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Optimization of a flame photometric detector for supercritical fluid chromatography of organotin compounds

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ABSTRACT

A single flame photometric detector has been optimized for capillary supercritical fluid chromatography (cSFC) of trialkyltin chlorides for the first time. Detection variables (temperature, hydrogen and air flow-rates) were optimized by a combination of factorial experimental design and simplex. Furthermore, the position of the restrictor in the flame and injection volumes were also considered. Optimum sensitivity was achieved using high hydrogen–air ratios (1.8). Using the optimum conditions, baseline was stable during pressure programming. The detection limit of tributyltin chloride ($S/N = 3$) was around 40 pg (as tin). Reproducibility was high (R.S.D. = 3.8%, $n = 5$) and dynamic range was measured over two orders of magnitude. Furthermore, dibutyl-, diphenyl- and triphenyltin chlorides were also successfully eluted for the first time using linear density programming (carbon dioxide, 50 °C).

INTRODUCTION

Organotin speciation is of paramount importance in environmental studies in order to distinguish the most toxic species from the less toxic degradation products. Until now most organotin speciation techniques have been based on the GC resolution of volatile derivatives (*i.e.* hydrides or alkyl) coupled to elemental detection techniques [atomic absorption spectrometry (AAS), flame photometric detection (FPD) and atomic emission detection (AED)]. Furthermore, the high toxicity of organotins requires analytical techniques with extremely high sensitivity and selectivity.

However, it is suspected that derivatization reactions for organotins in complex mixtures of compounds present in environmental samples are not quantitative and might modify the original composition of the sample, leading to significantly biased results [1]. Furthermore, derivatization procedures are time-consuming, and consequently their application to environmental monitoring programmes are of limited interest because they are difficult to automate.

On the other hand, the lack of UV-absorbing functional groups in alkyltin compounds restricts the application of LC to post-column derivatization techniques or linked systems (LC–MS, LC–inductively coupled plasma-MS) [2], which are not well suited to surveys dealing with a large number of samples.

At present, the use of supercritical fluid chromatography (SFC) to analyse organometallic compounds is still in its infancy [3–5], but it could be an alternative to classical speciation techniques. Its potential is associated to the versatility of detection systems, especially the capillary column versions, combined with the solvating properties of supercritical fluids, which allow the elution of analytes at low temperatures. Until now only the tetra-alkyl- and tetra-

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aryltins have been analysed by SFC–ICP-MS [6]. Nevertheless, these analytes can also be determined by capillary GC (cGC), in contrast to the lower substituted alkyl and aryltins, which require volatile derivatives.

Although capillary SFC (cSFC) coupled to FPD has been previously evaluated for the determination of sulphur heterocycles [7,8] and high-molecular-weight organosulphur compounds [9], similar attempts have not been undertaken for organotins, despite the fact that cGC using tin-selective FPD is one of the most sensitive detection techniques for the determination of derivatized compounds [10].

In this work, the optimization of a tin-selective single-flame FPD system for cSFC has been carried out for the first time, with the aim of evaluating its applicability to organotin speciation of the corresponding chlorides, which cannot be successfully analysed by cGC–FPD. Organotin chlorides are one of the most important intermediate derivatives, which are generated in sample pretreatments in order to displace more ionic counterions (CO_3^{2-}, SO_4^{2-}, S^-) from ionic organotin species present in the aquatic environment.

Chloride derivatives of organotin compounds are easily obtained after a hydrochloric acid treatment during the extraction step [11]. Unfortunately, GC analysis of these compounds is not successful because the strongly polarized tin–chloride bonds are presumably thermolabile. It requires carrier gas saturation with hydrochloric acid and is obviously not suited for routine analysis [12].

EXPERIMENTAL

Apparatus

SFC-grade carbon dioxide was obtained from Air Products (Barcelona, Spain). Carbon dioxide was cooled at 4 °C in the syringe pump. SFC analyses were performed with an SFC-3000 chromatograph equipped with a dual-syringe pump system (Fisons, Milan, Italy) coupled to an FPD 250 series instrument (Fisons) using a broad band-pass filter with peak transmission at 610 nm (LOT, Darmstadt, Germany). Nitrogen was used as a make-up gas at a flow-rate of 55 ml/min. Data were acquired by a Nelson-PE interface with a sampling frequency of 100 Hz and handled by a PS computer. Standard solutions were injected at 30 °C dissolved in hexane into a timed-split rotary injection valve (Valco, Houston, TX, USA) using an internal loop of 200 nl. The analytical capillary column was a 10 m × 0.1 mm I.D. column coated with 0.4 μm film thickness of SE-52, and was fitted directly into the injection valve and to an integral restrictor (J & W, Folsom, USA) (2 ml/min, as gas), using a zero-dead-volume connector. Carbon dioxide pressure was programmed from 0.2 g/ml to 0.65 g/ml at 0.02 g/ml/min.

