Journal of Chromatography, 641 (1993) 337–345
Elsevier Science Publishers B.V., Amsterdam

CHROM. 25 013

Comparison of flame ionization and inductively coupled plasma mass spectrometry for the detection of organometallics separated by capillary supercritical fluid chromatography☆

Nohora P. Vela and Joseph A. Caruso*

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 (USA)

(First received December 1st, 1992; revised manuscript received February 24th, 1993)

ABSTRACT

Organotin compounds are separated by capillary supercritical fluid chromatography (SFC) and a comparison of the detection by flame ionization (FID) and inductively coupled plasma mass spectrometry (ICP-MS) is presented. Resolution, detection limits, linear dynamic range and reproducibility are the parameters compared between SFC–FID and SFC–ICP-MS, for the detection of tri- and tetraorganotin compounds. The resolution obtained in the SFC–FID system is not always observed in SFC–ICP-MS. Degradation in resolution is due to fluctuations in transfer line temperature. Baseline resolution for the organotins considered is achieved in both systems by using a longer column. Detection limits (DLs) are calculated as $3\sigma/S$, where σ is the standard deviation of the blank signal and S is the slope of the calibration curve. Detection limits of 10.3, 12.5, 12.0 and 9.0 pg are obtained for tetrabutyltin, tributyltin chloride, triphenyltin chloride and tetraphenyltin, respectively, using SFC–FID. An improvement in detection limits of one order of magnitude is achieved by SFC–ICP-MS for the same organotins (0.26, 0.80, 0.57 and 0.20 pg, respectively). The relative standard deviations using SFC–FID for five 50-nl injections, containing 0.5 ng Sn, ranged from 3.2 to 6.4%. Using SFC–ICP-MS, five replicate injections of 0.05 ng Sn give R.S.D.s from 1.3 to 3.4%.

INTRODUCTION

Supercritical fluid chromatography (SFC) spans the gap between liquid chromatography (HPLC) and gas chromatography (GC), making it possible to separate non-volatile, thermally labile and high-molecular-mass compounds in short analysis time [1–5]. This approach is due to the liquid-like property (density) and gas-like characteristics (viscosity and diffusion coefficients) of the supercritical fluids. Another advantage of SFC is its compatibility with the existing detectors for HPLC and GC. Liquid-phase and gas-phase detectors are suitable for SFC, since detection can be performed before or after the decompression zone of the mobile phase [1–7]. Ultraviolet–visible (UV–Vis) detection was first used in SFC and is still the most common detector for packed-column SFC [4–7]. Fluorescence, light scattering and chemiluminescence are among other optical detection methods used for SFC [1,5,7].

Performance of GC detectors coupled to SFC has been the topic of several publications [4,5,8–14]. Flame ionization detection (FID) is a universal detector and is easy to interface to SFC [4,5,8–11]. Selective detection systems used in GC, such as flame photometric (FPD) [8–11], electron-capture (ECD) [8–12] and thermionic ionization (TID) [8,13,14] have been evaluated for SFC. A variety of papers have been pub-

* Corresponding author.

☆ This work was presented in part at the *Pittsburgh Conference, New Orleans, March 1992* (paper 084).

0021-9673/93/$06.00

lished concerning the interface of SFC with detectors that provide structural information, such as Fourier transform infrared spectroscopy [5,6,15] and mass spectrometry [5,6,16–18]. SFC with detection based on atomic emission has been used as an element-selective detector for organometallics and halogenated compounds [19–25].

High-molecular-mass organotin compounds are good candidates for SFC, since they are not easily amenable to GC or HPLC separation. In general, organotin compounds are used as biocides and as antifouling agents in marine paints. These applications are the main source for the continuous release and accumulation of organotins in water, sediments and aquatic organisms [26,27]. Studies demonstrate that tetra and triorganotin compounds are the most toxic, while a decrease in the number of organic substituents linked to the tin atom is related to lower toxicity. The chemical form of the organic group also determines toxicity, resulting in the need for speciation information [26,27].

Organotin compounds with butyl and phenyl substituents are the most frequently used and a variety of papers have been published concerning their determination [24–41]. Speciation is obtained by GC, HPLC or SFC separation coupled to a universal or selective detector [24–42]. Most of the papers that describe the separation of organotins by GC involve the preparation of volatile derivatives (hydrides or pentyl derivatives) prior to the injection into the GC system [27–37]. Different techniques have been coupled to detect the chromatographic effluent, including ECD [28–29], FPD [30–34], FPD using quartz surface induced luminescence [35], atomic absorption (AAS) [36], quartz furnace atomic absorption [37], direct current plasma (DCP) [34] and microwave induced plasma detection (MIP) [38]. Dual detection by FPD–DCP has also been suggested [34].

