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Optimization study for the speciation analysis of organotin and organogermanium compounds by on-column capillary gas chromatography with flame photometric detection using quartz surface-induced luminescence

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Abstract

A laboratory-designed flame photometric detector (FPD) using quartz surface-induced luminescence was used for the on-column capillary chromatographic determination of organotin and organogermanium compounds. The detector response depends on gas flow-rates, detector temperature and the operation mode. The linear range is up to four orders of magnitude for organotin and up to three orders of magnitude for organogermanium compounds. The minimum detectable amounts, defined as the signal equal to three times the standard deviation (3σ) of the baseline noise, vary with the species detected and range from 0.7 to 2.3 pg for ethylated butyl- and phenyltin species and from 50 to 100 pg for pentylated dimethyl-, trimethyl- and tetrabutylgermanium. The determination of butyltin compounds in water and sediments was evaluated in comparison with a GC–AAS system. The proposed method is simple, highly sensitive and reproducible.

Keywords: Detectors, GC; Environmental analysis; Water analysis; Sediments; Organotin compounds; Organogermanium compounds

1. Introduction

Owing to its potential environmental accumulation and harmful biological effects, organometallic compounds, such as butyltins, are of growing public concern. As a consequence, many accurate, precise and quantitative instrumental methods have been developed in recent years to monitor their occurrence in the environment. Methods developed mainly include coupled techniques, based on a chromatographic separation followed by atomic absorption spectrometric (AAS) [1–4], atomic emission spectrometric (AES) [5–7], mass spectrometric (MS) [8,9] or flame photometric detection (FPD) [10–15].

GC–FPD as a direct detection technique is widely recognized as one of the most interesting techniques for organotin speciation analysis owing to its wide availability, low cost, competitive performance and high detection sensitivity.

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During the last 15 years, numerous organotin studies in the environment were performed by using GC–FPD, thus placing this technique at the forefront of organotin speciation analysis [11,14,16].

Since Brody and Chaney [17] developed the first version of FPD for sulphur and phosphorus determinations, the design has subsequently been improved by a number of workers in order to increase the flexibility, reliability and sensitivity of flame photometric analysis [16,18–24]. Dagnall et al. [18] first demonstrated that in a cool nitrogen–hydrogen diffused flame, organotin compounds are converted into SnH, which gives a red emission in the gas phase at ca. 610 nm and can be used for a highly sensitive determination. In a typical FPD, about 0.1 ng of tetrapropyltin could be detected [16]. By choosing appropriate interference filters (e.g., 610 nm), further improvements in detection limits appeared possible [20,21]. Measurements at 610 nm emission are most commonly used and form the basis of a commercial instrument for the flame photometric detection of tin.

In a later study, another strong emission of metal hydrides, identified as quartz surface-induced luminescence in the blue region, centred at ca. 390 nm, was observed. For tin this emission is up to 100–1000 times more sensitive than the more commonly used gas-phase luminescence [16]. It was further proved that the response was influenced by the shape and the size of the quartz enclosure and, therefore, various burner configurations for flame photometric detection have been developed [22–25]. However, most of this research was designed to explore the response mechanism [26,27] and only a few publications have described the application of the more sensitive blue emission for determinations in real samples [28,29]. To our knowledge, no attempt towards the application of a similar blue emission mode for germanium has been carried out. Although this emission mode appears attractive owing to its sensitivity, initial problems related to instrumental aspects and the stability of the emission intensity limited its analytical utility.

This paper describes a laboratory-designed flame photometric detector using quartz surface-induced luminescence. An optimization study of the detector parameters was carried out with the aim of establishing an analytical protocol for the implementation of organotin and organogermanium detection in a GC effluent. This system was used for the determination of tin species in real samples and evaluated in comparison with a previously established GC–AAS technique [3,30,31].

