Journal of Chromatography, 566 (1991) 207–214
Biomedical Applications
Elsevier Science Publishers B.V., Amsterdam

CHROMBIO. 5778

Comparison of sulphur-mode and tin-mode flame photometric detectors for the gas chromatographic determination of organotin compounds

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(First received October 8th, 1990; revised manuscript received December 11th, 1990)

ABSTRACT

A comparison of sulphur-mode (393 nm) and tin-mode (610 nm) flame photometric detectors for the gas chromatographic determination of butyl- and phenyltin compounds is described. The chromatographic peaks of the butyl- and phenyltin compounds were well separated, and high sensitivity was achieved in both modes; however, the tin-mode was more specific for tin compounds than the sulphur-mode. The absolute detection limits with the sulphur-mode and the tin-mode were 3.9–7.6 pg and 2.6–5.1 pg as tin, respectively. The application of the tin-mode gas chromatographic method to the determination of organotin compounds in fish is presented. For this application, organotins are extracted (as chloride) with hydrochloric acid and *n*-hexane–benzene (3:2, containing 0.05% tropolone) and the extracts are pentylated by a Grignard reagent prior to gas chromatography. The absolute recoveries of butyl- and phenyltin compounds added to fish samples ranged from 68.5 to 84.4% (the coefficients of variation were less than 6.6% for all substances, $n = 8$). Significant amounts of three organotin compounds (di- and tributyltin and triphenyltin) in fish samples were detected by this method. This technique may have application for other organotin compounds and the monitoring of butyl- and phenyltin compounds in the environment.

INTRODUCTION

Organotin compounds have been used as agricultural pesticides, antifoulants and stabilizers for vinyl chloride polymers. The increased production and consumption of organotin chemicals are due primarily to its wide range of industrial applications [1]. Some derivatives of organotin compounds are comparatively highly toxic to mammals [2]. Environmental pollution from these compounds may be a serious problem.

Flame photometric detection (FPD) has been employed in the gas chromatographic (GC) determination of organotin compounds. Aue and Flinn [3] reported the use of FPD in the 'open-mode' (no filter or mask) for the selective detection of volatile tin species. In recent years, we have developed an analytical method for organotin compounds by using capillary GC with a sulphur-mode (S-mode) (393 nm) filter [4,5]. However, the determination of organotin compounds using an S-mode detector requires relatively complex and mathematical

0378-4347/91/$03.50

analyses, because concentrations are given by exponential responses of these compounds [5].

We have now examined tin-mode (Sn-mode) (610 nm) FPD for the GC determination of organotin compounds, and obtained a linear correlation between the peak heights and the amount of tin. We have also applied FPD equipped with an Sn-mode filter for the simultaneous GC-determination of organotin compounds in fish.

EXPERIMENTAL

Materials

Triphenyltin chloride (Ph_3SnCl), tributyltin chloride (Bu_3SnCl) and dibutyltin dichloride (Bu_2SnCl_2) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Diphenyltin dichloride (Ph_2SnCl_2), phenyltin trichloride ($PhSnCl_3$) and butyltin trichloride ($BuSnCl_3$) were obtained from Alfa Products (Danvers, MA, U.S.A.). Pentylmagnesium bromide (2.0 *M* in diethyl ether) was from Aldrich (Millwaukee, WI, U.S.A.). Tropolone was from Sigma (St. Louis, MO, U.S.A.). Florisil PR was from Wako (Osaka, Japan), activated at 130°C for 6 h and rinsed with *n*-hexane before use. All other chemicals and solvents used were commercial products of reagent grade.

Fish samples (yellow tails) were from retail markets.

Standard solution

Each organotin compound was dissolved in tetrahydrofuran (THF) at a concentration of 12.0–25 mg per 10 ml as a stock solution and stored at 4°C. Working standard solutions were prepared by diluting the stock solution with *n*-hexane–benzene (3:2, containing 0.05% tropolone). Recovery experiments were carried out by adding each tin stock solution, diluted with distilled water, to fish samples. The final THF concentration of both the *n*-hexane–benzene and water solutions was under 1.2%.