TABLE I

OPTIMIZATION OF SFC–FPD VARIABLES BY FACTORIAL DESIGN

Experiment No.	Hydrogen (ml/min)	Air (ml/min)	Temperature (°C)	Response[a] (%)
1	75	44	175	29
2	111	44	175	46
3	75	92	175	45
4	111	92	175	78
5	75	44	250	38
6	111	44	250	51
7	75	92	250	50
8	111	92	250	100

[a] Response normalized to the optimum value.

Reagents

Diphenyltin (DPhTCl) chloride and tetrabutyltin (TeBT) were obtained from E. Merck (Darmstadt, Germany). Dibutyltin (DBTCl), triphenyltin (TPhTCl), tributyltin (TBTCl) and tripropyltin (TPrTCl) chlorides were from Fluka (Buchs, Switzerland). Stock solutions were prepared with pesticide-grade hexane (Merck) and stored at 4°C in the dark.

Statistical optimization

An experimental design [13] focused on three variables was applied for FPD optimization, each one chosen at two levels (high and low). Variables and their values are presented in Table I. Response effects were calculated according to the Yates algorithm [14]. Optimum conditions for FPD were investigated by using two independent simplex runs, to ascertain that the maximum was reached [15].

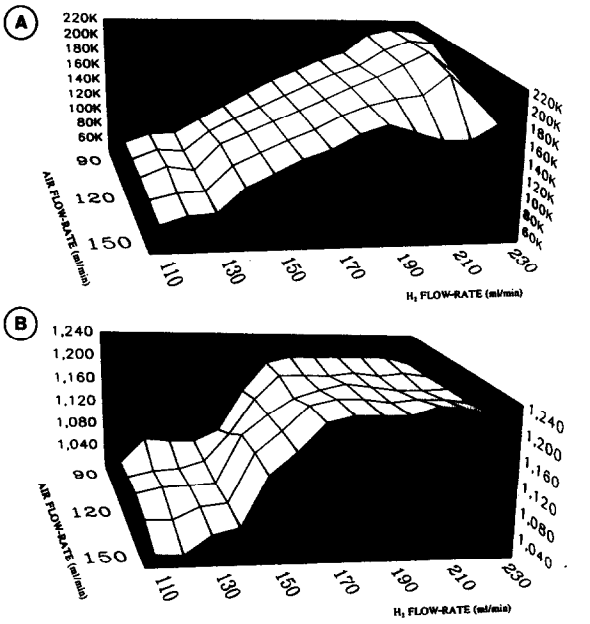

Fig. 1. (A) Variation of measured tin hydride emission (response $\times 10^3$) and (B) background emission as a function of hydrogen and air flow-rates. *y*-Axes are in arbitrary units.

RESULTS AND DISCUSSION

FPD response optimization

In order to evaluate the response of FPD variables to the organotin sensitivity, an experimental design was outlined and the TBTCl response was determined (Table I). Following the evaluation of response effects, significant variables were the FPD fuel gas composition, hydrogen and air. Conversely, the effect of temperature on sensitivity was negligible in the range 175–250°C, and it was kept constant in the subsequent experiments at 225°C.

In order to optimize the detector gases, simplex runs were carried out. Fig. 1 shows the response surface of TBT chloride as a function of hydrogen and air composition, where the maximum response was found at flow-rates of 220 and 120 ml/min, respectively (CO_2 at 76 μl/min). Background exhibited a moderate increase with hydrogen flow (0.2%), which is almost insignificant in comparison with the SnH response enhancement (30%). The high flow-rates of hydrogen required in the optimum conditions are in contrast to the moderate values used in cGC–FPD of alkyl-derivatized organotin compounds [10]. Similar results were also obtained in case of sulphur compounds and were tentatively attributed to a reaction between carbon dioxide and radicals of the flame gases [8] that are important to the formation of SnH, responsible for tin emission in FPD [16].

Another variable optimized was the distance of the restrictor from the flame. Fig. 2 shows that the optimum position was 1.2 cm lower than the flame base, while background was almost constant over the range of column positioning evaluated. The highest decrease in sensitivity was obtained when the restrictor was further beneath the flame, probably associated to band-broadening effects and excessive mixing with fuel gases. On the other hand, positioning the restrictor close to the flame leads to a poor mixing effects between hydrogen and air, which are flowing coaxially with the column effluent.