2. Experimental

2.1. Apparatus

2.1.1. GC–FPD

A CP-9001 gas chromatograph (Chrompack, Middelburg, Netherlands) equipped with an air-cooled on-column injection system was used. A schematic diagram of the GC–FPD system is shown in Fig. 1. The configuration of the detector is similar to that described previously [28], but with the following two improvements. First, possible adsorption of the organometallic compounds on the bottom part of the burner was circumvented by heating this part. Hydrogen and air were kept at the same temperature at their point of entry into the burner tip. Second, the chromatographic resolution was increased and the peak shape was improved by directly inserting the capillary column into the innermost tube of the FPD burner at about 10 mm below the burner tip. This ensured the direct transfer of the chromatographic effluent to the burner tip, avoiding premixing of the GC effluent with the flame gas.

The detector was mounted on the same housing by removing the commercial FPD system. It was a combination of a flame burner and an optical system. The burner was made of three coaxial silver-soldered stainless-steel tubes. The innermost tube was used for the column effluent. To obtain a stable flame, air was fed into the middle tube and hydrogen was fed into the outermost tube; this is the reverse arrangement compared with a commercial FPD burner. A 75 mm × 6 mm I.D. clean and transparent quartz tube was slipped over the burner to provide the

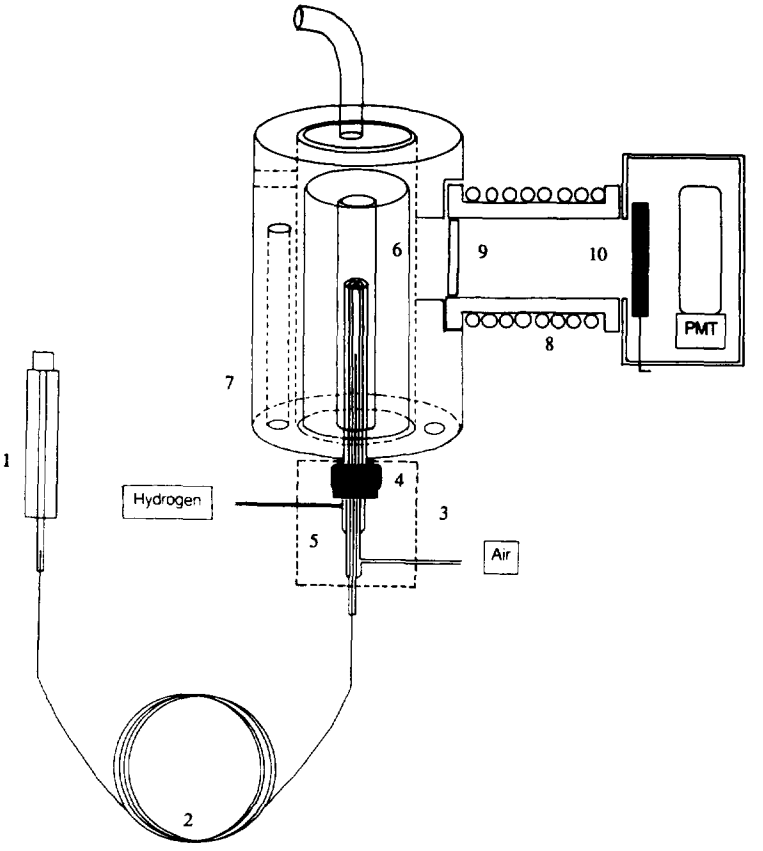

Fig. 1. Schematic diagram of the GC–FPD system. 1 = On-column injection port; 2 = capillary column with retention gap; 3 = temperature protecting block; 4 = adjustable screw; 5 = stainless-steel burner; 6 = quartz enclosure; 7 = heating cartridge; 8 = cooling water; 9 = quartz window; 10 = filter.

necessary quartz surface. Proper insulation of the optical part was ensured by means of water-cooled copper coils placed between the flame region and the photomultiplier tube (PMT), which allowed the detector to be operated over a wide temperature range. Nitrogen at flow-rate of 100 cm^3 min^{-1} was introduced at a point near the filter, to prevent water condensation. The emitted light was transmitted to a conventional photometric tube (PF-1042; Burle) via a straight aluminium delivery tube with a 394-nm interference filter. By displacing the attached slide bar, the filter mode could be easily and reversibly changed to a filterless mode of operation. The high-voltage supply and electrometer required to amplify the output from the PMT used the Chrompack 906A system. Output signals were recorded by a Chrompack PCI revision 5.0 data acquisition and processing system with a RS-232C interface.

