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Determination of organotin species by capillary gas chromatography with alternating current plasma emission detection

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ABSTRACT

An alternating current plasma (ACP) emission detector is used as a detector for capillary gas chromatography (GC) in the determination of organotin compounds in environmental marine samples. Detection limits for tributyltin chloride (TBT) and tetrabutyltin (TEBT) were found to be 131 and 116 pg/s (as Sn), respectively. Calibration curves exhibited linearity over three orders of magnitude. Precision was found to be less than 8.5% relative standard devision (n = 10) for both TBT and TEBT. Results for the separation and detection of organotin compounds in complex sample matrices are presented to illustrate the selectivity of the ACP emission detector. No prior hydride formation or alkylation reactions were performed on the organotin species prior to gas chromatographic detection. Recovery data ranged from 77 to 100%. The results obtained in this study demonstrate the variability, selectivity and ease of use of the GC–ACP detector for the determination of organotin compounds.

INTRODUCTION

Organotin compounds continue to generate considerable interest among environmental researchers because they exhibit extreme toxicity to a wide variety of aquatic organisms such as fish, mussels and mollusks [1–8]. Tributyltin chloride (TBT), $[CH_3(CH_2)_3]_3Sn$, and tetrabutyltin (TEBT), $[CH_3(CH_2)_3]_4Sn$, are two organotin compounds which are frequently used as fungicides, bactericides as well as anticancer and biochemical agents [2–4], the tri- and tetrabutyl moieties being more toxic than the mono- or dibutyl forms. Consequently, most published data on the toxicity of organotin in aquatic ecosystems focuses on TBT and TEBT [5–8].

Harrison *et al.* [9] have published a compilation of the various analytical techniques developed for the determination of organotin compounds. These include gas chromatography (GC) coupled with various detection modes such as microwave induced plasma [10–12], direct current plasma [13,14], atomic absorption spectroscopy [2,8,15–17] and flame photometric detection [5,18]. High-performance liquid chromatography (HPLC) has also been used in conjunction with several detection modes including plasma emission spectroscopy [3,10], laser-enhanced ionization detection [6], and furnace atomic absorption spectroscopy [15,19]. Uden [20] has provided an up-to-date review of on-line chromatographic detection by plasma emission spectroscopy in response to the resurgence and potential demonstrated by atomic emission techniques in the past decade.

In the majority of analytical approaches employed in the determination of tin compounds, hydride generation or alkylation [2,5,16] has been used to form volatile derivatives. Although most of these paths have provided low detection limits, they exhibit some minor drawbacks including unpredictable interferences from organic reagents used for hydride generation, contamination of Grignard reagents with TBT and the possibility of molecular rearrangement of organotin compounds accompa-

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nying the Grignard reaction [6].

Several recent studies in our laboratory have addressed the interfacing of a capillary gas chromatographic and a HPLC system with an alternating current plasma (ACP) emission detector for selective element detection [21–25]. With an ACP detector, a uniform discharge is generated across two copper electrodes (3 mm diameter) in a controlled helium atmosphere. Therefore, when a primary supply of 115 V at 60 Hz feeds a step-up furnace transformer, an unrectified output voltage of 10 000 V at a current of 23 mA is obtained. The discharge is contained within a quartz tube with emitted radiation incident on the entrance slit of a monochromator, detected and processed. The device produces a remarkably stable signal as it is self-seeding, reigniting itself every half-cycle (120 times/s) and is easily constructed at modest cost.

The results of the present investigation demonstrate the suitability of GC–ACP emission detection in the analysis of environmentally significant organotin compounds. No hydride formation or alkylation reactions were performed on the species prior to detection. The procedure was applied to mussel, sediment, industrial sludge and wastewater samples.

EXPERIMENTAL

Materials

All solvents employed in this study were pesticide grade. Concentrated hydrochloric acid (Ultrex, J. T. Baker, Philipsburg, NJ, USA), hydrobromic acid (48%) (Fisher Scientific, Fair Lawn, NJ, USA) and organotin standards as tributyltin chloride and tetrabutyltin (Alfa Products, Ward Hill, MA, USA) with stated purities of 96 and 93%, respectively, were used without further purification. Stock solutions of TBT and TEBT were prepared in benzene and refrigerated until use. A regular unleaded Shell gasoline sample was obtained locally.