Preparation of samples

Samples for GC were prepared by our previous procedure [5] with a slight modification. A fish sample was homogenized in a Universal Homogenizer (Nihon Seiki, Tokyo, Japan), and *ca.* 5 g of the homogenate were placed in a centrifuge tube with a glass stopper, and 10 ml of saturated sodium chloride solution and 0.5 ml of concentrated hydrochloric acid (35%) were added to the tube. The mixture was extracted twice with 10 ml of *n*-hexane–benzene (3:2, containing 0.05% tropolone) by agitating for 20 min in a mechanical shaker. After each shaking, the mixture was centrifuged for 10 min at 1800 *g*. Each organic layer was collected. The combined organic extracts were dried with 0.5 g of anhydrous sodium sulphate, then transferred to a separatory funnel, and 1 ml of pentylmagnesium bromide was added. The reaction mixture was allowed to stand for 20 min

at room temperature and subsequently extracted with 25 ml of hydrochloric acid (0.5 *M*) for 2 min. The organic layer was rinsed with 25 ml of distilled water and then evaporated at 40°C after drying with 0.5 g of anhydrous sodium sulphate. The residual material was dissolved in 2 ml of *n*-hexane and was applied to a Florisil column (8 g, I.D. 10 mm). The pentyl (Pe) derivatives of organotin compounds were eluted with 25 ml of *n*-hexane. The eluate was evaporated to near dryness and made up to 5 ml with toluene for GC. A 0.5-μl volume of the sample solution was injected into the chromatograph.

Calibration curves

A 20-ml volume of working standard solutions (each organotin compound 0.05–0.5 μg/ml) used for calibration curves was pentylated as above, but without any extraction and Florisil column chromatography. The calibration curves were constructed by plotting the peak heights *versus* the amount of tin.

Gas chromatography

Samples were analysed using a Hewlett-Packard (Avondale, PA, U.S.A.) Model 5890A gas chromatograph equipped with a flame photometric detector. The detector was operated in the S-mode (filter 393 nm) or Sn-mode (filter 610 nm). The detector output was recorded using an HP 3396A integrator (Hewlett-Packard). A 12.5 m × 0.2 mm I.D. Ultra 1 (Hewlett-Packard) capillary column (100% dimethyl polysiloxane gum, 0.33-μm film) was used. Injections were performed in the splitless mode, with a purge time of 2 min. The injector and the detector temperatures were 250°C. The oven temperature was initially 80°C for 2 min, then programmed at 30°C/min to 150°C, from 150 to 200°C at 5°C/min, and finally from 200 to 230°C at 10°C/min; it was then held isothermal until the end of the run (20 min). The flow-rate of nitrogen make-up gas was 28 ml/min. Helium was used as the carrier gas at a flow-rate of 2 ml/min and as the purge gas at 50 ml/min.

RESULTS AND DISCUSSION

Chromatographic characterization

The photometric detection mechanism is attributed to light emission of the excited organotin species in the detector flame [3]. Takahashi *et al.* [6] have reported that the flame emission band spectra, originating from SnH molecule in a strongly reductive hydrogen flame, have a strong band head at 609.5 nm. The wavelength of 610 nm was used in an analysis of organotin compounds by Müller [7].

We applied an Sn-mode filter for the GC determination of organotin compounds and compared the results with those obtained with an S-mode filter. Fig. 1 shows the gas chromatograms of pentylated organotins (mono-, di-, and tributyltin and mono-, di- and triphenyltin compounds). The chromatograms were

