APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 151–157 (1991)

Determination of butyltin species by GC/atomic emission spectroscopy

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A commercially available atomic emission detector coupled to a capillary column-containing gas chromatograph (GC/AE) was utilized to detect organotin compounds. The response for tin was found to be dependent on the flow rate of the make-up gas. At flow rates of 174 cm^3 min^{-1}, 6 × 10^{-12} g of tin could be detected. Lower flow rates decreased the sensitivity. Response curves for two different pressures were established and both plots exhibited curvature at low concentrations. Extracted fish and sediment samples were analysed on the GC/AE system. The technique is element-specific. The presence of tin compounds could be confirmed by examining the emission spectra taken at the retention time of the peak.

Keywords: Atomic emission detector, gas chromatograph, organotin, speciation, sediment, fish

INTRODUCTION

Organotins are mainly used as antifouling and stabilizing agents by industry and as pesticides in agriculture. Surveys[1] have shown that, with the widespread use of tin, there is a concurrent widespread contamination by organotin of the aquatic environment. Indeed, organotins have been found in sediments,[1] accumulated in the food chain by smaller organisms[2–4] and in fish tissue, both marine[5] and freshwater[1] species. In addition to these studies are the investigations of possible oxidation of tin by bacterial action[6] and other possible transformations of tin compounds in the environment.[7] In all these investigations, species differentiation and determination of the organotin compounds at environmental concentration levels are required. Analysis of these types is one of the most challenging areas of research in analytical chemistry today.

The most effective and sensitive techniques for speciation of trace organometallic compounds are the tandem analytical systems consisting of an element-specific detector coupled to a chromatographic separation instrument. Atomic spectrophotometers, in the absorption and emission modes, have been successfully used as detectors. Gas chromatography, as well liquid chromatography, has been widely applied in the separation of organometallic compounds. Reviews on these methods are available.[8–10]

For tandem analytical systems using gas chromatographic separations, derivatization is necessary to convert the polar and high-boiling ionic organometallic species, such as R_3Sn^+, R_2Sn^{2+} and RSn^{3+}, to volatile derivatives amenable to gas chromatographic separation. The most commonly used methods of derivatization are hydridization[11] or alkylation[12, 13] using appropriate Grignard reagents. The derivatized extract containing tin is then injected onto a gas chromatograph equipped with a capillary or megabore column, and the compounds are separated and analysed at a detector. A number of different detectors have been used for this purpose. Various modes of atomic spectrometry have been utilized for specific metal detection after gas chromatographic separation, including atomic absorption,[12] plasma-excited atomic emission[14] and flame photometric detectors in the sulphur mode.[15] Another detector used is quadrupole mass spectrometry (MS), in either the chemical ionization (CI) mode[16] or selective ion (SIM) mode.[17] The minimal detectable amount varies depending on the detector, values ranging from 0.01 ng to 5 pg depending on the detection system. Also these values are dependent on the compounds used,[18] and whether the cited value is experimentally measured[18] or extrapolated.[17]

It is this last aspect of detectors which is the focus of this report. Generally, the lower the detection limit, the more expensive the detection system. A detection limit similar to the lowest reported value for tin[18] (5 pg) was achieved using

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0268-2605/91/030151-07$05.00

Received 26 June 1990
Accepted 20 October 1990

a moderately priced, commercially available atomic emission detector. In addition, confirmation of the presence of tin in the eluting peak of the chromatogram can be obtained from the emission spectra at the retention time of the peak down to levels of the minimum detectable concentrations. The minimum detectable amounts for the compounds used as standards was 0.1 ng[12] to 5 pg[18] of the metal monitored at the detector. To analyse successfully for tin at these amounts, the operating conditions of the detector had to be altered from the manufacturer's recommendations.[18] It is the optimizing of the operating conditions which will be reported in this work, as will typical results from standards, sediment and fish samples. Ethylbutyltin compounds were used as standards.