Instrumentation

The GC–ACP detector system arrangement has been described in detail elsewhere [24,25]. The system includes a Hewlett-Packard 5890A gas chromatograph, a single-beam McPherson grating monochromator (Model EU700 McPherson, Acton, MA), an optical bench equipped with an adjustable optical mount and 75-mm biconvex quartz lens (Stratford, CT), a R212 photomultiplier tube (Hamamatsu, Middlesex, NJ, USA) coupled to a McPherson Model 7640 voltage supply and a Hewlett-Packard 3392A integrator. A picoammeter (Model 414S, Keithley instruments, Cleveland, OH, USA) monitored the current generated by the photomultiplier tube. Data acquisition was simultaneously achieved with a Chrom-1AT chromatography data acquisition board controlled by the Lab Calc software (Galactic Industries, Salem, NH, USA) in conjunction with a Zenith AT microcomputer. The Lab Calc software package provided data smoothing algorithms to reduce random noise and permitted selectable sampling rates.

A DB-1 fused-silica capillary GC column (30 m × 0.32 mm I.D., 1.5 μm film thickness) (J&W Scientific, Folsom, CA, USA) was employed. Helium (Linde, ultra-high-purity grade) served as carrier gas at a linear velocity of 30 cm/s and as the plasma supporting gas at a flow-rate of 1800 ml/min. The temperatures of the split injector (split ratio of 100:1) and the interface were maintained at 220°C and 250°C, respectively. The operational parameters for the GC–ACP system appear in Table I.

Preparation of marine samples

Mussels (*Mytilus edulus*) and sediments were collected by hand from Boston Harbor at low tide and were refrigerated to minimize possible changes in-

TABLE I

GENERAL ACP DETECTOR OPERATING CONDITIONS USED IN THIS STUDY

Parameter	Condition
Helium flow-rate	1800 ml/min
Alternating current power output	11 000 V a.c.
Slit width	200 μm
Slit height	5 mm
Analytical wavelength for Sn(I)	300.91 nm
Picoammeter gain	$0.03 \cdot 10^{-6}$ to $10 \cdot 10^{-6}$ A
Picoammeter time constant	0.2 s
Photomultiplier tube and voltage	R212, −1000 V d.c.
Discharge tube	1 mm I.D. × 6 mm O.D. quartz
RC low-pass filter	Time constant 0.2 s

duced by bacterial action. Mussels were transported to the laboratory in plastic bags while sediments were transported in polycarbonate containers which were prewashed with acid. The industrial sludge and wastewater samples were collected at a local manufacturer of printed circuit boards. Synthetic ocean water was prepared according to the procedure of Parsons *et al.* [26].

The procedure used for the extraction of tin species from mussel tissue and water samples was a modification of the method reported by Martin-Landa *et al.* [27]. After the exterior of the mussel shells was rinsed thoroughly with distilled water, the shells were then opened and the soft tissue removed and washed with distilled water. The analytical sample set consisted of 6 samples, a blank and a spiked blank. The blank consisted of distilled water, glassware and the extracting reagent. The spiked blank was the same except for the addition of known amounts of tributyltin chloride and tetrabutyltin. A 12-g amount of tissue or 100 ml of volume of water (for the case of wastewater and ocean water) were transferred into a 250-ml separatory funnel. A 40-ml volume of concentrated hydrochloric acid was added and the funnel shaken for 2 h followed by a 2-h equilibration period. A 10-ml aliquot of hydrobromic acid (48%) was then added and the solution was allowed to stand for 15 min. A 100-ml aliquot of benzene was then added to the separatory funnel which was subjected to vigorous shaking action for 5 min. After 1 h the organic layer was removed.