Detection of organotins after HPLC has been obtained by several techniques including graphite furnace–atomic absorption spectroscopy (GF-AAS) [39], flame-laser excited atomic fluorescence spectroscopy (LEAFS) [40], inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) [20,41,42]. The applicability of SFC for the speciation of tetra- and triorganotin compounds with ICP-MS detection has also been demonstrated [24,25]. In this study, capillary SFC with FID and ICP-MS detection is used for the speciation and detection of organotin compounds. Comparison of resolution, detection limits, linear dynamic range and reproducibility for tributyltin chloride, tetrabutyltin, triphenyltin chloride and tetraphenyltin using SFC–FID and SFC–ICP-MS is presented.

EXPERIMENTAL

Instrumentation

A description of the SFC–ICP-MS system used for the experiments was presented in a previous publication [24]. Fig. 1 illustrates the SFC–ICP-MS interface and detailed information was presented elsewhere [24]. Operating conditions for ICP-MS are: forward power: 1.35 kW; reflected power: <5 W; argon coolant flow: 15 l/min; argon auxiliary flow: 1.5 l/min and make-up gas flow: 0.65 l/min. Carbon dioxide, SFC-grade (Scott Specialty Gases, Plumsteadsville, PA, USA) was used as a mobile phase. An SB-Biphenyl-30 capillary column (0.25 μm film thickness, 50 μm I.D., 375 μm O.D.) with different lengths of 2.5 and 4 m were purchased from Lee Scientific (Salt Lake City, UT, USA). Frit restrictors (50 μm I.D.) with a linear velocity of 1.5 cm/s were also obtained from Lee Scientific. Calibration of the time split injector indicates that a duration of 0.075 s injection time corresponds to 50 nl injection volume.

A conventional flame ionization detector, obtained from Hewlett-Packard (Avondale, PA,

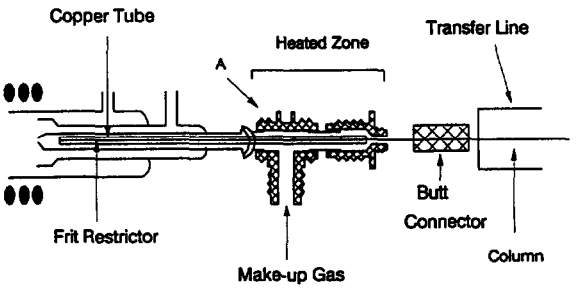

Fig. 1. SFC–ICP-MS interface.

USA) was installed in the gas chromatograph oven (Hewlett-Packard Model 5890). A jet tip (0.011 in. I.D.; 1 in. = 2.54 cm) that accommodates capillary columns was used for the detector. No additional modifications were required to convert the GC system into the SFC mode. The flow of the gases used with FID were: hydrogen: 45 ml/min; air: 400 ml/min and nitrogen (detector make-up gas): 32 ml/min. The temperature of the FID system was 300°C.

Reagents

The organometallic compounds, tetrabutyltin (TBT, 97% purity), tetraphenyltin (TPT, unknown purity), tetraphenyllead (TPL, 98% purity), tributyltin chloride (TrBT-Cl, 95% purity in metal basis) and triphenyltin chloride (TrPT-Cl, 95% purity), were obtained from Alfa Products (Danvers, MA, USA). They were used without further purification. Stock solutions of 1000 ppm (w/w) Sn corrected to the purity of the compounds, were prepared in HPLC grade methylene chloride (Aldrich, Milwaukee, WI, USA). Fresh working solutions were prepared daily by serial dilution with methylene chloride.

RESULTS AND DISCUSSION

The comparison between FID and ICP-MS for the detection of organometallics after SFC, is based on three aspects. The first is the effect of the detector temperature (SFC–FID) or interface temperature (SFC–ICP-MS) in the signal response, for organotins with different molecular weight and volatility. The second aspect investigated is with certain chromatographic conditions (pressure program and temperature) there are any variations in the resolution as a function of the detector used. Finally, analytical figures of merit are compared using SFC–FID and SFC–ICP-MS in the speciation of organotins.

A mixture of 50 ng of each TBT and TPT, 100 ng of TrBT-Cl and 150 ng of TrPT-Cl is injected to obtain SFC–FID chromatograms. A lower concentration, consisting of a mixture of 5 ng each of TBT, TrBT-Cl, TrPT-Cl and TPT is used during SFC–ICP-MS experiments.