Optimum flow-rates for organotin were hydrogen 170 cm^3 min^{-1} and air (high-purity grade) 80 cm^3 min^{-1}. High-purity nitrogen (99.9990%; Alphagaz) was used as a carrier and detector purge gas without further purification.

A 2-m piece of deactivated fused-silica column serving as the retention gap was installed between the on-column joint and the capillary column. A 25 m × 0.32 mm I.D. HP-1 (0.17 μm) (Hewlett-Packard, Avondale, PA, USA) cross-linked methylsilicone capillary column was used. The operating conditions are given in Table 1.

Table 1
GC–FPD operating conditions

On column injection parameters	
Cooling air flow-rate	300 cm^3 min^{-1}
Injection volume	0.5–5 μl
Injection port temperature	Air cooled
GC parameters for tin	
Column	HP-1 (25 m × 0.32 mm I.D.) 0.17-μm crosslinked methylsilicone
Column head pressure	150 kPa N_2
Oven temperature programme:	
Initial temperature	40°C, held for 1 min
Ramp rate	15°C min^{-1}
Final temperature	250°C, held for 1 min
GC parameters for germanium	
Column	HP-1 (25 m × 0.32 mm I.D.) 0.17-μm crosslinked methylsilicone
Column head pressure	150 kPa N_2
Oven temperature programme:	
Initial temperature	50°C, held for 1 min
Ramp rate	20°C min^{-1}
Final temperature	230°C, no hold
FPD parameters for tin	
PMT	PF-1042
Hydrogen	170 cm^3 min^{-1}
Air	80 cm^3 min^{-1}
Purge gas	N_2, 100 cm^3 min^{-1}
Detector temperature	120°C
FPD parameters for germanium	
PMT	PF-1042
Hydrogen	280 cm^3 min^{-1}
Air	150 cm^3 min^{-1}
Purge gas	N_2, 100 cm^3 min^{-1}
Detector temperature	230°C
Data processing	Chrompack PCI revision 5.0 software with RS-232 C interface

2.1.2. GC–AAS

A GC–AAS system described previously [3,30,31], consisting of an HP 5890 series II gas chromatograph and a Perkin-Elmer Model 2380 atomic absorption spectrometer, was used, but the system was adapted to the use of an HP-1 capillary column. The experimental conditions are given in Table 2. Chromatograms were recorded on a Spectra-Physics SP 4290 integrator in the peak-height mode.

2.2. Chemicals and reagents

Bu_3SnCl (96%), Bu_2SnCl_2 (95%), $BuSnCl_3$ (95%), Ph_3SnCl (95%), Ph_2SnCl_2 (96%), $PhSnCl_3$ (98%) and *n*-pentylmagnesium bromide (2.0 mol dm^{-3}) in diethyl ether were obtained from Aldrich (Milwaukee, WI, USA) and sodium tetraethylborate from Strem Chemicals (Bischheim, France), a 0.3% (w/v) aqueous solution being prepared daily. Ethylated organotin standards were prepared as described previously [32]. $(CH_3)_2GeCl_2$, $(CH_3)_3GeCl$ and Bu_4Ge were obtained from Alfa (Johnson Matthey). All other chemicals, of analytical-reagent grade, were obtained from Merck (Darmstadt, Germany), unless stated otherwise. Acetate buffer (pH 5, 0.1 *M*) was prepared by dissolving 13.6 g of sodium acetate trihydrate in 1 dm^3 of water, followed by pH adjustment with concentrated acetic acid. A

Table 2
GC–AAS operating conditions

GC parameters	
Column	HP-1 (25 m × 0.32 mm I.D.) 0.17-μm crosslinked methylsilicone
Injection port	Temperature programmable with Tenax trap
Injection temperature	Initial 20°C for 1 min, ramp at 12°C s^{-1}, final 270°C
Injection volume	2–40 μl
Carrier gas	Helium, 130 kPa
Oven temperature	Initial 40°C for 1 min, ramp at 20°C min^{-1}, final 270°C
Interface parameters	
Transfer line	2 m × 530 μm I.D. deactivated fused silica
Transfer line temperature	270°C
Heating block temperature	270°C
AAS parameters	
Light source	Sn EDL (8 W)
Wavelength	286.4 nm
Slit	0.7 nm
Hydrogen flow-rate	350 cm^3 min^{-1}
Air flow-rate	45 cm^3 min^{-1}
Atomizer	MHS-20 furnace, 900°C

0.05% tropolone solution was prepared by dissolving the appropriate amount in hexane–ethyl acetate (1:1). Deionized water, further purified in a Millipore (El Paso, TX, USA) Milli-Q system, was used.