Furthermore, under density programming conditions no baseline drift was apparent, probably because of reduced quenching effects at the wavelength monitored in the tin-selective FPD (610 nm). In fact, a great selectivity of tin over carbon is evident from the solvent peak in the

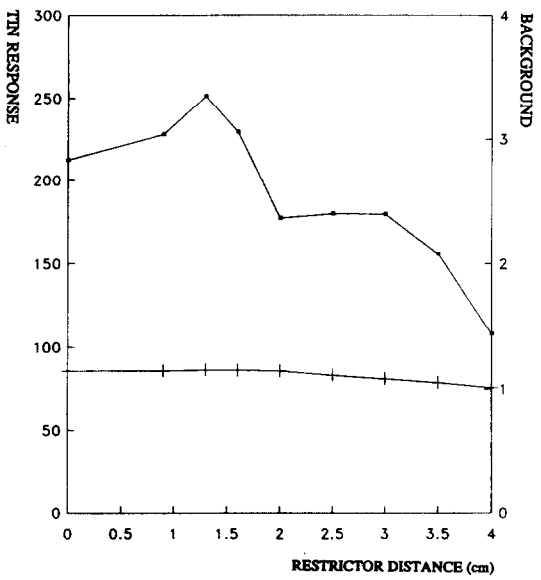

Fig. 2. Variation of measured tin hydride emission (□), and background emission as a function of position of restrictor from the flame base (+). *y*-Axes are in arbitrary units.

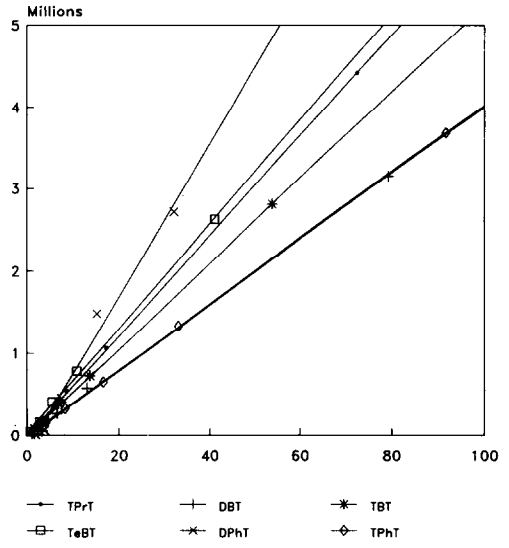

Fig. 3. Response in arbitrary units *vs.* injected amounts in ng (as organotin chlorides) under the optimum cSFC–FPD conditions.

optimum conditions. These results are clearly in contrast with those reported formerly for the cSFC–FPD of organosulphur and organophosphorus compounds, which exhibited a positive baseline drift under similar operating conditions, leading to a significant reduction in sensitivity [7].

Furthermore, in order to evaluate the optimum amount of sample to inject while maintaining column efficiency, injection time, and as a consequence injection volume, were also evaluated. The results show no significant band broadening when slow injections (2 s) were performed using the 200-nl loop in comparison with the fast injection technique (0.2 s). This could be because of the focusing effect in injection conditions involving low densities. Accordingly, further sensitivity evaluation was carried out using long injection times.

The dynamic range of the SnH response was

TABLE II

LIMIT OF DETECTION (LOD) OF ORGANOTIN COMPOUNDS (SIGNAL-TO-NOISE RATIO = 3)[a] AND REPRODUCIBILITY ($n = 5$) UNDER THE OPTIMUM CONDITIONS

Compound	LOD		R.S.D. (%)
	(pg as tin)	(pg as chloride)	
Tripropyltin chloride	122	291	–[b]
Dibutyltin chloride	334	1 099	14.6
Tributyltin chloride	40	110	3.8
Tetrabutyltin	50	147	5.7
Diphenyltin chloride	623	1 804	5.2
Triphenyltin chloride	123	400	5.4

[a] Noise was measured by peak-to-peak baseline.

[b] Injection amount at the picogram level. Tripropyltin chloride was used as internal standard.