Effect of interface temperature

Fig. 2 shows the variation in % normalized peak area for several organotins, as a function of the interface temperature, using SFC coupled to FID and ICP-MS. This figure indicates only minor variations in the organotin peak areas for FID temperatures ranging from 215 to 350°C. Variations are within the R.S.D. (1.1–5.5%) calculated for several injections at a constant FID temperature. On the other hand, the response obtained with SFC–ICP-MS is highly dependent on interface temperature. Interface temperature affects not only peak area, but also retention time and peak shape, mostly for the less volatile organotins that are TrPT-Cl and TPT, as it has been demonstrated in a previous study [25]. Variations in the results obtained between SFC–FID and SFC–ICP-MS, are explained by the different efficiency in which the heat is transferred to the restrictor tip. In the

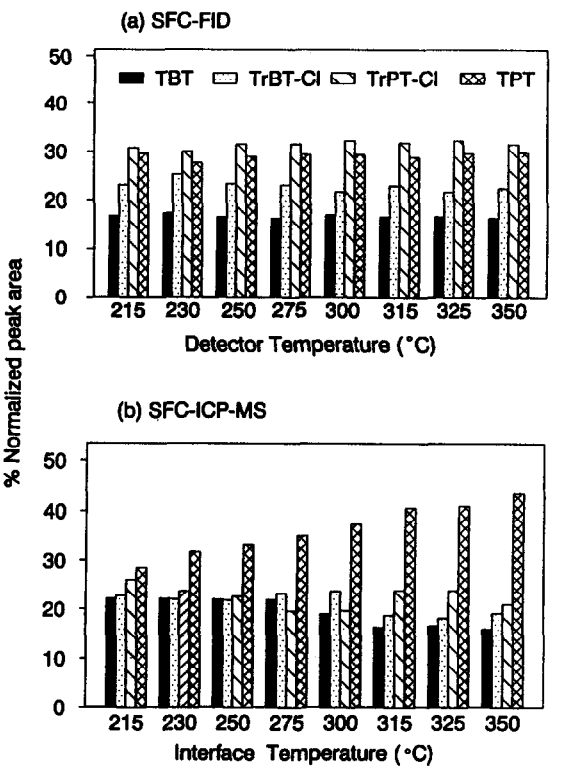

Fig. 2. Variation in peak area for several organotins as a function of (a) SFC–FID detector temperature and (b) SFC–ICP-MS interface temperature.

case of the FID, the proximity of the restrictor to the heating block allows an efficient heat transfer. For ICP-MS detection, heat to the frit is supplied by a preheated gas (see Fig. 1) that continuously flows along the restrictor. The temperature of the interface is taken at point A of the preheated zone. Results indicate that there is some temperature difference between point A and the tip of the restrictor in the ICP-MS interface. Nevertheless, chromatograms obtained for an SFC–ICP-MS interface temperature of 300°C are comparable to those obtained by SFC–FID [25].

Resolution as a function of chromatographic conditions

A pressure program, usually required to resolve a mixture, generally involves at least two steps. First, the pressure is maintained constant during enough time to allow solvent elution and second a pressure ramp is applied to resolve the components of the mixture. Fig. 3 indicates no significant variation in capacity factors for organotins using SFC–FID, when the pressure (70 atm; 1 atm = 101 325 Pa) is held constant for 1 and 1.5 min. Capacity factors as well as resolution are slightly increased by having a constant pressure of 70 atm for 2 min before the pressure ramp. Fig. 4 shows the chromatograms obtained at an oven temperature of 75°C for different hold times and for all of them baseline resolution is observed. An initial pressure of 70 atm held for 1 min, followed by a variable pressure ramp, is used for the next SFC–FID experiments.

An important difference between flame ionization and plasma detection is that the second detector is transparent to the solvent and to mobile phases that give response with FID [22,23,25] because ICP-MS is an element-selective detector. ICP-MS has a m/z resolution of better than 1 u, so a single-ion scan mode can be selected to detect a certain mass. Fig. 5 presents

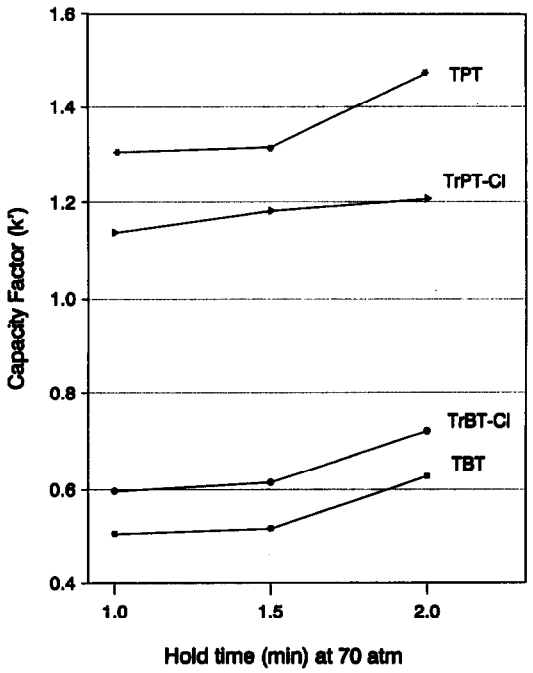

Fig. 3. Variation of capacity factor (k') for organotins with different hold times in the pressure program.

