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Note

Analysis of butyltin compounds by gas chromatography

Comparison of flame photometric and atomic absorption spectrophotometric detectors

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The presence of *n*-butyltin^{1,2} and methyltin²⁻⁴ species at concentrations of ng/l to µg/l has been reported in a variety of natural waters as well as rain, and is probably due to the use of organotin compounds as stabilizers for polyvinyl chloride, as catalysts and as pesticides⁵. Our determination of *n*-butyltin species in Canadian waters² was done by gas chromatography (GC) of their volatile *n*-pentyl derivatives (Bu_nPe_{4-n}Sn), with detection by a modified flame photometric detector⁶. Although this detector worked well initially, our experience over the past three years has shown that its response is severely diminished by injections of large amounts of (i) organotin compounds, *i.e.*, more than 10² ng, (ii) tropolone, which is used in extracting butyltin species and Sn⁴⁺ from water⁶, and (iii) organic co-extractives from natural waters and sediments. These difficulties can usually be avoided through a judicious choice of concentration of butyltin species to inject for GC, or the use of a silica gel column to remove tropolone and organic co-extractives from water and sediment; however, the inadvertent "poisoning" of the flame photometric detector necessitates a time-consuming disassembly of the detector and removal of a white powder (presumably SnO₂) by mechanical and chemical means from accessible metal and optical surfaces, followed by repeated injections of chlorofluorocarbons^{4,7} at 250°C to restore the sensitivity of the detector. The whole process has occasionally taken as long as 3 weeks. In addition, the flame needs to be kept on continuously in order to maintain detector sensitivity. Faced with these inconveniences, we have sought a more reliable method. The gas chromatographic-atomic absorption spectrophotometric (GC-AAS) method of Chau *et al.*^{8,9}, which used a heated quartz furnace in the light path for AAS, was appealing since there could be no fouling of the optical system by combustion products, and the relatively inexpensive (\$30 CDN) quartz furnaces could be replaced easily. This note compares the performance of AAS with that of flame photometric detection (FPD) for the detection of butylpentyltin species.

EXPERIMENTAL

Materials

Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) was obtained from Chroma-

tographic Specialties (Brockville, Ontario, Canada). The sources of all other chemicals, and the procedure for the preparation of the butylpentyltin standards ($\text{Bu}_n\text{Pe}_{4-n}\text{Sn}$) were given previously⁶.

GC-FPD analysis

The packed column and operating conditions were described previously⁶. For the four butylpentyltin species, the column temperature was held at 135°C for 10 min, followed by a 50°C/min rise to 230°C, at which temperature the column was held for 2 min. This temperature program was necessary to preserve the sensitivity of the detector, and to elute a high-boiling organotin compound which occasionally contaminated bottles of the *n*-pentylmagnesium bromide derivatizing agent.

GC-AAS analysis

A Tracor 550 gas chromatograph was connected via a heated transfer line to a quartz tube furnace in the light path of a Perkin-Elmer 4000 atomic absorption spectrophotometer. The following conditions were used.

GC. 1.8 m × 2 mm I.D. glass column packed with 3% OV-225 on Chromosorb W (80–100 mesh); carrier gas, N_2 , 20 ml/min; injection port temperature, 250°C; oven temperature program, 160°C for 2 min, then 6°C/min to 250°C, with final hold for 2 min.

Transfer line. 1 m × 1/32 in. I.D. nickel tubing, connected to the column and quartz tube furnace by Swagelok fittings. The transfer line extends into the furnace assembly, ending just above the light path of the furnace; the line is wrapped with heating tape and kept at 300°C.

Quartz tube furnace. This is supplied by a local glassblower, similar in dimensions to that described previously⁸. The furnace was wrapped with Chromel "A" electrical heating wire (Fisher Scientific, Toronto, Ontario, Canada), insulated with firebrick and mounted on the burner of the Perkin-Elmer 4000 atomic absorption spectrophotometer to take advantage of the light path alignment controls on the burner. The furnace temperature, with both electrical heating and the flame on, was 900°C. The combustion gases (H_2 at 100 ml/min and air at 20 ml/min) were introduced to the furnace through a T-joint at the top of the furnace assembly; they ignited automatically when the furnace was heated electrically.

AAS. Electrodeless discharge tin lamp at 224.6 nm, with deuterium background correction. It was necessary in our laboratory to have voltage regulators for both the atomic absorption spectrophotometer and the lamp power supply. The output from the spectrophotometer was filtered through a passive RC filter (*cf.*, ref. 10) and connected to a Spectra-Physics 4000 recorder-integrator. The RC filter ($R = 47$ kohm, $C = 0.24$ μF , in series, with time constant of 11.3 msec) lowered the detection limits of the butyltin species by factors of 2–3.

RESULTS AND DISCUSSION

The $\text{Bu}_n\text{Pe}_{4-n}\text{Sn}$ peaks detected by AAS are generally sharper than those detected by FPD, in which case tailing of organotin peaks has been ascribed to the geometry of the detector⁷. Table I shows that for the detection of the three butyltin species and Sn^{4+} , the response of the atomic absorption spectrophotometer is rough-

TABLE I

ANALYSIS OF BUTYLTIN SPECIES AND Sn^{4+} BY GC-FPD AND GC-AAS

The butyltin species and Sn^{4+} , injected together, are detected as pentyl derivatives; the FPD data are from ref. 6.

Species	Minimum detectable amount (pg)		Linear response range (pg)	
	FPD	AAS	FPD	AAS
Bu_3Sn^+	$1.5 \cdot 10^2$	$1.5 \cdot 10^2$	$1.5 \cdot 10^2$ – $3.0 \cdot 10^4$	$1.5 \cdot 10^2$ – $1.5 \cdot 10^4$
$\text{Bu}_2\text{Sn}^{2+}$	$1.2 \cdot 10^2$	$1.4 \cdot 10^2$	$1.2 \cdot 10^2$ – $3.0 \cdot 10^4$	$1.4 \cdot 10^2$ – $1.4 \cdot 10^4$
BuSn^{3+}	$1.0 \cdot 10^2$	$1.1 \cdot 10^2$	$1.0 \cdot 10^2$ – $2.0 \cdot 10^4$	$1.1 \cdot 10^2$ – $1.1 \cdot 10^4$
Sn^{4+}	$6.0 \cdot 10$	$6.3 \cdot 10$	$6.0 \cdot 10$ – $2.5 \cdot 10^4$	$6.3 \cdot 10$ – $6.3 \cdot 10^4$

ly equal to that of the flame photometric detector. Like the latter, the quartz furnace in the spectrophotometer can be poisoned by injections of more than 10^2 ng Sn, but unlike the latter, recovery of detector sensitivity by repeated injections of Freon 113 is faster, and in any event the furnace is easily replaced. Although the quartz furnace of the atomic absorption spectrophotometer is less sensitive to the presence of tropolone or organic co-extractives from water and sediment than is the flame photometric detector, it is good practice to remove these interfering substances with an activated silica column with hexane as eluant. We have found that the performance of the quartz furnace is maintained for 2–3 months of up to 25 injections per working day, and that the flame does not have to be left on continuously. In summary, although the sensitivity of the atomic absorption spectrophotometer is approximately the same as that of the flame photometric detector, we believe that the ease of replacement of contaminated quartz tube furnaces, and the potential applicability of the GC-AAS technique to the detection of other volatile organometallic compounds, make it preferable to the GC-FPD method.

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