivity and decreased material use.

* Organo Tin standards are available from Restek Corporation at 1-800-356-1688.

Organo Tin Analysis by Capillary GC

by Frank Dorman
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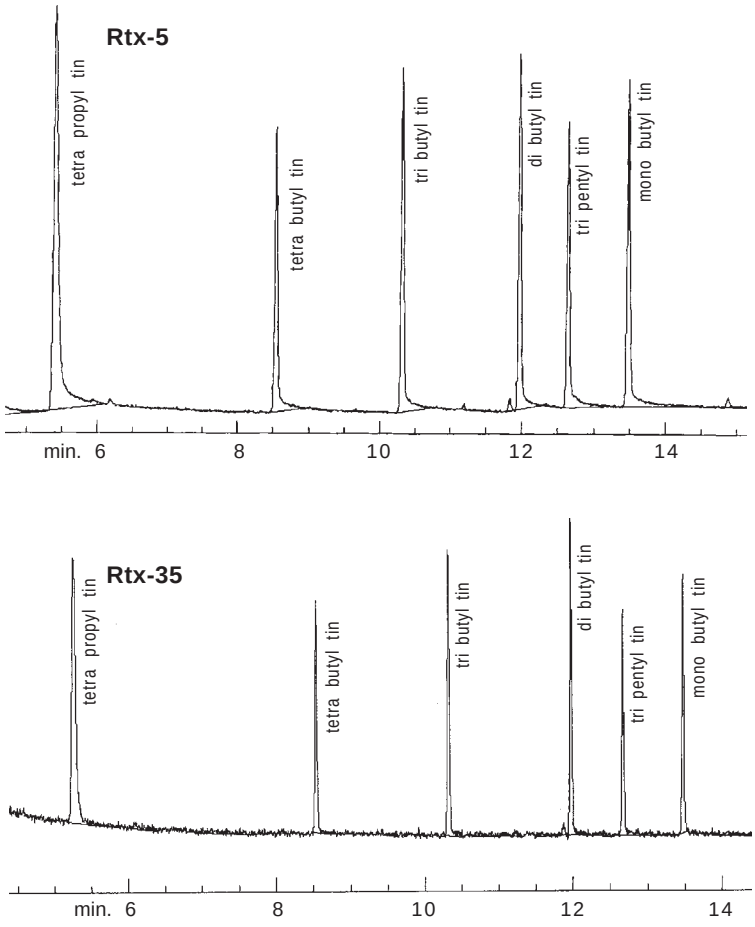
Tributyl tin was commonly used as an antifouling agent in marine paint, as well as a pesticide and fungicide before its use was discontinued in the 1980s. Tributyl tin has since been found to bioaccumulate and cause a number of health-related problems, and has been recently added to the growing list of possible endocrine disrupting compounds.[1] As awareness of endocrine disrupters grows and shipyards are remediated, many environmental laboratories are faced with requests for the analysis of tributyl tin and its breakdown products. Unfortunately, there is no "EPA accepted" method for this, so most laboratories have decided to either pass on these requests or subcontract the analysis to one of the few laboratories that perform this test. Generally, laboratories are under the impression that this analysis requires a considerable capital expenditure and complex techniques that would result in high cost. This does not have to be the case, however, and most laboratories could perform this analysis with the equipment they already have. The purpose of this proposed method is to make this analysis "available" to an environmental laboratory at low cost using common glassware and instrumentation.

Tributyl tin and its breakdown products of dibutyl tin and monobutyl tin present a preparation problem due to the wide range of polarity. These compounds usually exist as chlorides, and it is difficult to completely extract all of them quantitatively from the sample matrix, although there has been some promising data from open-vessel microwave extraction techniques. What is possible, however, is to quantitatively extract the tetra-, tri-, and dibutyl tin, and achieve reasonable and reproducible extraction of the monobutyl tin.

For this method it is very important to remove as much of the potential interferents as possible through a thorough extract cleanup. The primary interference is from sulfur-containing compounds, and these can be at relatively high concentration compared to

Figures 1 & 2: 500 pg Organo Tin Compounds on the Rtx®-5 and Rtx®-35 Columns by GC-FPD.



30m, 0.32mm ID, 1.0µm Rtx-5 and Rtx-35 columns (cat.# 10254 and 10454)
3µl direct injection. **Concentration:** ~500pg on-column. **Head pressure:** 15 psi, constant.
Oven temp: 100°C (hold 1 min.) to 285°C @ 10°C/min. hold 10 min.; **Inj. & det. temp.:** 250°C; **Carrier gas:** He

Figure 3: Commercial Laboratory Results using the Restek's Proposed Method.

Compound	Water Extraction Recovery (%)	Soil Extraction Recovery (%)	Restek SPE-Cleanup Recovery (%)	MDL Liquid (ng/L)	MDL Soil (µg/Kg)
tetrabutyl tin	83	86	92	29.9	0.45
tributyl tin	110	96	99	20.9	0.39
dibutyl tin	75	66	96	15.7	0.46
tripentyl tin (SSTD)	NA	NA	101	NA	NA
monobutyl tin	38	36	118	19.6	0.14

Organo Tin Analysis by Capillary GC, cont.