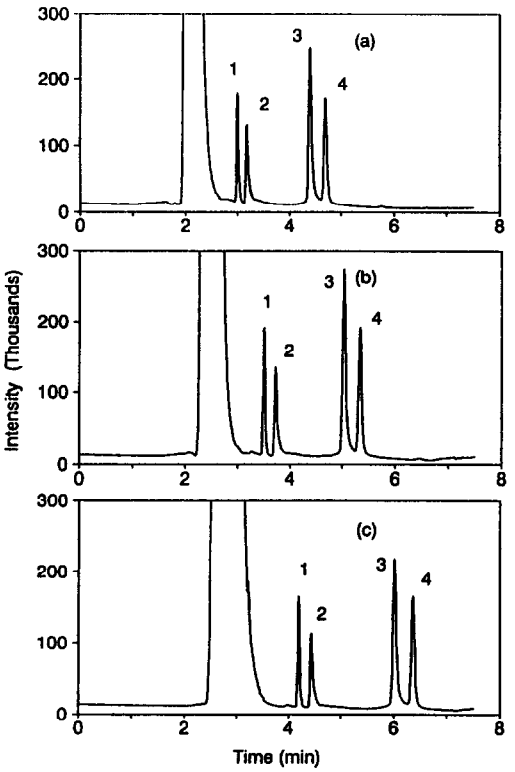

Fig. 4. Effect of hold time at an initial pressure of 70 atm. Pressure ramp: 60 atm/min; final pressure: 300 atm; oven temperature: 75°C. FID temperature: 300°C. Hold time: (a) 1 min, (b) 1.5 min and (c) 2 min. Peaks: 1 = TBT; 2 = TrBT-Cl; 3 = TrPT-Cl; 4 = TPT.

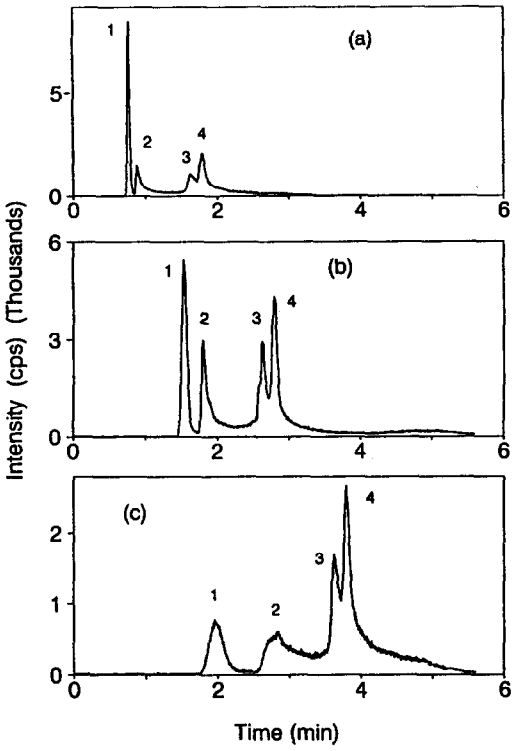

Fig. 5. Effect of hold time at an initial pressure of 70 atm. Pressure ramp: 60 atm/min; final pressure: 300 atm; oven temperature: 75°C. ICP-MS interface temperature: 300°C. Hold time: (a) no hold time, (b) 1 min and (c) 2 min. Peaks: 1 = TBT; 2 = TrBT-Cl; 3 = TrPT-Cl; 4 = TPT.

the chromatograms obtained for a 5-ng injection using SFC–ICP-MS and having different hold times at an initial pressure of 70 atm. The ICP-MS feature of detecting compounds that coelute with the solvent is illustrated in Fig. 5a. However, conditions are not always recommended where one of the compounds coelute with the solvent, since sensitivity and reproducibility are affected. Chromatograms presented in Fig. 5 demonstrate that retention time, peak shape and relative peak height, especially for TBT and TrBT-Cl are affected by the length of the hold time. As with SFC–FID, for the next SFC–ICP-MS experiments, the pressure was started at 70 atm and was held constant for 1 min before the pressure ramp was initiated.

Table I shows the effect of pressure ramp in the resolution of organotin compounds using ICP-MS and FID, at a fixed temperature of 50°C. The general trend observed is a decrease in resolution with the increase in pressure ramp. Comparing resolution between TBT and TrBT-Cl, better values are obtained with ICP-MS detection. As it was pointed out earlier, ICP-MS is transparent to the solvent and with FID, TBT and TrBT-Cl elute in the tail of the solvent peak, at a column temperature of 50°C (see Fig. 6). TrBT-Cl and TrPT-Cl are baseline resolved using both detectors, at pressure ramps between 20 and 60 atm/min. Table I also shows that better resolution between TrPT-Cl and TPT is observed with FID. Loss in resolution in SFC–ICP-MS is due to peak broadening attributed to fluctuations in transfer line temperature.