METHODS

Each of the ethylbutyltins was prepared individually by dissolving the appropriate chloride precursor in distilled water, extracting with tropolone/hexane (0.5%) at pH 1.5, then alkylating the extract with ethylmagnesium bromide.[19] Aliquots of triethylbutyl-, diethyldibutyl-, and ethyltributyltin were combined to provide an injection standard of 0.2 ng μl^{-1} of each compound in spectrograde hexane. This standard was injected at increasing make-up gas flows. In another part of the study, the injection standard was diluted by a factor of two after duplicate injections. This solution was sequentially continually diluted by a factor of two until no response was observed on the chromatogram. Fish and sediment samples were extracted and prepared using procedures described elsewhere.[20] These samples were stored in darkness at 4°C until needed for analysis. Duplicate injections were made of each sample as well as for each set of conditions where a standard was used.

The gas chromatograph used was a Hewlett-Packard model 5890 equipped with a split/splitless injector for capillary columns. A pressure of 115 kPa was maintained at the column head. Helium carrier gas had a flow rate of 5 cm^3 min^{-1} at an oven temperature of 90°C. The oven was programmed to have an initial temperature of 90°C which was increased to 200°C at a rate of 20°C min^{-1} and kept at this temperature for 5 min before cooling for the next determination. It was found that there was no evidence of thermal decomposition of the standards in the injector at 250°C, which was the temperature used for the study. All injections were performed in the splitless mode with the purge delay set at 0.8 min. The injection volume was 1 μl for all samples. An automatic sampler (Hewlett–Packard model 7321A) was used for all injections.

The detector was a Hewlett-Packard model 5921A atomic emission (AE) detector, which uses an induced microwave helium plasma to excite the various atoms.[21] This was coupled to the gas chromatograph by a transfer line through which the end of the capillary column was directed to the plasma. The line was kept at a constant temperature of 210°C. For the initial studies the response of the spectral lines at Sn (303.4 nm), C (496 nm) and H (486 nm) were used to construct the chromatograms. For most of the study, only the Sn (303.4 nm) line was needed. To obtain maximum emission for this line, the reagent gases of hydrogen and oxygen were utilized. As the C (496 nm) and H (486 nm) emission lines require only oxygen as reagent gas, two separate injections on the same sample were needed when the three elements were analysed. With hexane as the solvent, the solvent valve was activated at 1.5 min and shut off at 3.0 min to avoid extinction of the plasma. The detector cavity temperature was set at 210°C, and the plasma burned at a temperature of greater than 3000°C. Results were

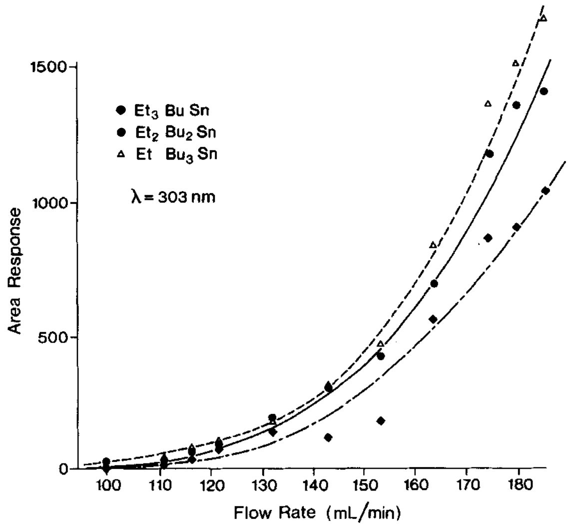

Figure 1 Effect of make-up gas flow rate on the response to the butyltins.

transferred to an HP GC/AED/Data System work-station to facilitate analysis. Occasionally between runs, oxygen was turned on for about a minute to burn off any tin and carbon residues that might have collected at the end of the discharge tube. Make-up gas flow rates were measured at the cavity vent outlet. Figures showing the emission spectra are presented with background noise subtracted from the spectra.

Columns, supplied by Hiresco (Mississauga, Ont., Canada), were 25 m in length and had an internal diameter of 0.255 mm. The liquid phase was XE-52XL (5% phenylmethylpolysiloxone) with a film thickness of 0.25 μm. Flow rates were measured using a Humonics Optiflow 520 digital flowmeter (Fairfield, CA, USA) which permits an objective measure of the flows at higher values. Make-up gas flow rates were measured at the cavity vent outlet with the reagent gases and the spectrophotometer window purge gas turned off.