The extraction method used for sediments and sludge was a modification of the method reported by Schebek and Andreae [8]. A 50-ml volume of benzene and 1 ml of 30% HCl were added to an appropriate amount of sediment. A PTFE-coated stirring bar was added and the mixture boiled under reflux conditions for 30–40 min in a water bath. After cooling to room temperature, the mixture was distributed among six 10-ml acid-washed glass tubes and centrifuged for 1 h at 1500 *g*. The supernatants were decanted, combined and transferred into a 50-ml volumetric flask and diluted to the mark with benzene. Each sediment sample was extracted and analyzed in triplicate.

Recovery studies with TBT and TEBT were performed by analyzing a given original sample (*e.g.* mussel tissue, sediment or water) and then spiking another portion of the original sample at a known level of TBT and TEBT and repeating the same procedure in triplicate; all subsequent GC analyses were also performed in triplicate.

RESULTS AND DISCUSSION

Spectral considerations

A general description of GC–ACP detector interface and the plasma discharge tube appears elsewhere [24,25]; however, in this study a modified quartz plasma discharge tube (2 cm × 1 mm I.D. × 6 mm O.D.) was utilized to enclose the plasma. Approximately 0.5 cm of the capillary column was inserted into the discharge tube after removal of the protective polyimide coating from this segment. A schematic diagram of the GC column–plasma discharge tube interface is shown in Fig. 1. The ACP detector plasma image was focused on the monochromator entrance slit by means of an adjustable optical mount and lens.

An ultrasonic nebulizer (common room humidifier) was subsequently used to generate headspace vapor of TEBT which was transported to the ACP by helium make-up flow. This procedure provided a constant mass introduction of TEBT into the plasma and the emission wavelength-intensity profile of

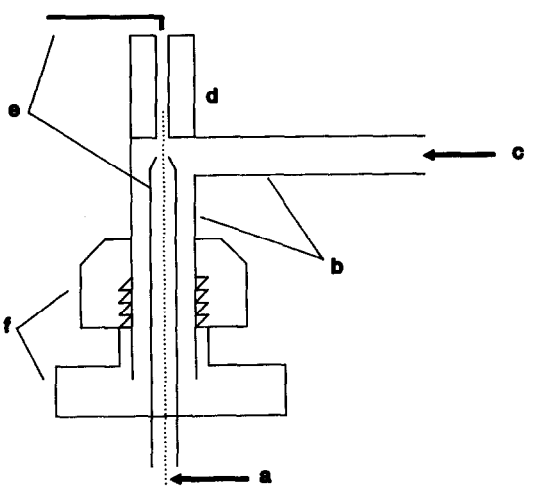

Fig. 1. Gas chromatographic column–plasma discharge tube interface. a = Column from the oven; b = 4 mm I.D. × 6 mm O.D. transfer and electrode holding tubing; c = helium plasma gas inlet; d = 1 mm I.D. × 6 mm O.D. plasma discharge tube; e = copper electrodes; f = 1/4 in O.D. Swagelok tee union.

the tin lines were then determined. Emission intensities at wavelengths of 231.72, 242.95, 254.66, 270.65 and 300.91 nm were observed and corresponded to relative intensities of 0.12, 0.67, 1.00, 0.07 and 0.75, respectively. The 300.91-nm line was selected as the analytical wavelength for this study because of its favorable relative intensity and location in background emission spectrum where no interference from OH, N_2, NH, H, He and O is observed. A tin hollow cathode lamp (Perkin-Elmer, Norwalk, CT, USA) was employed to confirm the analytical emission line (300.91 nm) by positioning the lamp such that its emission lines were incident on the entrance slit of the monochromator. The ACP spectral profile of this region is displayed in Fig. 2. The carbon backbone of TEBT was also eliminated as a source of molecular emission in this spectral region because a scan of benzene vapors in the ACP detector did not produce any major emission bands.