2.3. Preparation of germanium standards

Tetrabutylgermanium (Bu_4Ge) standard was prepared by directly diluting the pure compound with hexane. Pentylated methylgermanium standard [$(CH_3)_2Pe_2Ge$, $(CH_3)_3PeGe$] were prepared by direct pentylation in hexane solutions of the methylgermanium salts, by adding an excess of *n*-pentylmagnesium bromide (PeMgBr) in diethyl ether (0.5 cm^3 of a 2 mol dm^{-1} solution). The reaction mixture was gently swirled for 5 min at room temperature and then treated with 5 cm^3 of 0.5 mol dm^{-3} H_2SO_4 to destroy the excess of Grignard reagent. The upper hexane layer containing about 1 μg cm^{-3} of Ge was removed and used as a stock solution.

2.4. Procedures for organotin extraction

2.4.1. Water [33]

A 50–100-cm^3 volume of water sample was placed in an extraction vessel, 0.5 g of sodium acetate was added and the pH was adjusted to 5 with acetic acid. Then 1 cm^3 of an aqueous 0.3% (w/v) $NaBEt_4$ solution and 1 cm^3 of hexane, containing Pe_3EtSn as an internal standard, were added. The mixture was shaken manually for 5 min. After phase separation (5 min), the hexane phase was collected with a micropipette and transferred into a conical vial and 1–5 μl of solution was injected into the chromatograph depending on the organotin concentration in the sample.

2.4.2. Sediment [34]

A 0.5–1-g portion of dry sediment was placed in a centrifugation vessel with a glass stopper. A 2-cm^3 volume of hydrochloric acid (32%) and 8 cm^3 of water were added followed by 25 cm^3 of 0.05% tropolone in hexane–ethyl acetate (1:1). The mixture was sonicated for 1 h, and then centrifuged at 2000 rpm for 5 min. The organic phase was transferred into a vessel and evaporated to dryness using a rotary evaporator, then 0.5 cm^3 of hexane, containing Pe_3EtSn as an internal standard, was added and the complexes were derivatized by adding 1 cm^3 of the $NaBEt_4$ solution together with 50 cm^3 of acetate buffer solution. The mixture was shaken manually for 5 min and after phase separation the hexane phase

was ready for clean-up or direct injection into the chromatograph.

3. Results and discussion

3.1. Chromatographic operation

3.1.1. On-column injection

The use of an on-column injection technique has been shown to yield important advantages over conventional injection techniques as discrimination caused by selective vaporization cannot occur and thermal and catalytic decomposition are minimized because the sample is injected into a cold column and no vaporization takes place.

3.1.2. Retention gap

For organotin determinations, especially for extracts of real sediment samples, it is essential to use a retention gap with the on-column injection port. The benefits of the use of a retention gap include the following: the chance of band broadening and/or peak splitting is reduced; phase stripping of a non-chemically bonded analytical column is prevented; and contamination caused by components remaining in the column inlet is prevented.

3.1.3. Separation

Two typical chromatograms, one for an injection of an ethylated mixture of $BuEt_3Sn$, Bu_2Et_2Sn, Bu_3EtSn, $PhEt_3Sn$, Ph_2Et_2Sn and Ph_3EtSn organotin species, and the other for an injection of a pentylated mixture of Me_2Pe_2Ge, Me_3PeGe and Bu_4Ge, using the HP-1 capillary column are shown in Fig. 2a and b, respectively. The chromatograms illustrate the sensitivity and specificity of the system. It should be noted that for a quartz surface-induced tin or germanium emission, the spectrum is much wider and higher (360–460 nm) than with a commercially used FPD system (600–640 nm). The peak is clearly broadened by the surface effect. The extent of broadening and mainly its tailing depend on the detector conditions and the geometry of the quartz enclosure. By careful selection from a bunch of quartz tubes, almost symmetrical peaks can be obtained.