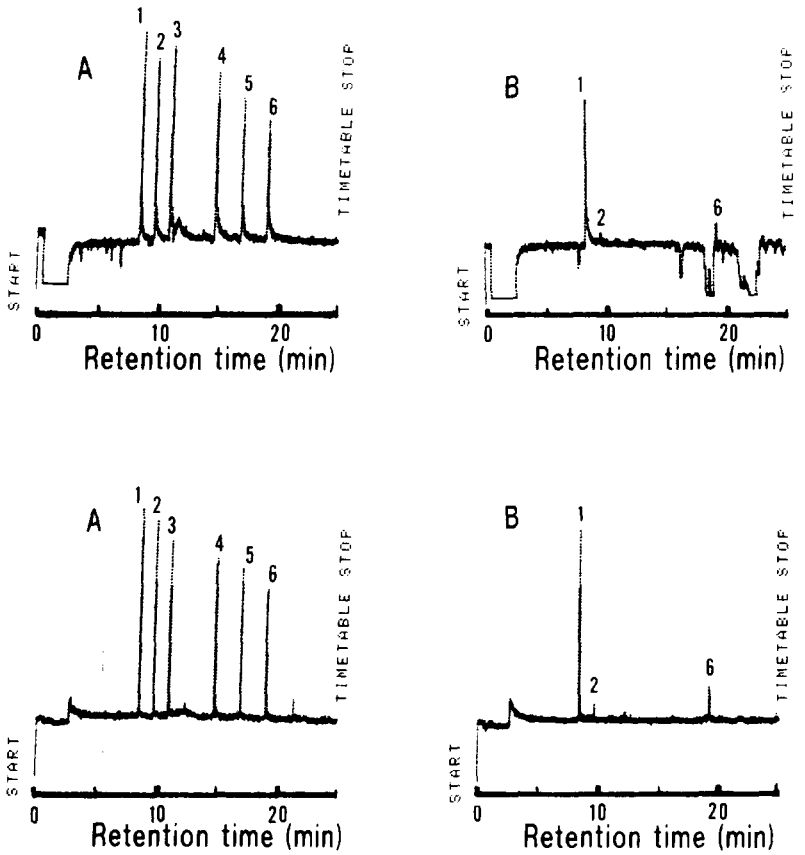

Fig. 1. Comparison of S-mode (upper) and Sn-mode (lower) chromatograms obtained with pentyl derivatives of organotin compounds. (A) Standard mixture; (B) non-spiked samples from fish. Peaks: 1 = $PeBu_3Sn$; 2 = Pe_2Bu_2Sn; 3 = Pe_3BuSn; 4 = Pe_3PhSn; 5 = Pe_2Ph_2Sn; 6 = $PePh_3Sn$. GC conditions are given in Experimental.

obtained with standard solutions (the amounts of compounds injected were as follows: $PeBu_3Sn$, 38.5 pg; Pe_2Bu_2Sn, 40.7 pg; Pe_3BuSn, 40.1 pg; $PePh_3Sn$ 64.1 pg; Pe_2Ph_2Sn, 51.1 pg; and Pe_3PhSn 75.8 pg as tin) and with the extracts from fish samples. All peaks corresponding to organotin compounds were well separated and showed high sensitivity in both modes. The Sn mode was more specific for tin compounds than the S mode. Consequently, the chromatograms with the Sn-mode filter have a more stable baseline and sharper peaks than those with the S-mode filter, as shown in Fig. 1.

The absolute detection limits with the S mode, determined on the basis of a signal-to-noise ratio of 2, were in the range 3.9–7.6 pg as tin. In the case of the Sn mode, the absolute detection limits were in the range 2.6–5.1 pg as tin.

Calibration

The calibration curves were determined as described in the text and are shown in Fig. 2. The detector response with the S-mode filter is linearly related to the working range concentration of organotin compounds on the log–log paper. In contrast, response with the Sn-mode filter is linearly related on the ordinary