RESULTS AND DISCUSSION

The AE detector was previously used for analysis of heteroatom-containing hydrocarbons. For these analyses the make-up gas flow rate is optimized at 60 $cm^3 min^{-1}$. Analysis for metals requires a higher flow rate, generally at 140 $cm^3 min^{-1}$. To check the reproducibility of the system, ten injections of the standard were made, six with a make-up flow rate of 175 $cm^3 min^{-1}$ and four at 167 $cm^3 min^{-1}$. At 175 $cm^3 min^{-1}$. At 175 $cm^3 min^{-1}$, the triethylbutyl-, diethyldibutyl- and ethyltributyltin mean responses were 999, 1587 and 1274 area counts respectively with corresponding relative standard deviations of 1.5%, 3.0% and 7.2%. Lowering the make-up flow to 166 $cm^3 min^{-1}$ resulted in mean area responses of 759, 1118 and 958 respectively with corresponding relative standard deviations of 5.0%, 2.2% and 13.0%.

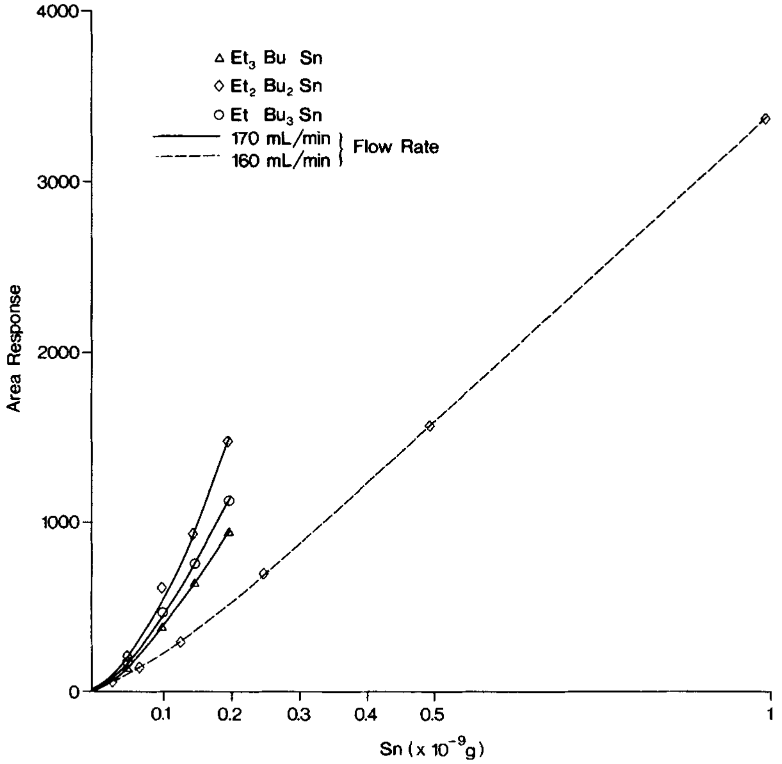

Figure 2 Response to butyltin compounds as a function of concentration, shown for two make-up gas flow rates.

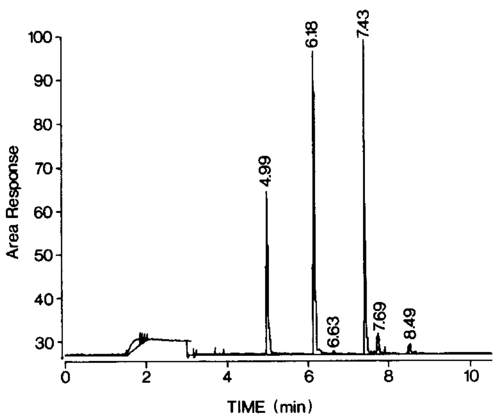

Figure 3 Typical chromatogram of standard butyltin solution of 0.2 ng μl^{-1}.