Variation in resolution for the same pressure program, as a function of the temperature is presented in Table II. Using FID, better resolution is obtained at 100°C, although baseline resolution is also observed at 75°C. Resolution between TBT and TrBT-Cl with ICP-MS detection is slightly affected by variation in column

TABLE I

EFFECT OF THE PRESSURE RAMP IN THE RESOLUTION OF ORGANOTIN COMPOUNDS USING SFC COUPLED TO ICP-MS AND FID

Pressure program: 70 atm held for 1 min; variable pressure ramp up to 320 atm. Column temperature: 50°C.

Ramp (atm/min)	TBT and TrBT-Cl		TrBT-Cl and TrPT-Cl		TrPT-Cl and TPT	
	ICP-MS	FID	ICP-MS	FID	ICP-MS	FID
20	1.105	1.428	3.702	7.330	0.908	2.000
40	1.200	0.833	3.417	4.555	0.867	1.300
60	0.933	0.571	3.200	4.133	0.692	1.125

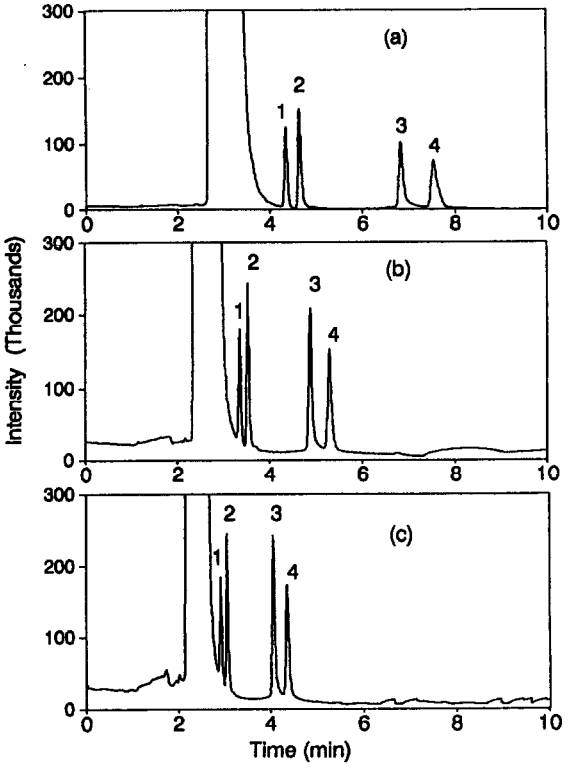

Fig. 6. Effect of pressure ramps at an oven temperature of 50°C: (a) 20 atm/min, (b) 40 atm/min and (c) 60 atm/min. FID temperature: 300°C. Initial pressure: 70 atm held for 1 min; final pressure: 350 atm. Peaks: 1 = TBT; 2 = TrBT-Cl; 3 = TrPT-Cl; 4 = TPT.

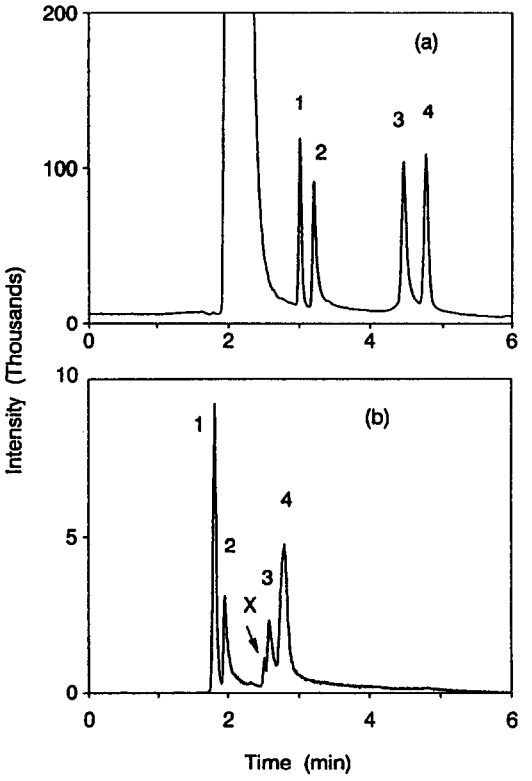

Fig. 7. (a) SFC–FID using the following conditions: Oven temperature: 75°C; initial pressure 70 atm held for 1 min, pressure ramp: 60 atm/min, final pressure: 360 atm. (b) SFC–ICP-MS chromatogram using an oven temperature of 50°C and the same pressure program described for (a). Peaks: 1 = TBT; 2 = TrBT-Cl; 3 = TrPT-Cl; 4 = TPT.

temperatures, however, better peak shape is obtained at 50°C. The same tendency is observed for the resolution between TrPT-Cl and TPT using SFC–ICP-MS. Another factor involved in peak broadening for ICP-MS detection is related to interface design and operation. The distance between the tip of the restrictor and the detection zone is longer in ICP-MS than in FID. The lower temperature at the tip of the restrictor for SFC–ICP-MS causes a slow release of the analyte and as a consequence, peak broadening

TABLE II

EFFECT OF TEMPERATURE IN THE RESOLUTION OF ORGANOTIN COMPOUNDS USING SFC INTERFACED TO ICP-MS AND FID

Pressure program: 70 atm held for 1 min; ramp: 60 atm/min to 320 atm.

