Analysis of Organotin Compounds in Biological and Environmental Samples by Gas Chromatography and Pulsed Flame Photometric Detection (GC-PFPD)

Introduction

Organotin compounds have a great many applications which include stabilizers, catalysts, biocides, and pesticides. One of the more significant uses was that of biocides employed as anti-fouling paint on sea-going vessels which has contributed to coastline contamination throughout the world.[1] Although their use as a biocide in anti-fouling paint was completely banned in 2008, residual contamination is still present in water and sediment.[2,3] Organotins are also significant in the plastics industry because they are used in place of heavy metals such as lead and cadmium. They are an important heat stabilizer additive in the manufacture of PVC.[4] Organotins have been found to bio accumulate and cause a number of health related problems including being a possible endocrine disrupting compound.[5] Many laboratories are faced with requests for organotin analysis as public awareness of the toxicity of these compounds grows. Presently their use is strongly regulated because of the high degree of toxicity. At this time, there is no EPA accepted method for this analysis and many labs pass up work or subcontract the analysis to one of the few labs that analyze for organotin because they are under the impression that it would be a significant capital expense and take a great deal of expertise to successfully run the analysis.[5]

The purpose of this paper is to present a sensitive, selective method which may easily be incorporated into laboratories day-to-day analyses. The PFPD offers ppb sensitivity along with great selectivity for tin versus hydrocarbons. The derivatization procedure using sodium tetraethylborate alkylation for the standards, optimum GC-PFPD conditions, and calibration data will be presented. Sample data for blood plasma, urine, wastewater, and dewatered sludge will also be presented.

5383 PFPD Detector

O·I·Analytical
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Methodology

The analysis was performed at three locations: The City of San Diego, California PUD, OI Analytical, and the University of Iowa. A Shimadzu GC and Agilent GC's were used with OI Analytical PFPD's. The California and Iowa locations ran derivitized standards and "real world" samples while the OI Analytical location ran studies on detector contamination which may be experienced running the analysis. Standards which are received as tin chlorides and sample extracts must be derivitized in order to be detected by gas chromatography. Ethylation is performed using 1 mL 1% Sodium tetraethyl borate (STEB) in Tetrahydrofuran or Methanol and 1 mL Sodium acetate buffer in water acidified to ~pH 4.9 with acetic acid. Great care must be used when preparing the STEB solution because it is pyrophoric (handle under inert gas).

The PFPD's were tuned for optimum sulfur response by adjusting the hydrogen and air flows. A multi-point calibration was run and calibration curves were generated using linear regression. Please see Table 1 for instrument configurations and operating conditions.

Table 1. Instrument Configurations and Operating Conditions

	Laboratory: San Diego PFPD Model 5380	Laboratory: OI Analytical PFPD Model 5383	Laboratory: University of Iowa PFPD Model 5383
PFPD Settings			
Combustor Size	3 mm	3 mm	3 mm
Filter Type	BG-12	BG-12	BG-12
PMT	1924	1924	1924
Element/Gate	Sn/6-15 ms	Sn/6-20 ms	Sn/6-24.5 ms
PMT VOLTAGE	550	625	500
Trigger Level	500	800000	500000
Detector Temperature	325 °C	325 °C	350 °C
H_2 Flow (measured)	11.5 mL/min	13.5 mL/min	13.0
Air 1 Flow (measured)	11.0 mL/min	13.5 mL/min	12.0 mL/min
Air 2 Flow (measured)	10.0 mL/min	13.0 mL/min	10.0 mL/min
Gas Chromatograph			
Model	Shimadzu GC2010 Plus	Agilent 7890A	Agilent 7890A
Inlet Type	Split/Splitless	Split/Splitless	Split/Splitless
Inlet Temperature	250 °C	250 °C	250 °C
Inlet Liner	Restek 3.4 mm Sky Liner, Split, Open tube	Restek 4mm Topaz, single taper, gooseneck	Agilent 4 mm single taper, splitless
Column	Restek Rtx-1 and Rtx-5	Restek Rxi-5MS and Rxi-35SIL MS	Supelco SPB-1
Column Dimensions	30 meter, 0.25 mm ID, 1.0 µm df	30 meter, 0.25 mm ID, 1.0 µm df	30 meter, .25 mm ID, 0.25 µm df
Column Flow	1.5 mL/min	1.2 mL/min	2.1 mL/min
Split Ratio	Splitless with 2 µl injection	Splitless with 2 µl injection	Splitless with 1 µl injection
Oven Program	Hold at 70 °C for 1 minute 4 °C/min to 190 °C 30 °C/min to 250 °C, hold 3 minutes Total run time 34 minutes	Hold at 100 °C for 1 minute 10 °c/min to 285 °C, hold 1 minute Total run time 19.5 minutes	Hold at 80 °C for 1 minute 2 °C/min to 130 °C 0.5 °C/min to 138 °C 15 °C/min to 280 °C, hold 15 minutes Total run time 57 minutes