Linearity and detection limits

Calibration plots for TBT and TEBT were prepared by injecting seven repetitive injections of known amounts of each solute into the GC–ACP system. Linearity for each solute extended over three orders of magnitude. Correlation coefficients of the log–log plots were found to be 0.999 for TBT and 0.998 for TEBT, respectively. The detection limits of TBT and TEBT were estimated based on integrated baseline noise [28,29]. Detection limit may be defined as the amount of organotin species needed to produce a signal that is three times the standard deviation of the baseline noise divided by the sensitivity whereas sensitivity is defined as the slope of the calibration plot [30,31] multiplied by the peak-width at half height of the analyte peak to account for k' (capacity factor) [32]. Detection limits were calculated to be 131 and 116 pg/s as Sn for TBT and TEBT, respectively. These detection limits, when converted to mass detection limits, become 0.88 and 0.53 ng as Sn for TBT and TEBT, respectively, and compare favorably with the detection limits of 2.5 ng as Sn for TBT reported by Weber and Han [2]. The precision in response at twice the detection limit was under 8.5% relative standard deviation (n = 10) for both TBT and TEBT.

Selectivity

The selectivity ratio may be defined as the ratio of peak area response of the ACP detector at 300.91 nm per unit mass of tin to the response per gram weight of carbon in a given compound. The selectivity ratio of the ACP detector towards tin was determined by means of injecting 1-μl aliquot of standard solutions of selected organics and TEBT with a column temperature of 200°C and a slit width of 200 μm, after which the responses were then compared. Selectivity ratios of TEBT relative to several organic solvents are listed in Table II and compare favorably with those reported with a GC–microwave-induced plasma [11,12], exhibiting a range of $2.1 \cdot 10^4$ to $5 \cdot 10^5$ for the organic probes under consideration.

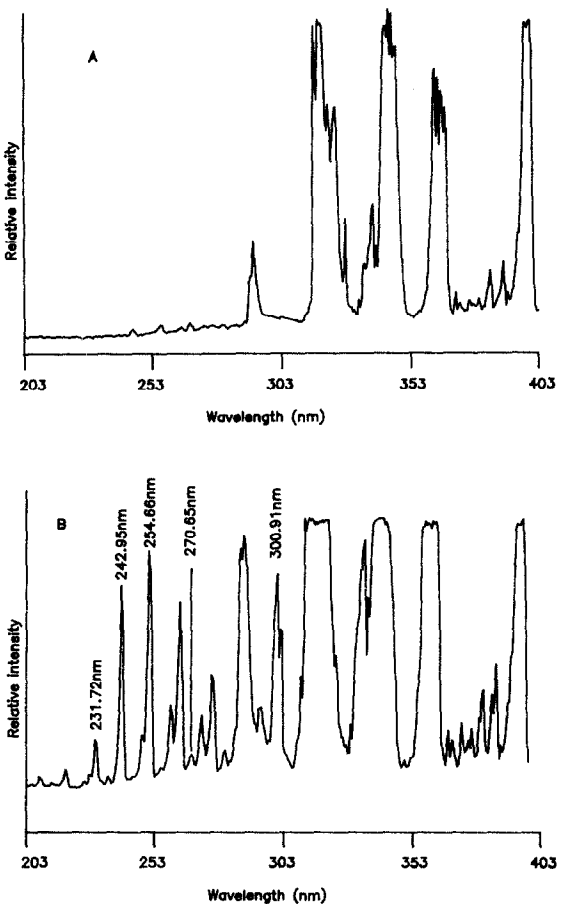

Fig. 2. (A) Background spectrum of the helium alternating current plasma from 203 nm to 403 nm; (B) emission wavelength profile of TEBT in the same spectral region as in (A) (see Table I for experimental conditions of the ACP detector).

TABLE II

ACP SELECTIVITIES OF TETRABUTYLTIN RELATIVE TO SELECTED ORGANICS

The selectivity ratio is defined as the ratio of the peak area response per gram Sn to the peak area response per gram of carbon in the indicated compound.