To establish the effect the make-up gas flow rate has on the signal, duplicate injections of a 0.25 ng μl^{-1} standard containing the three butyltin compounds were made with increasing flow rate. The results of this are illustrated in Fig. 1. Below a flow rate of 100 cm^3 min^{-1} no signal was detected for all three tin compounds. A practical upper limit of 180 cm^3 min^{-1} was adopted as higher flow rates could result in damage to the ferrules about the discharge tube which directs the column effluent into the plasma area. The curve in Fig. 1 exhibits a slow increase at low flow rates and increases rapidly above flow rates of 120 cm^3 min^{-1}. The responses for all three tin compounds were still increasing at the 180 cm^3 min^{-1} upper limit. A flow rate of 170 cm^3 min^{-1} was used in this study and the rate was constantly monitored during analysis of standards and samples. No variation in rate of flow was observed. Other elements such as carbon, sulphur and nitrogen were normally monitored at make-up flow rates of 60 cm^3 min^{-1}. Increasing the flow rate diminished the response for these elements and they could not be monitored at the make-up gas flow rates used to measure the various tin compounds. Therefore, no effort was made to check the response of the organic portion of the molecule during the tin analysis. Increasing the flow rate of the make-up gas also increased the retention times of the peaks. Over the range of flow rates examined, the increase was 0.1 min.

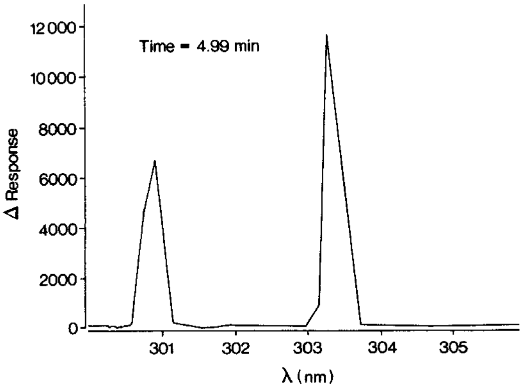

Figure 4 Emission spectra of Et$_3$BuSn, showing the expected tin emission lines at 300.9 and 303.4 nm with background correction.[22]

Two calibration plots are shown in Fig. 2. One illustrates the responses for a flow rate of 171 cm^3 min^{-1} and a maximum concentration of each tin species of 0.2 ng injected. The other represents the responses for a flow rate of 160 cm^3 min^{-1} and a maximum concentration of 1 ng of each compound injected. At both flow rates, the points in the two plots are not linear over the concentration ranges studied, especially below concentrations of 10^{-10} g (0.1 ng). As expected, the lower detection limits for the three ethylbutyltin compounds are higher for those measured at 160 cm^3 min^{-1} flow rate of the make-up gas than those measured at 171 cm^3 min^{-1}. Also, the responses for equal quantities of the three tin compounds, shown in Fig. 2, do not coincide when measured under the same conditions.

A typical chromatogram of the three tin compounds at concentrations of 0.2 ng cm^{-3} each is shown in Fig. 3. The three peaks have retention times of 4.99 min (Et$_3$BuSn), 6.17 min (Et$_2$Bu$_2$Sn) and 7.42 min (EtBu$_3$Sn). When the emission spectrum is examined at one of these retention times, a plot similar to that in Fig. 4 is obtained. The peaks at 300.9 and 303.4 nm confirm that the compound examined does contain tin. The very minor peaks at 6.63, 7.69 and 8.49 min in Fig. 3 were examined and their emission spectra exhibited the two characteristic tin peaks, indicating that these peaks were tin containing impurities in the standard solution.

As the three compounds in the standard did not exhibit the same AE response with identical concentrations of each, it was necessary to ascertain if the difference in response originated in the injector. This was done by comparing the results of a split injection (50 : 1 split ratio) of a standard butyltin solution (10^{-9} μg cm^{-3}) with those from a splitless injection from the same solution. This was done in duplicate. The average area res-