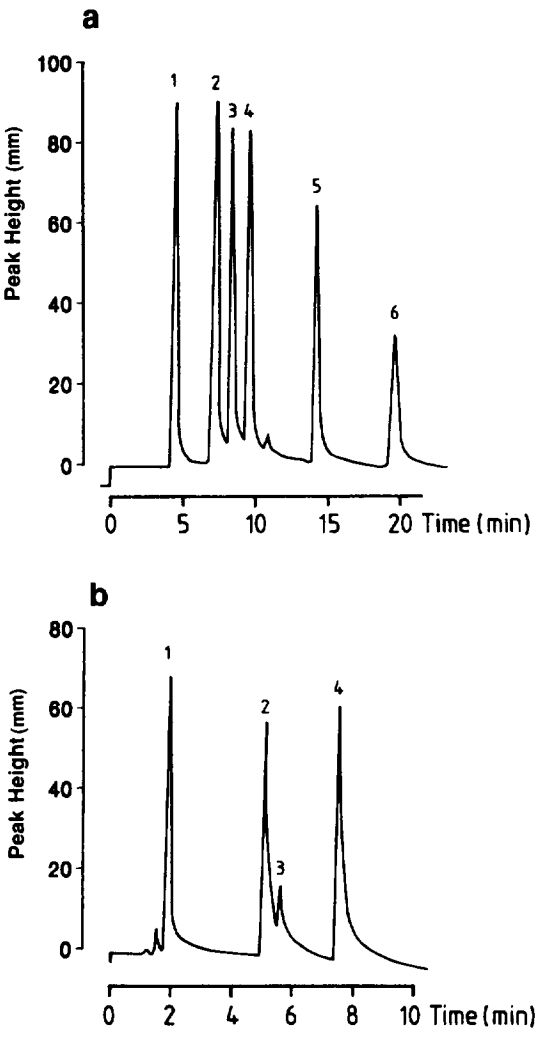

Fig. 2. (a) Typical on-column capillary chromatogram of six ethylated organotin derivatives under optimized GC–FPD conditions: amount injected, 1 μl, 80 pg (as Sn) each. Compounds: 1 = $BuEt_3Sn$; 2 = Bu_2Et_2Sn; 3 = $PhEt_3Sn$; 4 = Bu_3EtSn; 5 = Ph_2Et_2Sn; 6 = Ph_3EtSn. (b) Typical on-column capillary chromatogram of two pentylated organogermanium derivatives and tetrabutylgermanium under optimized GC–FPD conditions: amount injected, 1 μl, 0.5 ng (as Ge) each. Compounds: 1 = Me_3PeGe; 2 = Me_2Pe_2Ge; 3 = unidentified; 4 = Bu_4Ge.

3.2. Detector optimization

3.2.1. Hydrogen and air flow-rates

Preliminary experiments indicated that a hydrogen-rich flame had a strong effect on the detector response. In fact, the optimum hydrogen and air flow-rates varied strongly for different burner systems and detector configurations. Fig. 3a shows the peak height of $BuEt_3Sn$ measured for different hydrogen and air flow-rates. Other organotin compounds, such as Bu_2Et_2Sn, Bu_3EtSn, $PhaEt_3Sn$ and Ph_2Et_2Sn, showed a similar trend. The optimum detector response was obtained at 170 cm^3 min^{-1} for hydrogen and 80 cm^3 min^{-1} for air, which provides a hydrogen-to-air ratio of about 2:1. However, raising the hydrogen flow-rate to more than 400 cm^3 min^{-1} caused a high detector signal background that significantly decreased the detector sensitivity and caused peak distortion. On lowering the flow-rate to less than 120 cm^3 min^{-1} a smaller flame was observed, which not only resulted in a slight decrease in the detector signal background (10–30%) but also caused flame instability and even flame-out.

The effect of hydrogen and air flow-rates on organogermanium was not as strong as for organotin compounds. As shown in Fig. 3b, the optimum response was obtained at 280 cm^3 min^{-1} for hydrogen and 150 cm^3 min^{-1} for air.