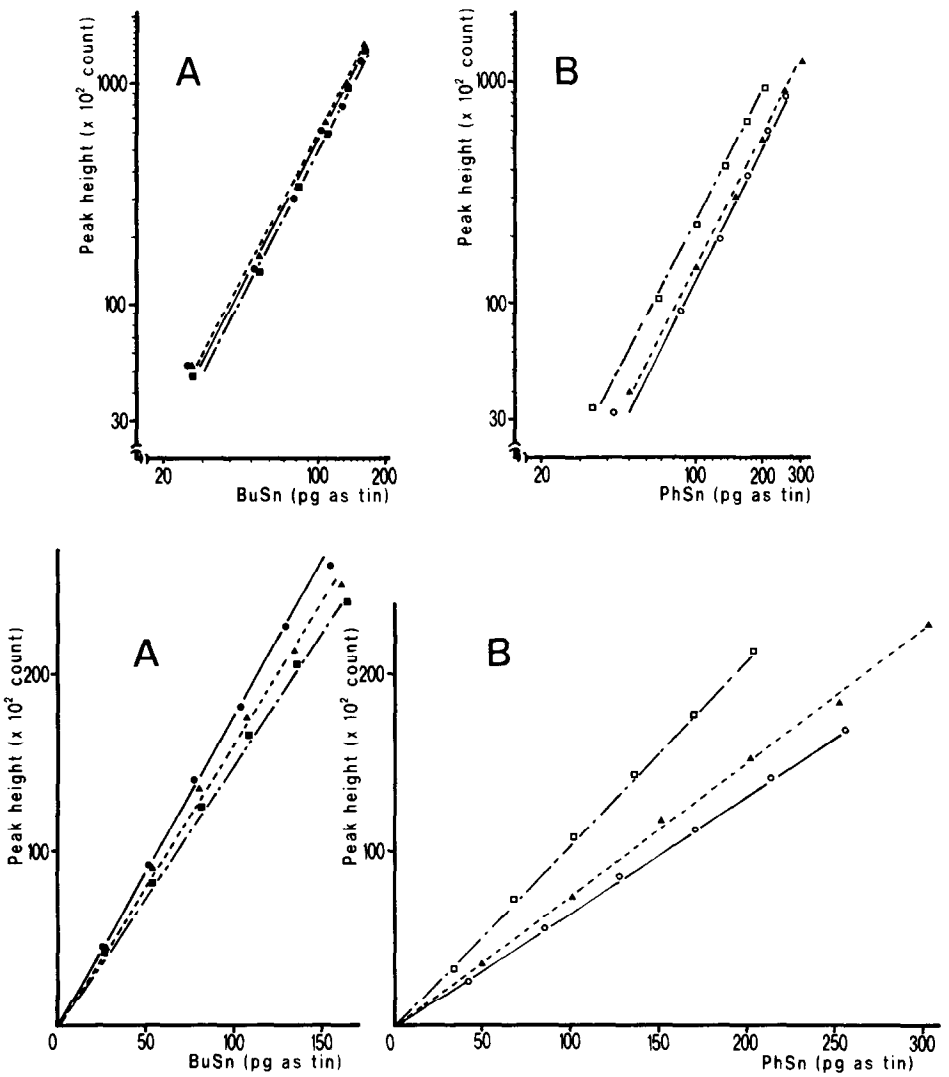

Fig. 2. Calibration curves of organotin compounds using the S-mode (upper) and the Sn-mode (lower) detectors. (A) Butyltin compounds; (B) phenyltin compounds. (●) $PeBu_3Sn$; (■) Pe_2Bu_2Sn; (▲) Pe_3BuSn; (○) $PePh_3Sn$; (□) Pe_2Ph_2Sn; (△) Pe_3PhSn.

section paper. With the Sn-mode filter, the order of the relative sensitivity from the calibration curve slopes was as follows: tributyl > monobutyl > dibutyl > diphenyl > monophenyl > triphenyl.

Precision and accuracy

The precision (estimated as the coefficients of variation, C.V.) and the accuracy (estimated as the percentage differences between the mean values and the known concentrations) of the S-mode and the Sn-mode detectors were quantified using five aliquots of the same fish samples spiked with organotin compounds (concentrations: $PeBu_3Sn$, 77.0 ng; Pe_2Bu_2Sn, 81.4 ng; Pe_3BuSn, 80.2 ng; $PePh_3Sn$, 128.2 ng; Pe_2Ph_2Sn, 102.2 ng; and Pe_3PhSn 151.6 ng as tin per gram of tissue) on five consecutive days. The calibration curve was used to determine the precision and the accuracy, by analysis of the same fish samples containing six organotin compounds at four different concentrations.

The values of the C.V. were less than 3.8% for all organotin compounds (range 2.5–3.8%) in the S-mode detector and 3.4% (range 2.1–3.6%) in the Sn-mode detector. The accuracy was less than 3.6% (range 2.1–3.6%) in the S-mode detector and 3.2% (range 1.9–3.2%) in the Sn-mode detector.

Application of Sn-mode detector

The Sn-mode GC–FPD method was applied to the determination of organotin compounds in fish. The samples were prepared as described in Experimental. Corresponding gas chromatograms are shown in Figs. 1 and 3. These chromatograms indicate that there are no serious interferences from other substances in fish.