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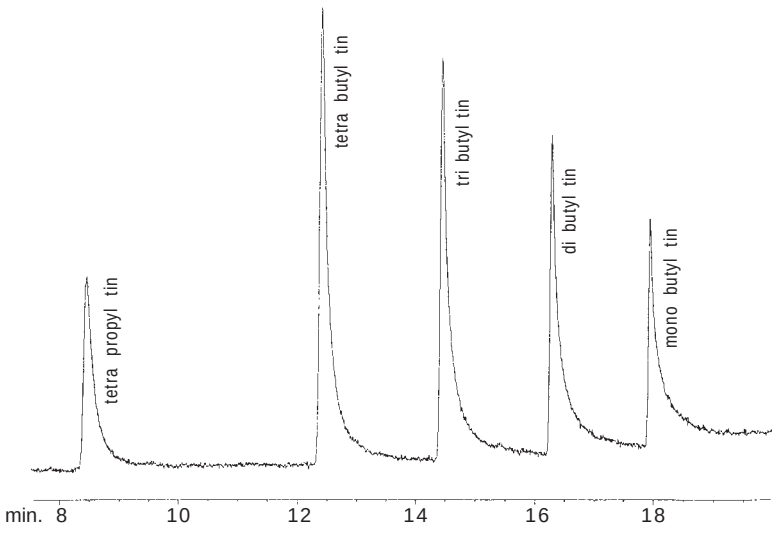
Figure 4: Organo Tin compounds using Pulsed FPD. Detector courtesy of OI Analyical, College Station, TX, Model 5380.



30m, 0.32mm ID, 1.0µm Rtx-35 (cat.# 10454). **Concentration:** 5pg on-column. **Head pressure:** 15 psi, constant. **Oven temp.:** 100°C (hold 1 min.) to 285°C @ 10°C/min. hold 10 min.; **Detector:** PFPD from OI Analytical

the organo tin compounds. The 16 gram Florisil and 5 gram silica gel method[2] has a large capacity and works well for all three sample matrices: water, soil, and biota. The cleanup column can be made in glass prep-scale chromatography columns, or purchased as SPE cartridges from Restek (cat.# 53305). In either case, the extract is applied to a hexane-wetted column and eluted using 100 mL of hexane. The extract is again collected and the internal standard, tetra-*n*-propyl tin, is added before final concentration.

There are many reported methods of analysis in the literature, but since the goal of this method was to be adaptable to an environmental laboratory, gas chromatography (GC) with flame photometric detection (FPD) was chosen. The FPD must be operated under fuel-rich conditions for efficient conversion of the alkyl tin compounds into tin hydrides. The only other necessary modification is to use a 610-nm wavelength filter to collect the molecular emission from the tin hydride. Tin chlorides are analyzed as hexyl derivatives, which are formed by a Grignard reaction using *n*-hexyl magnesium bromide. The surrogate tripentyl-tin chloride is added to the sample prior to extraction and tetra-*n*-propyl-tin is the recommended internal standard. The calibration compounds, surrogate and internal standard solutions are available from Restek as custom reference materials.

Figures 1 and 2 show the resulting chromatograms from the mid-point calibration standard on the Rtx-5 and the Rtx-35 columns by GC-FPD. **Figure 3** shows the method performance obtained by a commercial laboratory using this method.[3]

The method presented easily meets the requirements of 50 ng/L. In order to meet a possible proposed detection limit of 1 ng/L, some method modification will be necessary. The easiest modification would be to switch from using a regular FPD to a pulsed FPD (PFPD) detector. This detector gives a sensitivity enhancement of 10 to 100 times over the standard FPD for the organo tin compounds. **Figure 4** shows the chromatogram obtained for 5 pg of each tin compound on the Rtx-35 using PFPD detection. Comparing this chromatogram to **Figure 1 and 2** it is observed that a similar signal to noise ratio is obtained with 100 times less material. This demonstrates roughly an increase of 100 in sensitivity using the PFPD with the same preparation method, resulting in the ability to meet the proposed 1 ng/L detection limit being considered by the EPA.

In summary, this method allows laboratories to perform organo tin analysis with minimal start up and implementation costs. It is reliable, rugged, and utilizes equipment that most laboratories already have. To meet current and proposed detection limits, it is not necessary to use tandem MS or GC-AED, which have high purchase and operating costs, and are typically not found is most laboratories. Finally, Restek can provide the technical training and supplies required to perform this method so that literature and vendor research is not required.

[1] Special Report on Environmental Endocrine Disruption: An Effects Assessment and Analysis, EPA/630/R-96/012, Feb. 1997.
[2] Sampling and Analytical Methods of the National Status and Trends Program, National Benthic Surveillance and Mussel Watch Projects 1984–1992, Vol. IV, NOAA Technical Memorandum, NOS ORCA 71.
[3] ITS - Environmental, 55 South Park Drive, Colchester, VT 05446.

Columns and Accessories

30m, 0.32mm ID, 0.50µm Rtx-5: cat.# 10239, $415
30m, 0.32mm ID, 0.50µm Rtx-35: cat.# 10439, $415
Florisil/silica gel SPE cartridge: cat.# 24049, $120 16-pack

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