Results and Discussion

Please see Table 2 for calibration results. Peak tailing can be severe when running this analysis at the normal PFPD operation temperature of 250 ˚C. Running the detector from 325˚ to 350˚ is recommended to reduce tailing.[6] Frequent inlet maintenance including changing out the liner is also recommended to keep the system optimized.

Table 2. Calibration Data

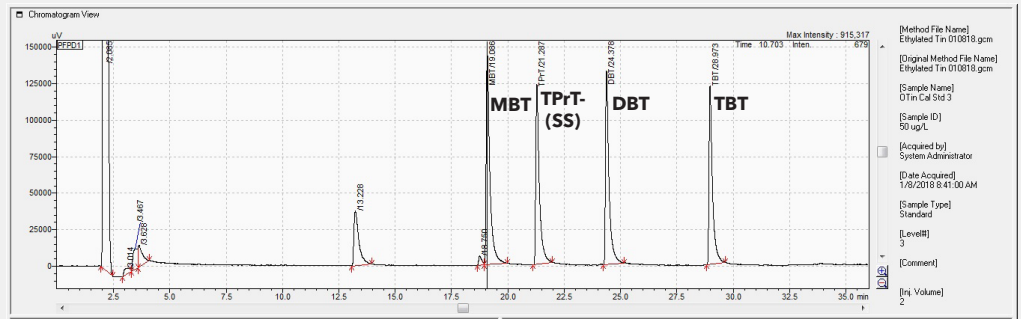
Lab	Compound	Calibration Range (ppb)	Retention Time (min)	Coeff Of Det
San Diego	Monobutyltin (MBT)	10-200	19.09	0.998
	Tripropyltin (TPrT) - SS	10-200	21.29	0.999
	Dibutyltin (DBT)	10-200	24.38	0.998
	Tributyltin (TBT)	10-200	28.97	0.998
U of Iowa	Tetraethyltin (TET) - SS	0.5 - 250	6.19	1.00
	Monobutyltin (MBT)	0.5 - 250	11.84	0.997
	Dibutyltin-d18 (DBT-d18)	0.5 - 250	19.00	0.999
	Dibutyltin (DBT)	0.5 - 250	19.55	0.999
	Tributyltin-d27(TBT-d27) - SS	0.5 - 250	26.78	1.00
	Tributyltin (TBT)	0.5 - 250	27.70	1.00
	Tetrabutyltin-d36 (TeBT-d36) - SS	0.5 - 250	36.17	0.997
	Tetrabutyltin (TeBT)	0.5 - 250	37.97	1.00
	Tetraphentyltin (TPhT) – IS	0.5 - 250	52.82	0.997

Data for environmental samples were obtained from the City of San Diego, Public Utilities Department. Figure 2 shows a chromatogram of 1 liter raw sewage concentrated to a final volume of 10 mL. Figure 3 shows 1 liter treated wastewater concentrated to a final volume of 10 mL. Figure 4 shows 1 gram of dewatered sludge concentrated to a final volume of 10 mL. MBT, DBT, and TBT were not detected in any samples. Clean-up using florisil/silica gel SPE Cartridges was experimented with, but did not have a positive effect on the sewage extracts. This may be due to the specific wastewater or sludge matrix. All samples were run under instrument conditions listed in Table 1.

Data for human urine and blood samples were obtained from the University of Iowa, College of Public Health, Occupational, and Environmental Health. Figure 6 shows a chromatogram of 2 mL human urine concentrated to a final volume of 200 µl. Results were 0.6 ppb for MBT and 3.7 ppb for DBT. Figure 7 shows 2 mL human blood concentrated to a final volume of 200 µl. An activated alumina clean-up was performed on blood samples. All samples were run under instrument conditions listed in Table 1.