Compound	Selectivity ratio
Carbon disulfide	21 000
Chloroform	37 200
Ethylene disulfide	53 200
n-Butanol	87 400
Trichloroethylene	90 100
n-Heptane	99 400
Cumene	133 200
n-Hexane	142 300
Pyridine	225 200
Benzene	500 300

TABLE III

RECOVERY OF TRIBUTYLTIN CHLORIDE AND TETRABUTYLTIN COMPOUNDS FROM SPIKED SAMPLES

	Recovery ± S.D. (%) (n = 3)	
	Tributyltin chloride	Tetrabutyltin
Distilled water	98.78 ± 1.19	101.44 ± 1.08
Ocean water	89.54 ± 0.76	91.11 ± 1.22
Sediment	97.67 ± 0.78	93.29 ± 1.74
Wastewater	77.26 ± 1.94	83.33 ± 1.10
Sludge	79.97 ± 1.10	84.81 ± 1.37

Analytical applications

Several applications were conducted in order to demonstrate the practicality and selectivity underlying the ACP response to organotin species present in complex matrices. An appropriate amount of each sample was spiked with a known amount of organotin standard and the appropriate extraction procedure carried out as previously described. The chromatogram presented in Fig. 3 illustrates the separation of TBT (4.8 ng) and TEBT (4.4 ng) in a benzene extract of distilled water initially containing TBT and TEBT at concentrations of 120 and 106 μg/ml, respectively; likewise a chromatogram of a benzene spiked extract (containing TBT and TEBT) of mussels from Boston Harbor appears in Fig. 4. Percent recovery data for TBT and TEBT spiked in various matrices is listed in Table III and ranges from 77 to 101%. The lower recoveries of organotin from wastewater may be due to associ-

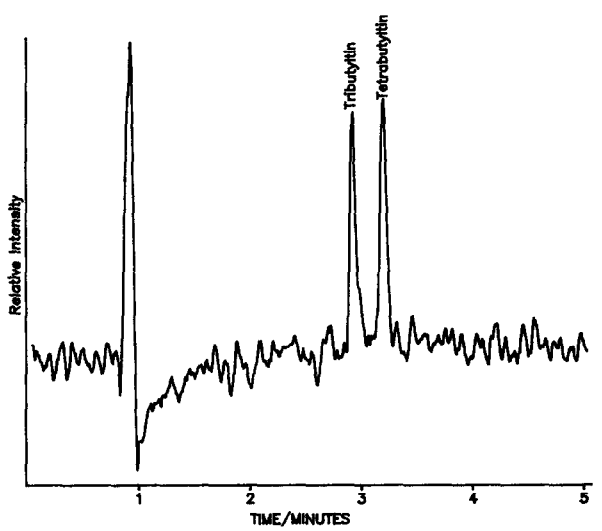

Fig. 3. Chromatogram of spiked distilled water extract; indicated peaks represent 4.8 ng of tributyltin chloride and 4.4 ng of tetrabutyltin. Conditions: column temperature, 170°C; interface temperature 200°C; split ratio, 100:1; amount injected, 1 μl; 0.03 · 10^{-6} A f.s.

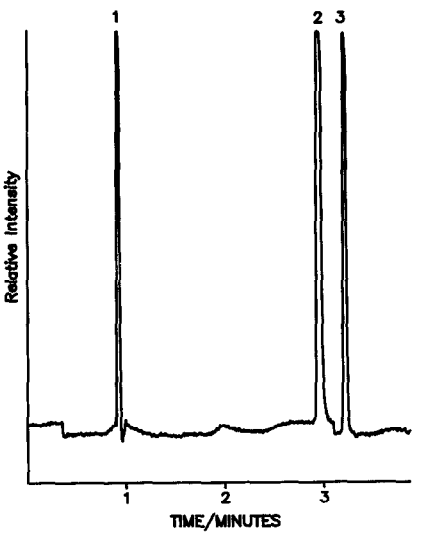

Fig. 4. Chromatogram of extract of mussel tissue from Boston Harbor spiked with tributyltin chloride and tetrabutyltin. Peaks: 1 = solvent; 2 = TBT; 3 = TEBT. Conditions: column temperature, 170°C; interface temperature, 200°C; split ratio, 100:1; 0.1 · 10^{-6} A f.s.