Oven temperature (°C)	TBT and TrBT-Cl		TrBT-Cl and TrPT-Cl		TrPT-Cl and TPT	
	ICP-MS	FID	ICP-MS	FID	ICP-MS	FID
50	0.933	0.571	3.200	4.133	0.692	1.125
75	1.067	1.002	2.355	5.250	0.540	1.455
100	1.071	1.263	1.654	5.308	0.513	1.467

and decrease in resolution are observed. Fig. 7 presents the best chromatograms obtained using a 2.5-m capillary column for the separation of organotins using SFC coupled to FID and ICP-MS. Variations in the temperatures of the oven, of the transfer line and of the restrictor tip affect mobile phase density and mobile phase velocity. As a consequence, there are changes in retention times and peak widths as well as in resolution comparing the two systems (SFC–FID and SFC–ICP-MS). A comparison of the chromatograms obtained using a longer column (4 m) is presented in Fig. 8. Baseline resolution between TrPT-Cl and TPT is now possible for the SFC–ICP-MS system (see Fig. 8b). Also, the impurity detected in the standard solutions and labeled as X in Fig. 7b is resolved into two peaks when a 4-m column is used. These impurities correspond to compounds containing tin and they were not detected by SFC–FID, most likely because of the difference in sensitivity of the detectors.

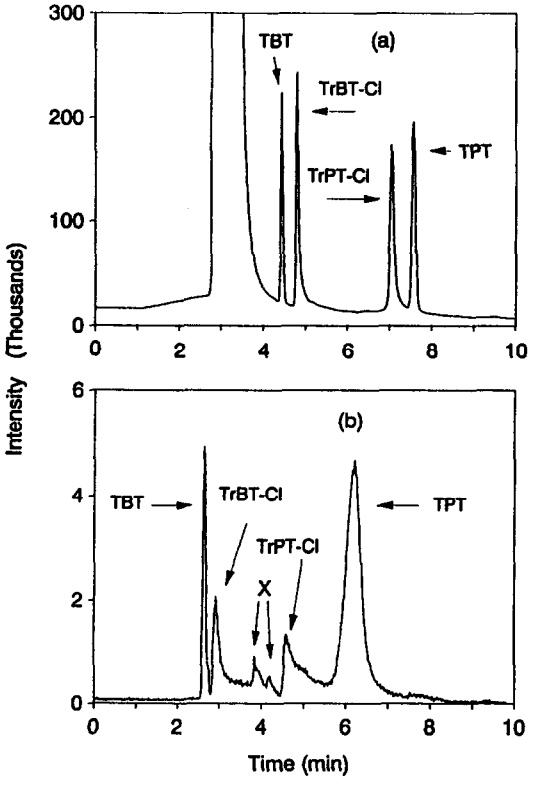

Fig. 8. Separation of organotins using a 4-m SB-Biphenyl-30 column: (a) SFC–ICP-MS and (b) SFC–FID. Initial pressure: 80 atm held for 2.5 min, followed by a pressure ramp of (a) 150 atm/min for ICP-MS and (b) 60 atm/min for SFC–FID; final pressure: 400 atm held for 5 min.

FID vs. ICP-MS: sensitivity and selectivity

Analytical figures of merit for tri- and tetra-organotins using SFC–FID and SFC–ICP-MS are presented in Table III. Five 50-nl injections containing 0.5 ng Sn gives a reproducibility range from 3.2 to 6.4% R.S.D. in the SFC–FID experiments. Using the same number of injections, but samples containing 0.05 ng Sn, reproducibility varies from 1.3 to 3.4% R.S.D. with the SFC–ICP-MS system. Detection limits are calculated as three times the standard deviation