Matrix interference can be a challenge with some dirty or complex samples. Extract concentration, column selection, and GC oven programming appeared to help the most in regards to matrix interference with analytes of interest. It is possible that the analysis of different matrices may benefit from other forms of clean-up not mentioned in this paper.

Figure 1. 50 ppb Organotin Standard



City of San Diego PUD

Figure 2. Raw Sewage

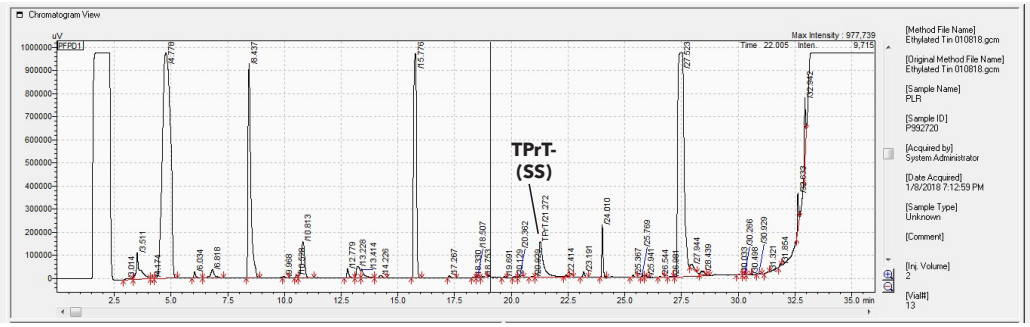


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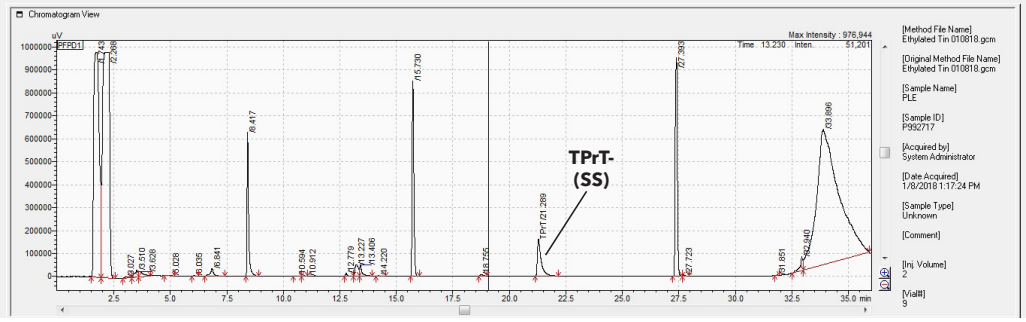
Figure 3. Effluent