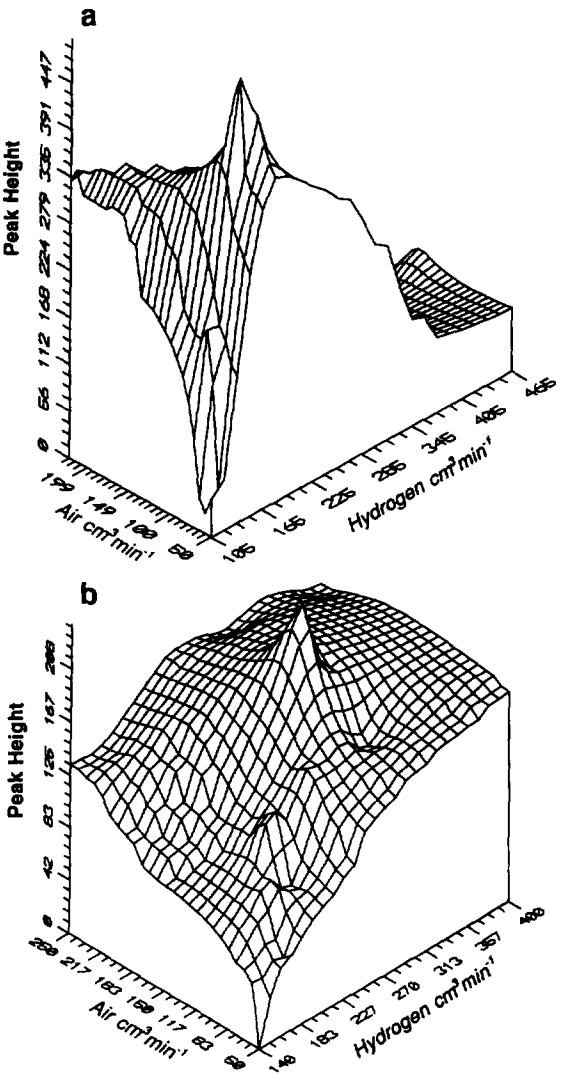

Fig. 3. Influence of hydrogen and air flow-rates on detector response with (a) 1 μl, 80 pg of Sn as $BuEt_3Sn$ and (b) 2 μl, 1 ng of Ge as Bu_4Ge injected.

3.2.2. Influence of detector temperature

The detector temperature appeared to be related to both the emission mechanism and the volatility of the species. The details and mechanisms of the reactions that are responsible for the emission intensity are not entirely clear. However, it is observed that the tin molecular band emission does not occur at the tip of the burner [20], but between the hydrogen–air flame and the quartz inner surface, hence it is influenced by the surrounding temperature. Consequently, the temperature dependences of the detector response for organotin and organogermanium were measured.

As shown in Fig. 4a, the detector response for organotin compounds increases initially with increasing detector temperature, reaches a maximum at about 120°C and then drops quickly with increasing temperature. The following explanations can be proposed to explain these observations. First, the response increase before the maximum is due to the increase in the volatility of the tin compounds. Actually, the maximum response can only be reached when the detector temperature is higher than the boiling-point of a