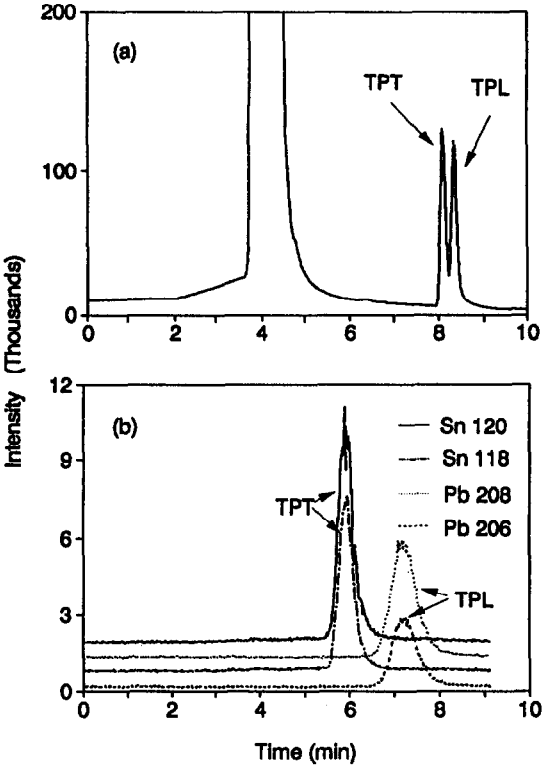

Fig. 9. Chromatograms for a mixture of tetraphenyltin (TPT) and tetraphenyllead (TPL). Column: SB-Biphenyl-30, 4 m length. Oven temperature: 75°C. (a) SFC–FID. Conditions: initial pressure: 70 atm held for 2 min followed by a pressure ramp of 40 atm/min up to 320 atm; detector temperature: 350°C. (b) SFC–ICP-MS. Conditions: initial pressure 80 atm held for 2 min followed by a pressure ramp of 150 atm/min up to 400 atm (held for 4 min); interface temperature: 350°C.

TABLE III

COMPARISON OF ANALYTICAL FIGURES OF MERIT FOR ORGANOTIN COMPOUNDS USING SFC–FID AND SFC–ICP-MS

		TBT	TrBT-Cl	TrPT-Cl	TPT
Reproducibility (%)[a]	SFC–FID	4.64	4.92	6.43	3.20
	SFC–ICP-MS	1.29	1.52	1.67	3.42
Absolute detection limit (pg), 50-nl injection	SFC–FID	10.3	12.5	12.0	9.0
	SFC–ICP-MS	0.26	0.80	0.57	0.20
Linear range[b]	SFC–FID	3	3	3	3
	SFC–ICP-MS	3	3	3	3
Slope (log–log)	SFC–FID	1.0006	0.9736	1.0130	0.9816
	SFC–ICP-MS	0.9647	1.1749	1.0980	1.0310
R^2 (correlation coefficient)	SFC–FID	0.9990	0.9981	0.9969	0.9991
	SFC–ICP-MS	0.9936	0.9960	0.9870	0.9803

[a] Reproducibility in peak area; 5 and 0.5 ng injection for SFC–FID and SFC–ICP-MS, respectively.
[b] Linear range between 0.5 and 50 ng for SFC–FID and between 0.05 and 5 ng using SFC–ICP-MS.

(σ) of the blank signal divided by the slope of the calibration curve. Absolute detection limits (50 nl injection volume) for organotins with SFC–FID range from 9.0 to 12.5 pg. An improvement of one order of magnitude in sensitivity is found for SFC–ICP-MS detection (absolute detection limits range from 0.2 to 0.8 pg). Linearity over three orders of magnitude is presented for both SFC–FID and SFC–ICP-MS in the detection of organotins.

Differences in mobile phase velocity, comparing SFC–FID and SFC–ICP-MS have some advantages. This is the case of the baseline resolution obtained using SFC–ICP-MS for the separation of TPT and TPL (see Fig. 9b). Different chromatographic conditions were evaluated in SFC–FID to resolve TPT and TPL, but no baseline resolution was possible and the best chromatogram is shown in Fig. 9a. Another relevant advantage of ICP-MS over FID is the element-selective capability of the former detector. Non-baseline resolution and coelution of compounds with a different central atom can be resolved using the time-resolved acquisition software of the VG PlasmaQuad, that allows monitoring several m/z positions by moving rapidly between them. Fig. 9b also demonstrates the ICP-MS capability to detect selected isotopes and the potential to obtain multielement chromatograms.

CONCLUSIONS

Control of the temperature for the SFC–ICP-MS interface is vitally important, while variations for the detector temperature for SFC–FID, in the same range of temperatures (215 to 350°C), do not affect the results. Fluctuations in the transfer line temperature for the SFC–ICP-MS system is the main source of peak broadening. Better resolution among organotins is obtained in SFC–FID at a column temperature of 75°C; while in SFC–ICP-MS the best results (but non-baseline resolution between TrPT-Cl and TPT) is obtained at 50°C. The use of a 4-m column improves separation, and baseline resolution is obtained among tri- and tetra-organotins in both SFC–FID and SFC–ICP-MS. The major advantages of FID are low cost and ease of operation, while ICP-MS as a detector for SFC is more sensitive and selective than FID. In addition ICP-MS allows the use of modifiers. Application of the technique for the analysis of real samples, will yield more interferences by SFC–FID than by SFC–ICP-MS since FID is an universal detector and ICP-MS is an element-

selective detector. Thus a cleaner and more conclusive chromatogram will be obtained by using SFC–ICP-MS.