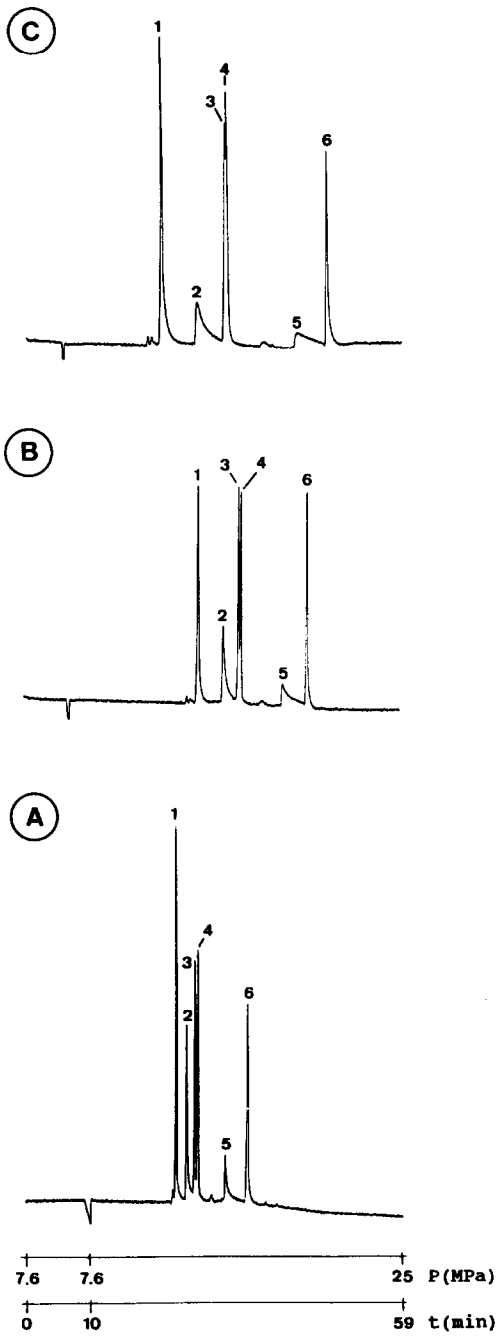

Fig. 4. cSFC–FPD chromatograms of organotin compounds obtained at different column temperatures: (A) 50°C, (B) 80°C and (C) 110°C. Injection was performed at 7.6 MPa and then programmed to 25 MPa at 0.35 MPa/min, after a 10-min isobaric period. Compounds are as follows: 1 = TPrTCl; 2 = DBTCl; 3 = TBTCl; 4 = TeBTCl; 5 = DPhTCl; and 6 = TPhTCl. Injected amount of organotin chlorides was in the low-ng range (0.5–5 ng).

evaluated from near the detection limits to injected amounts around 500 pg. In this range, a linear response was found for all the components ($r > 0.999$) (Fig. 3). This behaviour is similar to the cGC–FPD of alkyl derivatives of organotin compounds (tetraalkyltins), although response factors are slightly higher in the GC conditions.

The limit of detection (LOD) and reproducibility of butyltin and phenyltin chlorides under the optimum conditions are shown in Table II. Trialkyltins and tetraalkyltins exhibited lower LOD than triphenyltin, but the highest LOD values were obtained for dialkyl- and diaryltins, probably because of the lower stability of these compounds in the analysis conditions.

As far as precision is concerned, dibutyltin chloride exhibited the highest R.S.D. (14.6%), while the R.S.D. was considered acceptable for the rest of components (3.8–5.7%), taking into account the low volume injected (< 200 nl). It is interesting to note the difference in precision between diaryltin and dialkyltin. In this regard, the R.S.D. of DPhTCl was much lower than that of DBTCl, despite the fact that DPhTCl is more labile than DBTCl. Therefore, the poor precision of DBTCl seems not to be related to the compound instability. In spite of this, co-elution with another component seems a more reasonable explanation of the high R.S.D. for the latter compound.

Application to organotin speciation

In order to evaluate the feasibility of cSFC–FPD for organotin speciation in environmental samples, a standard mixture containing tributyltin and triphenyltin chlorides and the most toxic degradation products, dibutyltin and diphenyltin, was analysed at different temperatures under pressure programming conditions. As soon as column temperature increased, significant peak tailing of DBTCl and DPhTCl became apparent, probably due to compound decomposition during analysis. In this regard, DPhTCl is eluted very poorly at 110°C and co-elution of TeBT and TBTCl is apparent. As a consequence, temperatures as low as possible are preferred for the analysis of these thermolabile compounds. However, temperatures lower than 50°C were not evaluated in order to keep the

TABLE III

CORRELATION BETWEEN CAPACITY FACTOR (k') IN SFC AND CARBON (C) AND CHLORINE (Cl) NUMBERS OF SIX ORGANOTIN CHLORIDES: TRIPROPYLTIN, DIBUTYLTIN, TRIBUTYLTIN, DIPHENYLTIN, TRIPHENYLTIN CHLORIDES AND TETRABUTYLTIN

Temperature (°C)	a^a	b^a	c^a	r^a
50	−0.368	0.128	0.429	0.973
80	−0.641	0.287	1.010	0.984
110	−4.01	0.520	1.840	0.965

[a] a, b and c correspond to the constants in the correlation equation $k' = a + b\mathrm{C} + c\mathrm{Cl}$; r is the corresponding correlation coefficient.

analysis time as short as possible. At this temperature, the resolution of six organotin compounds exhibited reasonable peak shape and an acceptable analysis time (35 min) was obtained (Fig. 4).