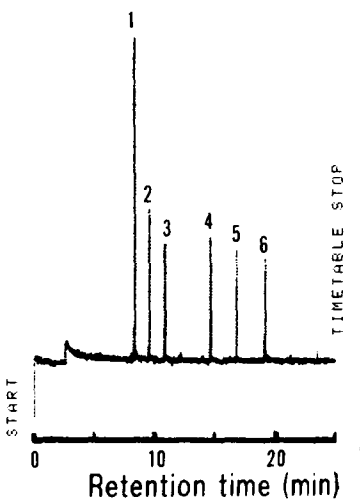

Fig. 3. Gas chromatogram of fish samples spiked with butyltin (Bu_3SnCl 77.0 ng/g, Bu_2SnCl_2 81.4 ng/g, $BuSnCl_3$ 80.2 ng/g) and phenyltin compounds (Ph_3SnCl 128.2 ng/g, Ph_2SnCl_2 102.2 ng/g, $PhSnCl_3$ 151.6 ng/g as tin). Peaks as in Fig. 1.

TABLE I

ABSOLUTE RECOVERY OF BUTYLTIN AND PHENYLTIN COMPOUNDS FROM FISH TISSUE

Compound	Amount added (μg of tin compounds)	Recovery (mean ± S.D., $n=8$) (%)
$BuSnCl_3$	0.95–3.81	76.2 ± 1.2
Bu_2SnCl_2	1.04–4.16	78.8 ± 2.4
Bu_3SnCl	1.06–4.22	68.5 ± 4.5
$PhSnCl_3$	1.93–7.71	74.4 ± 2.2
Ph_2SnCl_2	1.48–5.92	84.4 ± 1.1
Ph_3SnCl	2.08–8.32	72.5 ± 3.4

The absolute recoveries of six organotins added to 5 g of homogenized fish samples were evaluated (Table I). The C.V. of the yield were less than 6.6% for all the substances (range 1.3–6.6%). Some variations in the average absolute recoveries were seen for different tin compounds. The detection limits were dependent on the concentration of the sample solution injected into the chromatograph. In the present experiment, the detection limits of the six organotin compounds in fish samples were in the range 3.8–4.3 ng/g for butyltin compounds and 5.4–7.2 ng/g for phenyltin compounds (expressed as tin) for a GC sample volume of 5 ml.

Peak heights showed a linear relationship with the concentrations of the butyl- and phenyltin compounds in the Sn mode. Therefore, it is possible to use the standard addition method to calculate the amount of organotin compounds in

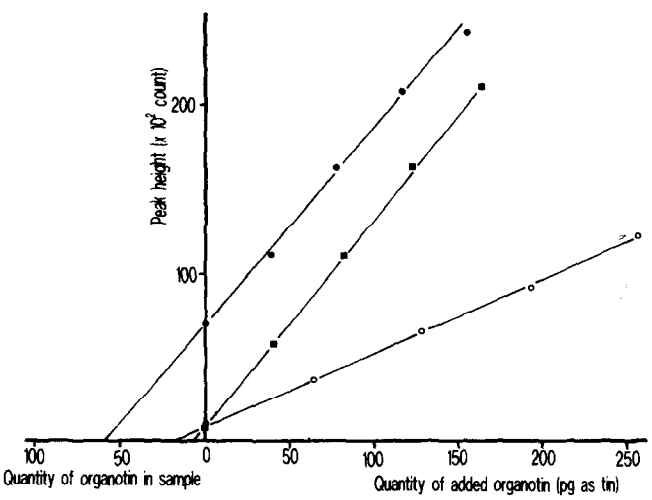

Fig. 4. Determination of organotin compounds in fish using the standard addition method. (●) Tributyl tin; (■) dibutyltin; (○) triphenyltin.

the fish. Fig. 4 shows calibrations of di- and tributyltin and triphenyltin. The concentrations of the compound in fish samples were 13 ng/g for dibutyltin, 119 ng/g for tributyltin and 34 ng/g for triphenyltin (as tin).

We think this method will be applicable for the monitoring of butyl- and phenyltin compounds in the environment.

ACKNOWLEDGEMENTS

The authors thank Ms. Katsuko Takakuwa and Ms. Tahori Sekiya for valuable technical assistance.

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