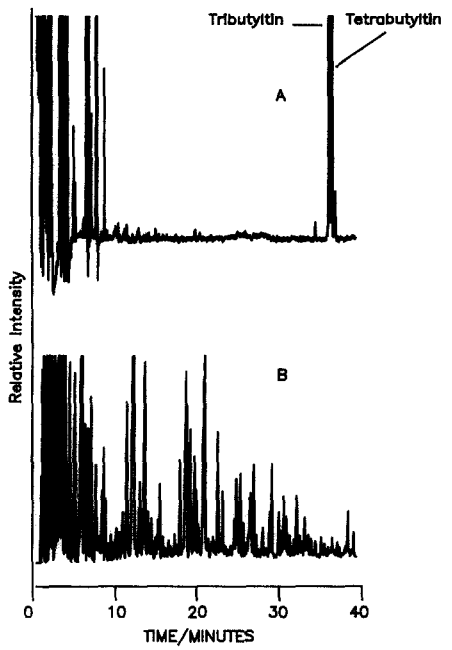

Fig. 5. (A) Chromatogram of regular unleaded gasoline illustrating the detection of 64 ng TBT (26 ng Sn) and 28 ng TEBT (9.6 ng Sn) with ACP detector at 300.91 nm, $0.1 \cdot 10^6$ A f.s. (B) Chromatogram of regular unleaded gasoline detected by flame ionization detection; conditions: 35°C (5 min) to 100°C at 4°C/min then to 230°C at 5°C/min.

ative effects with other organics present whereas secondary partitioning effects may be responsible for the lower recoveries in the sludge samples studied.

An additional application of the detection of organotin in gasoline, a potentially interfering matrix, was then examined to demonstrate the sensitivity and selectivity of the ACP detector. A 5-ml sample of regular gasoline was spiked with 500 μl of a solution containing 192 ng of TBT and 85 ng of TEBT and a 1-μl aliquot was then chromatographed. Parallel ACP and flame ionization detection chromatograms are shown in Fig. 5 where the indicated peaks represent 64 ng TBT (26 ng Sn) and 28 ng TEBT (9.6 ng Sn). Although TBT is not a additive to gasoline, the gasoline matrix may be viewed as potentially problematic, as evidenced by the irregular appearance at the beginning of the chromatogram in Fig. 5A due to the rapid coelution of many hydrocarbons associated with gasoline. This coelution results in plasma instability and carbon background emission and has been observed in previous studies [21,22]. The coelution of these components in Fig. 5 also demonstrates that the ACP detector does not extinguish with the injection of a large solvent plug.

Hydrogen doping of plasma gas

The addition of hydrogen as a doping agent to helium-supported plasmas has been shown to produce signal enhancement in some determinations [12]; signal enhancement factors of two and three have been reported for elements capable of undergoing hydride formation [33]. In the present study, however, the addition of 0.5 to 3 ml/min of hydrogen gas to the helium flow did not produce any enhancement of organotin signals. Also, the hydrogen flow creates intense heating of the plasma and causes added stress on the walls of the discharge tube resulting in reduced life-time of the discharge tube.

CONCLUSIONS

The ACP detector is a viable alternative to other element-selective devices for the detection of organotin species and offers considerable potential. The detector is easily assembled and interfaced with chromatographic equipment at modest cost. The device exhibits a remarkably stable signal because the plasma is self-seeding and reignites itself every half cycle which is 120 times per second for the 60 Hz power supply. A tesla coil is not required to commence operation of the plasma if the ac voltage is greater than the breakdown voltage. As a result, the ACP detector can tolerate high mass flow-rates of solvent without extinguishing and, thus, requires no venting valve which lends itself to a less complex interface design and minimizes band broadening.

The reduction of background spectral interference produced by molecular emission has not been investigated with the ACP detector to date. The use of techniques such as lock-in amplifiers, oscillating quartz plates incorporated within a monochromator and pulsed power sources often lead to an improved signal to noise ratio and better selectivity. These fruitful avenues remain to be studied.

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