Application Note: 10092

Analysis of Organotin Compounds in Tissues and Sediments Using Accelerated Solvent Extraction and Large Volume Injection GC/FPD

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Key Words

- Accelerated Solvent Extraction
- Large Volume Injection
- Organotin Compounds

Introduction

The analysis of organotin compounds such as: Tetrabutyltin, Tributyltin, Dibutyltin, and Monobutyltin from environmental and marine tissue samples is an application of considerable interest. These compounds were used in anti-fouling coatings for marine use for many years. Now there is concern over their impact on marine life in the bays and harbors where the greatest concentration has accumulated. Construction or remediation work in any of these sites where the concentration of organotin is suspected requires testing for these compounds.

One of the difficulties with any analytical method used with biological samples is separating the components of interest away from the biological interferences. This report describes a methodology which yields excellent sensitivity while reducing the extraction and solvent concentration workload.

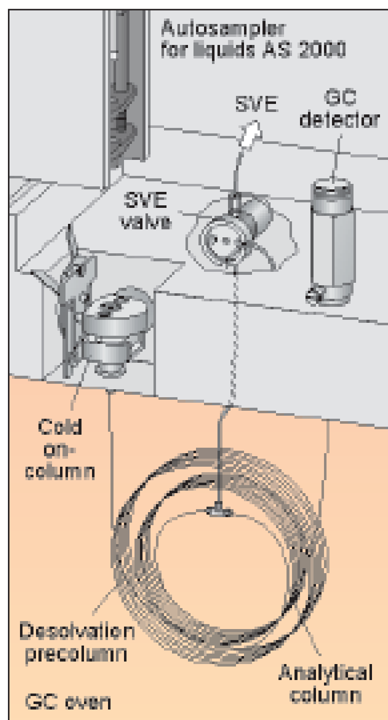

Figure 1: Components of an on-column Large Volume Injection instrument.

Description

The analysis of these compounds is usually done by extracting the organotin compounds into a solvent followed by derivatization before analysis. This requires considerable expenditure of labor and materials to carry out the extraction part of the method. The sol-vent must be concentrated to maintain good detection limits, and large quantities of solvent must be disposed of or reclaimed and tested before reuse.

In this method, an On-Column Large Volume Injection (OCLVI) technique eliminates the concentration step, yet still maintains good detection limits. The instrumentation used for OCLVI consisted of an Autosampler with injection parameters calculated and controlled from a unique software program, a patented Cold-on-Column inlet, a desolvation precolumn, a tee fitting, and a heated Solvent Vapor Exit valve (Figure 1).

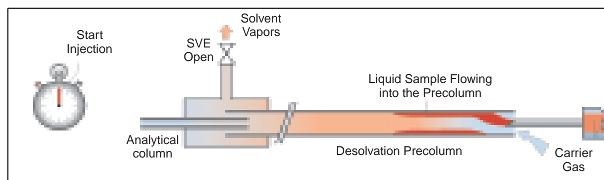

Figure 2A: Sample Injection

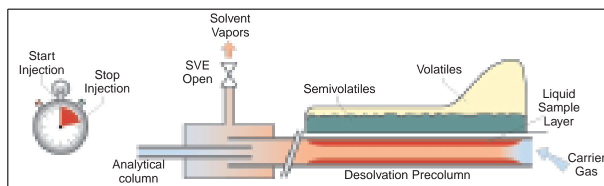

Figure 2B: Solvent Evaporation

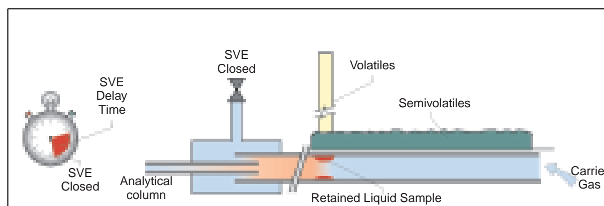

Figure 2C: Component Transfer

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In OCLVI, 50 to 200 microliters of extract are injected into a desolvation precolumn (Figure 2A). The injection conditions for both the Autosampler and the Gas Chromatograph are under computer control to allow precise evaporation of the solvent without loss of the components of interest (Figure 2B). After most of the solvent has been vented, the remaining liquid containing the volatile compounds is allowed to proceed onto the analytical column very much like a splitless injection (Figure 2C). The OCLVI technique can be used to achieve lower detection limits if the sample is concentrated before injection. It can also be used to increase productivity with standard detection limits by eliminating the need for the time consuming concentration step. In this case, the intent was to maximize productivity.