City of San Diego PUD

Figure 4. Dewatered Sludge

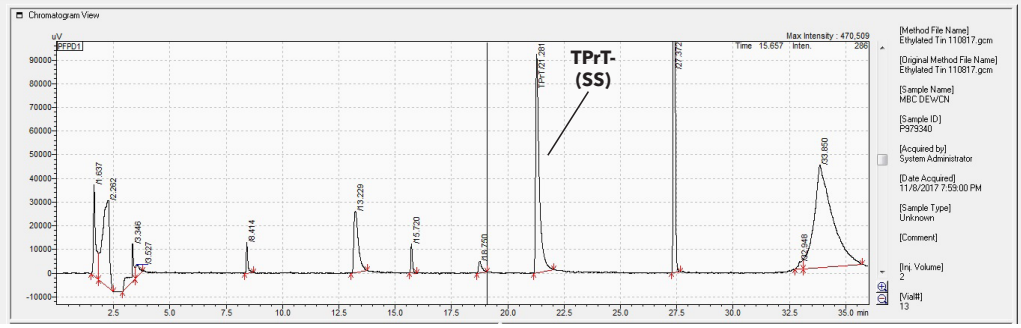


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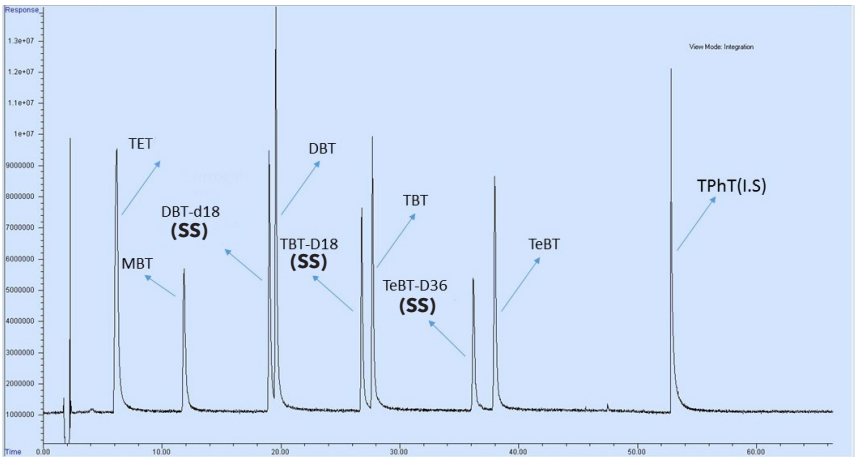
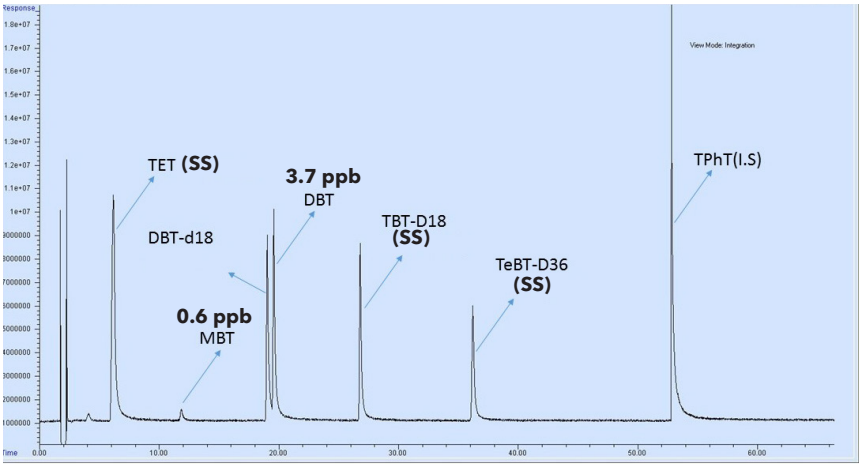
Figure 5. 5 ppb Organotin Standard



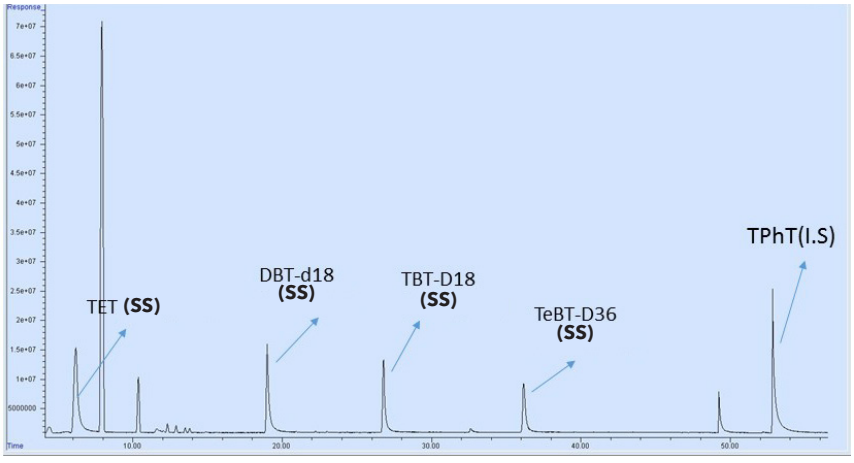
University of Iowa

Figure 6. Human Urine



University of Iowa

Figure 7. Human Blood



University of Iowa

It had been noted by some OI Analytical customers that, after running the instrument for an extended period of time, a contamination peak at ~3-4.5 ms formed after the hydrocarbon emission at ~1-3 ms. Various tests were run at OI to duplicate this. Build-up varied according to injections made and concentration. If high concentrations of >1 ppm were run successively over a two day period, the contamination was fairly significant. Some decrease over time was observed because of the self-cleaning properties of the combustion zone. Replacing the combustor, baking out the system, and performing inlet maintenance helped somewhat but the only action that completely removes the contamination is clipping the column at the detector end. Installing a guard column at the detector end may help extend column life. Setting the Tin gate after the contamination will ensure that it does not interfere with the analysis.