Table 1 Concentrations of butyltin compounds in selected fish samples

		Concentration (ng g^{-1})[a]		
		$BuSn^{3+}$	Bu_2Sn^{2+}	Bu_3Sn^+
Location/Sample	Retention time:	4.97 min	6.18 min	7.40 min
Whitby Harbour, Ontario				
F1		22.0 ± 0.7	36.0 ± 0.3	56.0 ± 2.9
F2		25.1 ± 2.2	25.2 ± 0.2	28.8 ± 0.5
F3		19.4 ± 2.2	42.4 ± 1.2	54.6 ± 1.2
F7		46.8 ± 0.6	109.2 ± 0.6	178.8 ± 0.2
F8		37.2 ± 1.8	102.0 ± 1.2	106.8 ± 1.4
F9		38.4 ± 1.2	85.9 ± 3.1	109.2 ± 6.2
F10		—[b]	57.6 ± 16.3	58.4 ± 3.3
Kingston Harbour, Ontario				
F4		14.2 ± 0.0	24.4 ± 0.3	59.6 ± 2.1
F5		15.8 ± 0.9	21.6 ± 2.9	15.8 ± 0.0
F11		21.6 ± 1.2	14.4 ± 2.1	16.8 ± 1.1
Port Dover Harbour, Ontario				
F6		4.3 ± 0.1	4.3 ± 0.3	40.1 ± 3.6

[a]Concentration unit ng g^{-1} g expressed as Sn (whole fish wet weight). [b]—, Not detectable.

ponses were 3365 ± 10, 3325 ± 10 and 3688 ± 26 for Et_3BuSn, Et_2Bu_2Sn and $EtBu_3Sn$ respectively in the splitless mode. The peak area responses of 59 ± 5.2, 78 ± 0.1 and 129 ± 5.3 were measured for the split mode for the same compounds. This indicated that there were more serious problems with the material being eluted in the split mode than in the splitless. Clearly, the minimal detectable amounts are a function of the system including the injector and detector.

A number of sediment and fish samples were analysed and the results are shown in Tables 1 and 2. As the recovery for the butyltins using this method is greater than 85%, no correction factor was applied to these concentrations. With the exception of sample F10, all of the fish samples listed in Table 1 contained measurable amounts of the three butyltin compounds. The measured quantities of the tin compounds ranged from 5×10^{-12} to 149×10^{-12} g. Generally, for each

Table 2 Concentrations of butyltin compounds in selected sediment samples

		Concentration (ng g^{-1})[a]				
		$BuSn^{3+}$	Unknown	Unknown	Bu_2Sn^{2+}	Bu_3Sn^+
Location/Sample	Retention time:	4.97 min	5.20 min	5.30 min	6.15 min	7.40 min
Port Dover Harbour, Ontario						
S1		18.8 ± 1.7	122.0 ± 7.6	128.3 ± 9.2	97.0 ± 0.9	106.4 ± 2.9
S2		15.5 ± 1.9	161.2 ± 2.7	158.1 ± 1.1	62.1 ± 2.3	58.9 ± 11.4
S3		58.5 ± 7.9	120.0 ± 4.0	141.5 ± 6.5	67.7 ± 2.6	147.7 ± 11.5
S7		—[b]	126.0 ± 9.1	104.4 ± 9.0	—	36.0 ± 4.1
S8		35.4 ± 2.0	127.4 ± 3.4	145.1 ± 3.2	36.0 ± 2.4	46.8 ± 9.2
S9		—	21.6 ± 1.8	59.2 ± 1.9	21.6 ± 2.2	18.0 ± 2.4
S10		—	86.4 ± 1.9	97.2 ± 5.2	—	18.0 ± 1.3
S11		—	115.2 ± 1.8	126.0 ± 13.1	79.2 ± 2.9	86.4 ± 4.5
Wheatley Harbour, Ontario						
S4		—	—	—	—	9.2 ± 1.2
S5		—	—	—	—	18.5 ± 0.4
S6		—	—	—	21.6 ± 1.7	64.8 ± 5.0

[a]Concentration unit: ng g^{-1} as Sn (dried wt). [b]—, not detectable.