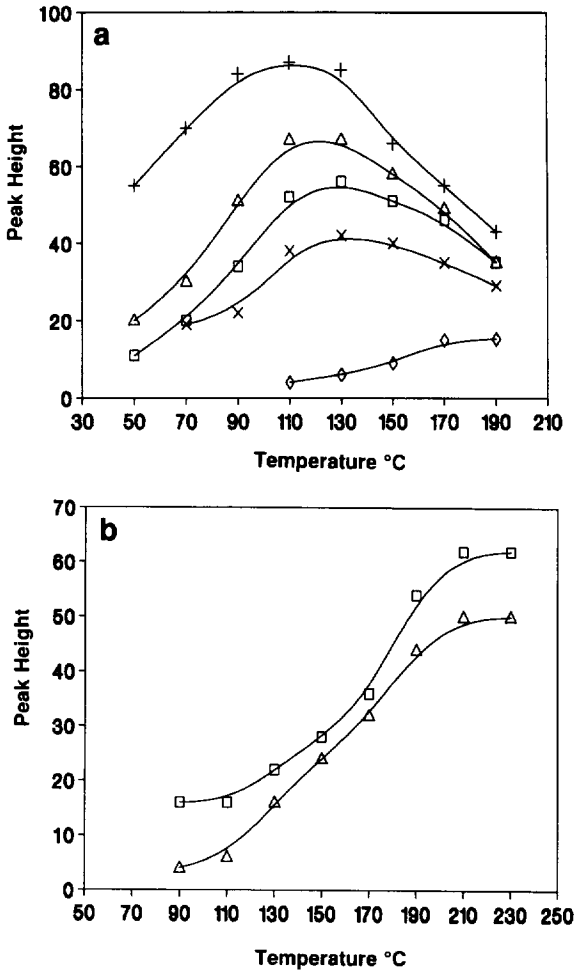

Fig. 4. (a) Effect of detector temperature on organotin compounds. + = $BuEt_3Sn$; △ = Bu_2Et_2Sn; □ = $PhEt_3Sn$; × = Bu_3EtSn; ◇ = Ph_2Et_2Sn. (b) Effect of detector temperature on organogermanium compounds. □ = Me_3PeGe; △ = Bu_4Ge.

compound. Hence the maximum temperature is dependent on the boiling-point of each species: higher volatility compounds correspond to a relatively high maximum detector temperature. For some compounds of low volatility, such as Ph_2Et_2Sn, the optimum detector temperature was higher than 200°C. Analyses performed at detector temperatures below the maximum suffer more from effluent condensation and adversely influence the detector sensitivity. After the maximum, the response drop can be attributed to the surface effect mechanism of the blue tin emission, in line with observations by some workers that the FPD response to sulphur compounds decreases with increasing detector temperature [35–37]. The highest detector response for sulphur was obtained at a relatively low detector temperature. In the present FPD system, the blue tin emission was found to be affected in a similar way by the surrounding temperature.

The detector response for organogermanium compounds is shown in Fig. 4b. In contrast to organotin compounds, the detector response increases quickly with increasing temperature with a maximum at temperatures above 210°C. This behaviour suggests that the mechanism of germanium emission is different from that of tin. By comparison of Fig. 4a with Fig. 4b, it can be concluded that the experimental conditions for high organotin responses give lower responses for organogermanium. This offers the possibility of detecting organotin compounds selectively in the presence of excess organogermanium species.

3.2.3. Burner position

The detector sensitivity in the surface emission mode is dependent on the burner position. In order to monitor the different parts of the flame, the burner was designed so that it can be easily moved up and down by adjusting a screw at the bottom part of the burner. By repeated injection of ca. 0.8 ng of butyltins at different burner position, the optimized position was found to be when the burner jet tip was situated at the bottom of the aluminium delivery tube.

3.2.4. Operation mode

Owing to its wide emission range at 360–460 nm, the 610-nm filter is of no use, and the 394-nm interference filter also decreases the sensitivity. Therefore, measurements in a filterless mode are preferred. Despite the detector noise, which increases by a factor of up to two, the signal gain is about 8–10-fold and the signal-to-noise ratio increases significantly.

3.3. Detector evaluation

3.3.1. Reproducibility

Reproducibility is a critical factor to illustrate and evaluate the stability of the blue tin and germanium emissions. The reproducibility for organotin was determined by performing ten consecutive manual on-column injections of 1 μl of standard solution containing 0.08 ng (as Sn) of $BuEt_3Sn$, Bu_2Et_2Sn, Bu_3EtSn and $PhEt_3Sn$. A 10 m $\times$ 0.25 mm I.D. CP-Sil 5 CB capillary column was used with the temperature initially at 40°C for 1 min then ramped at 15°C min^{-1} to 250°C and held there for 1 min. The peak-height measurement gave relative standard deviations (R.S.D.s) of 2.6%, 1.7%, 3.1% and 3.0% for the four compounds, respectively. Another test was carried out by nine replicate injections of 1 μl of standard solution containing 1 ng (as Ge) of Me_3PeGe and Bu_4Ge using the HP-1 capillary column. The R.S.D.s were 2.9% and 4.7%, respectively.