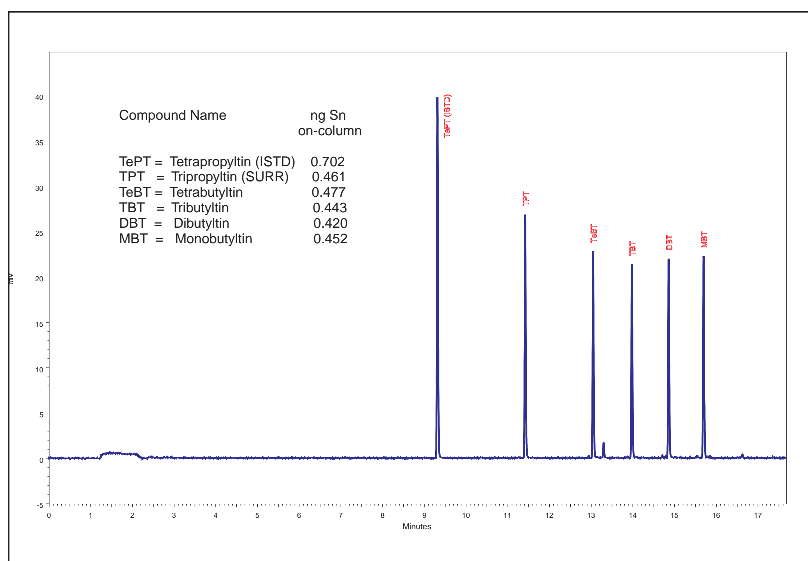

Figure 3: Chromatogram of 50 µL injection of mid level standard.

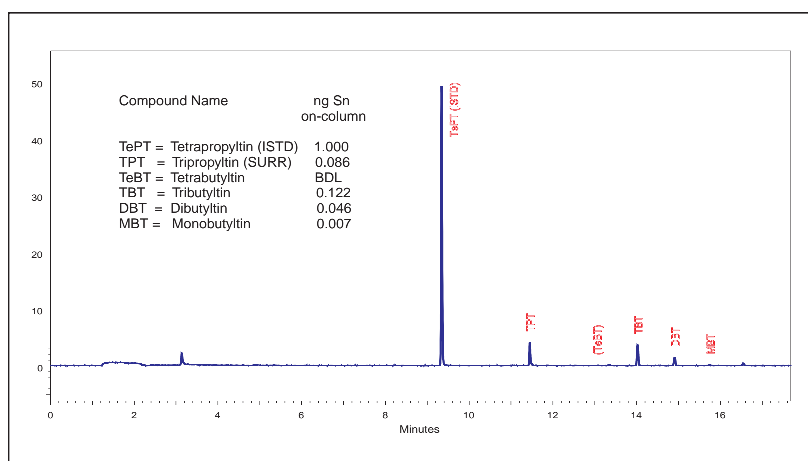

Figure 4: Chromatogram of 50 µL injection of sample extract from tissue.

Experimental

Water, tissue, and sediment method detection limit studies were performed using traditional extraction methods. The extraction solvent was 0.05% Tropolone in Hexane. Water samples were extracted in separatory funnels, tissues were macerated with Sodium Sulfate and a Tissuemizer, and sediments were mixed with Sodium Sulfate and extracted on a shaker table. The Hexane extracts were concentrated to 10 mL, after which 1 mL of Grignard reagent (Pentylmagnesium Bromide) was added and the samples were gently shaken for 1 hour.

The Pentylmagnesium Bromide reacts with the Chloride of the mono, di, and tri Butyl Tin compounds substituting the pentyl group and making them chromatograph more easily. Adding approximately 4 mL of concentrated Hydrochloric Acid to the samples then neutralized the Grignard reagent. The upper Hexane layer was removed from the sample using a pipet, and the acid fraction was back extracted twice more with Hexane. The extract was concentrated to 1 mL and passed through a cleanup column packed with 16 grams of 60/100 mesh Florisil. The final extract was concentrated to 10 mL, spiked with Tetrapropyltin as an internal standard, and 50 µL was then injected into the GC. The chromatogram shows excellent peak shapes, indicating the transfer into the analytical column is a narrow band. A chromatogram of a standard mix is shown in Figure 3. There is minimal detector response to the solvent, and peak shapes are narrow and well defined. All the compounds of interest are well separated from the solvent response and the other peaks. Figure 4 shows a chromatogram of a tissue sample extract. Note the clean baseline with virtually no interfering peaks in the region of the organotin compounds. The amount of Tin injected on-column is approximately 0.1 ng TBT for this sample showing the sensitivity of this method. The detection limit was 0.01 ng TBT on-column calculated on the lowest standard. This was based on a 50 microliter injection from a 10 mL solvent volume. The detection limits could have been lowered further by either concentrating this solvent volume, or extracting a larger sample. This procedure was chosen to balance laboratory productivity with sensitivity. The combination of selective detection of Tin compounds with the Flame Photometric Detector and a relatively simple sample cleanup procedure gives a method which is robust and sensitive.

Minimum Detection Limits for Butyltin Compounds in Various Samples			
	Water (1000 mL) ng Sn/mL	Tissue (10 g wet) ng Sn/g wet ng	Sediment (15 g dry) Sn/g dry
Monobutyltin	0.010	0.174	0.224
Dibutyltin	0.012	0.539	0.292
Tributyltin	0.009	1.311	0.370
Tetrabutyltin	0.007	0.763	0.434

Table 1: Detection limits obtained from water, tissue and sediment samples

Conclusion

The use of the Large Volume Injection technique allows higher productivity while maintaining method sensitivity. This is an important consideration for an analytical laboratory utilizing methods where sample preparation time is lengthy. Solvent extraction and evaporation is a labor intensive procedure which is not easily automated. The injection of large volumes of solvent extracts can be carried out reproducibly with proper instrumentation, as shown here.

In this application, the use of OCLVI allowed the extraction of smaller samples, increasing sample throughput for the laboratory. The extracts were less concentrated than the traditional larger sample sizes, but the ability to inject large volumes maintained the detection limits for the method at the same levels.

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