In order to model the retention behaviour of the organotins analysed, the capacity factor (k') was correlated with chlorine and carbon number for every compound by applying a multiple linear regression at the three temperatures evaluated. Table III shows that a significant correlation was obtained at each temperature. Previous studies of ethyl derivatives of organotin compounds using cGC–FPD have shown a simple linear correlation between carbon number and k' [17].

The retention time was dependent on compound volatility and the column temperature. At intermediate temperatures, the retention time of all components increased as a result of a decrease in density. Conversely, at higher temperatures the more volatile components (*i.e.* trialkyltin chlorides and tetrabutyltin) showed a decrease in retention time owing to the predominance of partition mechanisms, in contrast to the low-volatility components (*i.e.* di- and triphenyltins).

CONCLUSIONS

The suitability of single-flame FPD coupled to cSFC for the determination of organotin chlorides is demonstrated for the first time. Although detection limits are slightly higher than in cGC, the possibility of analysing tributyltin and triphenyltin chlorides and their degradation products (*i.e.* dibutyltin and diphenyltin chlorides), which are the most toxic organotin compounds, is of great interest for the speciation of organotin compounds in environmental samples since tedious and time-consuming derivatization steps can be avoided. Further, retention of organotin chlorides can be modelled at every temperature under density programming conditions by applying a linear regression with two variables, carbon and chlorine number in the molecule.

Recent findings regarding the suitability of FPD for the detection of the main group of elements [18,19] could expand the applications of FPD to the less volatile organometallic compounds using modified carbon dioxide as mobile phase.

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REFERENCES

1 X. Dauchy, A. Astruc, M. Borsier and M. Astruc, *Analusis*, 20 (1992) 41–48.
2 Ph. Quevauviller, Bureau Community of Reference (EC), Brussels, personal communication.
3 K. Jinno, H. Mae and C. Fujimoto, *J. High Resolut. Chromatogr.*, 13 (1990) 13–17.
4 K.E. Lainz, G.M. Shieh and C.M. Wai, *J. Chromatogr. Sci.*, 30 (1992) 120–123.
5 K.E. Lainz, J.-J. Yu and C.M. Wai, *Anal. Chem.*, 64 (1992) 311–315.
6 W.-L. Schen, N.P. Vela, B.S. Sheppard and J.A. Caruso, *Anal. Chem.*, 63 (1991) 1491–1496.
7 K.E. Markides, E.D. Lee, R. Bolick, and M.L. Lee, *Anal. Chem.*, 54 (1986) 740–743.
8 S.V. Olesik, L.A. Pekay and E.A. Paliwoda, *Anal. Chem.*, 61 (1989) 58–65.
9 L.A. Pekay and S.V. Olesik, *Anal. Chem.*, 61 (1989) 2616–2624.
10 I. Tolosa, J.M. Bayona, J. Albaigés, L.F. Alencastro and J. Tarradellas, *Fresenius' J. Anal. Chem.*, 339 (1991) 646–653.

11 H.A. Meinema, T. Burger-Wiersma, G. Verselius-de Haan and E.Ch. Gevers, *Environ. Sci. Technol.*, 12 (1978) 288–293.
12 K.W. Siu, P.S. Maxwell and S.S. Berman, *J. Chromatogr.*, 475 (1989) 373–379.
13 E.D. Morgan, *Chemometrics: Experimental Design*, Wiley, Chichester, 1991, Ch. 4 and 5 .
14 G.E.P. Box, W.G. Hunter and J.S. Hunter, *Statistics for Experimenters*, Wiley, New York, 1978.
15 S.N. Deming and S.L. Morgan. *Anal Chem.*, 45 (1973) 278A–283A.
16 R.M. Dagnall, K.C. Thompson and T.S. West, *Analyst*, 93 (1968) 518–521.
17 M. Müller, *Anal. Chem.*, 59 (1987) 617–623.
18 W.A. Aue, X.-Y. Sun and B. Millier, *J. Chromatogr.*, 606 (1992) 73–86.
19 W.A. Aue, B. Millier and X.-Y. Sun, *Anal. Chem.*, 63 (1991) 2951–2955.