3.3.2. Detector noise

In addition to the original electronic noise of the detector, it was observed that the stray light including sun and lamp light incident upon the burner housing or the optical system contributed more significantly to the detector noise level than flame noise. Hence it is preferable to operate the instrument in the dark. Simply covering the detector with a dark box also resulted in some decrease in the detector noise. In the case of "open-mode" (filterless) operation, it is difficult to prevent moisture from entering the electronic parts and condensing on the PMT surface, hence increasing the PMT dark current. A significant improvement can be obtained by passing dried nitrogen or air to purge the optical system.

3.3.3. Linear range

The linear range of the detector was established by injection of 1 μl standard solution with different concentrations. For Me_3PeGe, Me_2Pe_2Ge and Bu_4Ge, the linear range is up to three orders of magnitude. For $BuEt_3Sn$, Bu_2Et_2Sn, Bu_3EtSn, $PhEt_3Sn$, and Ph_2Et_2Sn, the linear range is up to four orders of magnitude, providing a working range of up to 8 ng of Sn with a 1-μl injection volume. However, when more than 1 ng of organotin or 10 ng of organogermanium were injected, significant peak tailing was observed. It was also noted that for the analysis of sediment samples, dilution reduced the possibility of detector poisoning. Generally, injections of 0.01–0.5 ng of Sn and 0.1–5 ng of Ge into the chromatograph were preferred.

3.3.4. Detection limits

To determine the minimum detectable amounts (MDAs), defined as the signal equal to three times the standard deviation (3σ) of the baseline noise, the filterless mode was used. For 1 μl of standard solution, the MDAs were 0.8, 0.7, 0.8, 0.8 and 2.3 pg (as Sn) for $BuEt_3Sn$, Bu_2Et_2Sn, Bu_3EtSn, $PhEt_3Sn$ and Ph_2Et_2Sn, respectively. These MDAs are approximately three orders of magnitude lower than those obtained with the commercial FPD system and about two orders magnitude lower than those with most GC–AAS systems [3,38,39]. Moreover, the relative detection limits of the whole procedure were dependent on the tin species involved, the response decreasing for higher boiling compounds.

For Me_3PeGe, Me_2Pe_2Ge and Bu_4Ge, the MDAs were found to range between 50 and 100 pg (as Ge); there are no comparable literature data because no reports on methylgermanium compounds measured by GC–FPD are available.

3.4. Determination of organotin compounds in real samples

Analyses of real water and sediment samples were carried out to illustrate the applicability of the proposed GC–FPD method. Each set of analyses was performed in triplicate at least. For all samples measured, butyltin species, such as MBT, DBT and TBT, were found to be present at high concentrations, but no phenyltin species were detected. In order to evaluate the accuracy of the proposed method, a number of samples were analysed independently by GC–AAS.

Table 3
Determination of butyltin compounds in water and sediments

Sample	Species	GC–AAS (μg Sn dm^{-3} or g^{-1})	GC–FPD (μg Sn dm^{-3} or g^{-1})
River water 1	MBT	0.207 ± 0.005	0.201 ± 0.016
	DBT	0.385 ± 0.008	0.350 ± 0.024
	TBT	0.523 ± 0.009	0.512 ± 0.028
River water 2	MBT	0.209 ± 0.007	0.189 ± 0.004
	DBT	0.343 ± 0.009	0.298 ± 0.008
	TBT	0.373 ± 0.008	0.333 ± 0.022
Sediment	MBT	0.081 ± 0.008	0.098 ± 0.002
	DBT	0.232 ± 0.024	0.219 ± 0.007
	TBT	1.112 ± 0.012	1.255 ± 0.033

Results given are averages of at least triplicate analyses.

Table 3 gives the results for two sets of water samples and one set of sediment samples. The two methods provided comparable results, with the difference ranging between 2% and 13% for all species determined.

4. Conclusions

A laboratory-designed flame photometric detector using quartz surface-induced tin emission was optimized for organotin and organogermanium determination with regard to the standard analytical figures of merit. The system was found to be reproducible and offered trouble-free operation over an operating period of 6 months. The analytical results for organotin compounds in several real samples obtained by GC–FPD and GC–AAS were in fair agreement.

The quantitative analytical use of the blue germanium emission shows potentially interesting features, which are now under further investigation.

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