Figure 8. Sulfur Emission

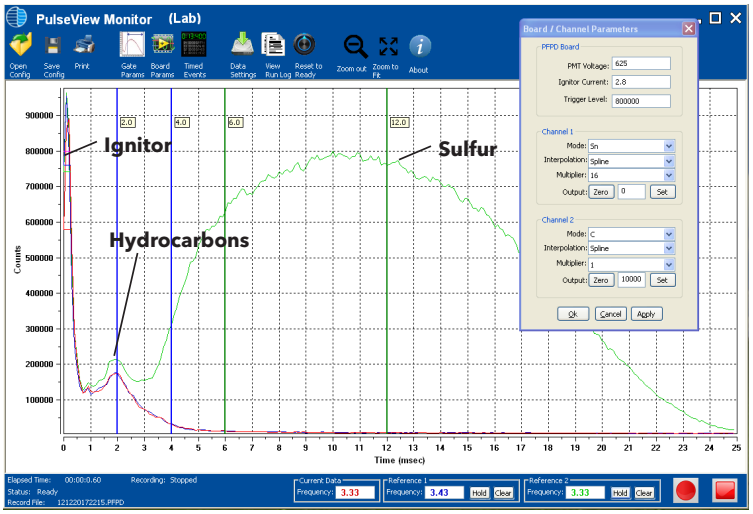


Figure 9. Tin Emission

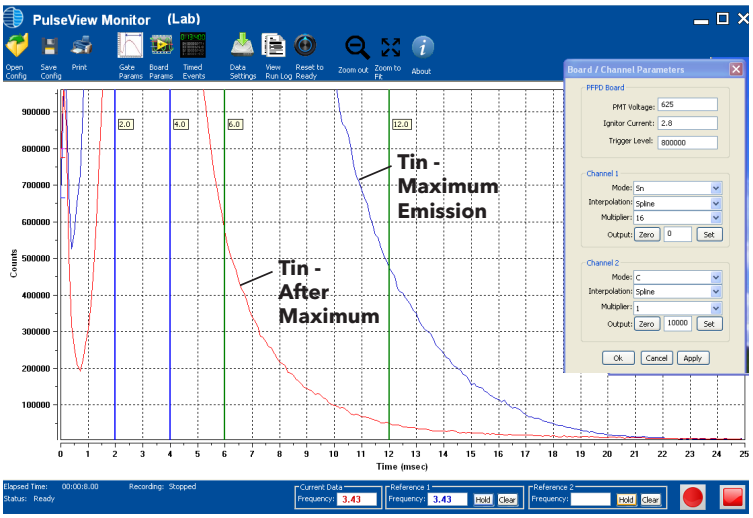
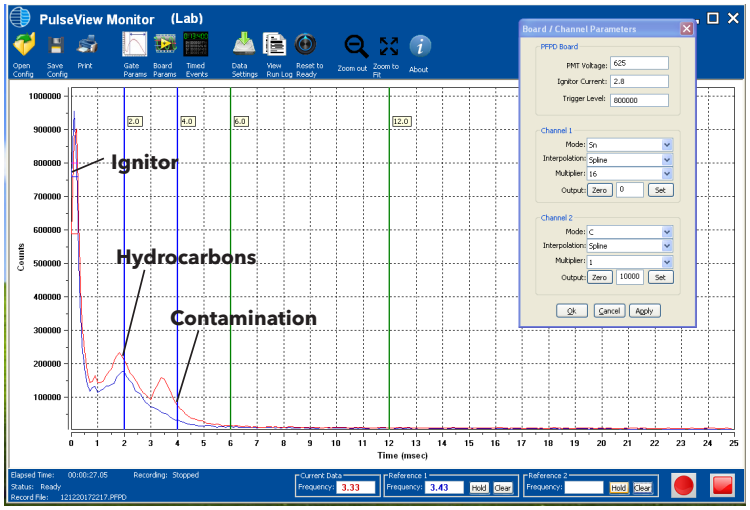


Figure 10. Emission after Multiple High Concentration Injections



Conclusions

Because of its persistence in the environment and its dangers as an endocrine disrupter, organotin will continue to be a compound of concern. As a result, more laboratories will want to offer the analysis with minimal start up and implementation cost which is possible using GC/PFPD. The method is reliable, rugged, and requires glassware and resources most full service labs already have. The PFPD offers the selectivity and sensitivity required with an easy to operate and maintain detector.

References

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