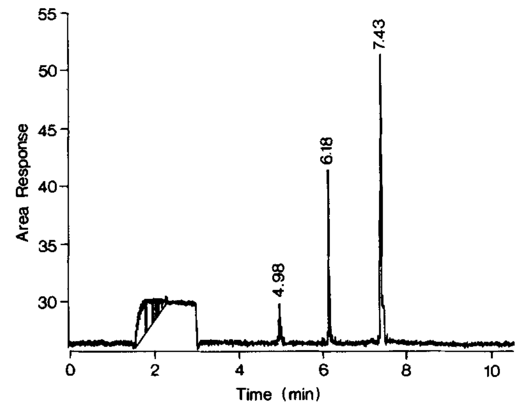

Figure 5 Typical emission chromatogram from a fish sample.

sample, the concentration of the tributyltin was greater than the dibutyltin, which was greater than the monobutyltin. A typical chromatogram is shown in Fig. 5 for fish sample F7. Only the three butyltin peaks are present, with no other organotin compounds being detected. At lower concentrations, such as in sample F6, the monobutyltin peak is less than four times the background noise. In this instance the presence of the tin compound was confirmed by inspection of the emission spectra.[22]

The results for the sediment samples are listed in Table 2. Butyltin compounds were detected in all samples but two samples contained only small amounts of the tributyltin compounds. Monobutyltin was detected in four of the eleven samples at low concentrations. The AE chromatogram for sample S2 is shown in Fig. 6. This chromatogram contains five integrated peaks, three of which are the ethylbutyltins and there are also two unidentified peaks which elute shortly after the triethylbutyltin at 5.20 and 5.29 min respectively. As in the case of the chromatogram from the fish extract (Fig. 5), this chromatogram contains no interferences from other compounds extracted from the matrix, illustrating the selectivity of the AE detector. To ensure that the two unidentified peaks represented tin containing compounds, the emission spectra were checked and found to contain tin. The emission spectra for the 5.29 min peak of sample S9 is shown in Fig. 7. This particular sample was chosen to be illustrated here as the concentrations of the components in the system are low, with the peaks heights being closest to the value of twice the background level. The emission spectrum shows two peaks at 303.4 and 300.9 nm, confirming the presence of tin. The emission spectrum for the peak at 5.21 min contains both tin emission lines, confirming that the compound also contains tin. Values for the concentrations of these two compounds were estimated using the response curve for the monobutyltin. When detected, both unknown compounds are present at about the same concentration and their concentrations are usually greater than that of monobutyltin.

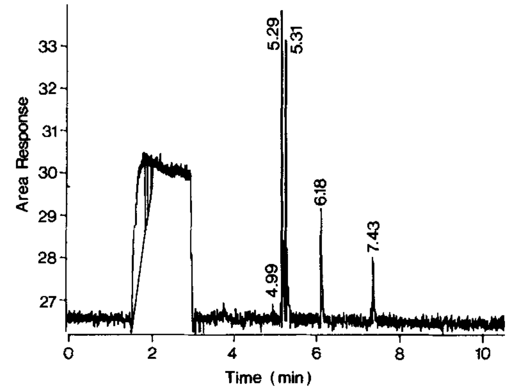

Figure 6 Typical emission chromatogram of a sediment sample.

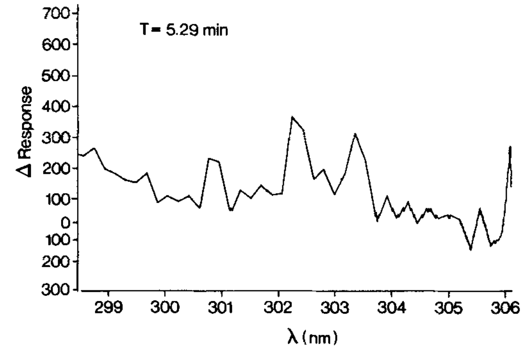

Figure 7 Emission spectra of eluting peak at 5.29 min showing anticipated tin lines at 300.9 and 303.4 nm (with background correction[22]).

CONCLUSION

In this study, the results derived from a new method to analyse organotin compounds have been reported. The AE method has a detection limit for tin comparable with the lowest reported in the literature. By using a capillary column, the method allows the operator to discern between peaks representing different compounds which may not be resolved on larger-diameter columns. The ability to confirm the presence of a suspected tin complex by inspecting the emission of tin is a feature of this method not available in others. Finally, although not discussed in this work, the instrument can also be used to detect for sulphur-, nitrogen- and phosphorus-containing compounds in extracts from oil-contaminated water without modifications needing to be made to the instrument between studies.

Acknowledgements The authors wish to thank Dr B. Quimby of Hewlett–Packard for valuable suggestions at the beginning of this study which enhanced the sensitivity of the method presented.

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