ACKNOWLEDGEMENTS

The authors are grateful to the National Institute of Environmental Health Science for support through research grants ES-03221 and ES-04908. We also acknowledge the NIH-BRS Shared Instruments Grants gram for providing the VG PlasmaQuad through grant number S10 RR02714. VG Elemental and Lee Scientific are credited for providing partial instrument support. Special thanks to Uma Kumar and Jeff Giglio for helping with the manuscript.

REFERENCES

1 J.C. Fjeldsted and M.L. Lee, *Anal. Chem.*, 56 (1984) 619A.
2 C.M. White and R.K. Houck, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 4.
3 P.J. Schoenmakers and F.C.C.J.C. Verhoeven, *Trends Anal. Chem.*, 6 (1987) 10.
4 R.D. Smith, B.W. Wright and C.R. Yonker, *Anal. Chem.*, 60 (1988) 1323A.
5 M.L. Lee and K.E. Markides (Editors), *Analytical Supercritical Fluid Chromatography and Extraction*, Chromatography Conferences, Provo, UT, 1990.
6 D.W. Later, D.J. Bornhop, E.D. Lee, J.D. Henion and R.C. Wieboldt, *LC · GC*, 5 (1987) 804.
7 D.J. Bornhop and J.G. Wangsgaard, *J. Chromatogr. Sci.*, 27 (1989) 293.
8 B.E. Richter, D.J. Bornhop, J.T. Swanson, J.G. Wangsgaard and M.R. Andersen, *J. Chromatogr. Sci.*, 27 (1989) 303.
9 J.C. Fjelested, R.C. Kong and M.L. Lee, *J. Chromatogr.*, 279 (1983) 449.
10 M.A. Morrissey and H.H. Hill, Jr., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 375
11 L.A. Pekay and S.V. Olesik, *Anal. Chem.*, 61 (1989) 2616.
12 H-C.K. Chang and L.T. Taylor, *J. Chromatogr. Sci.*, 28 (1990) 29.
13 W.R. West and M.L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 161.
14 E.R. Campbell and B.E. Richter, *LC · GC*, 10 (1992) 40.
15 K.D. Bartle, M.W. Raynor, A.A. Clifford, I.L. Davies, J.P. Kithinji, G.F. Shilstone, J.M. Chalmers and B.W. Cook, *J. Chromatogr. Sci.*, 27 (1989) 283.
16 P.J. Arpino, J. Cousin and J. Higgins, *Trends Anal. Chem.*, 6 (1987) 69.
17 A.J. Berry, D.E. Games, I.C. Mylchreest, J.R. Perkins and S. Pleasance, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 61.
18 J.D. Pinkston, G.D. Owens, L.J. Burkes, T.E. Delaney, D.S. Millington and D.A. Maltby, *Anal. Chem.*, 60 (1988) 962.
19 R.J. Skelton, Jr., P.B. Farnsworth, K.E. Markides and M.L. Lee, *Anal. Chem.*, 61 (1989) 1815.
20 P.C. Uden (Editor), *Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy (ACS Symposium Series*, No. 479), American Chemical Society, Washington, DC, 1992, p. 19.
21 C.B. Motley, M. Ashraf-Khorassani and G.L. Long, *Appl. Spectrosc.*, 43 (1989) 737.
22 M. Ashraf-Khorassani, J.W. Hellgeth and L.T. Taylor, *Anal. Chem.*, 59 (1987) 2077
23 C. Fujimoto, H. Yoshida and K. Jinno, *J. Microcol. Sep.*, 1 (1989) 19.
24 W.L. Shen, N.P. Vela, B.S. Sheppard and J.A. Caruso, *Anal. Chem.*, 63 (1991) 1491.
25 N.P. Vela and J.A. Caruso, *J. Anal. At. Spectrom.*, 7 (1992) 971.
26 P.G. Harrison, in P.G. Harrison (Editor), *Chemistry of Tin*, Chapman & Hall, New York, 1989, p. 358.
27 R.M. Harrison and S. Rapsomanikis, in R.M. Harrison and S. Rapsomanikis (Editors), *Environmental Analysis using Chromatography Interfaced with Atomic Spectroscopy*, Wiley, New York, 1989, p. 189.
28 O. Evans, B.J. Jacobs and A.I. Cohen, *Analyst*, 116 (1991) 15.
29 T. Tsuda, H. Nakaniski, S. Aoki and J. Takebayashi, *J. Chromatogr.*, 387 (1987) 361.
30 J.J. Sullivan, J.D. Torkelson, M.M. Wekell, T.A. Hollingworth, W.L. Saxton and G.A. Miller, *Anal. Chem.*, 60 (1988) 626.
31 S. Ohhira and H. Matsui, *J. Chromatogr.*, 525 (1990) 105.
32 K.W.M. Siu, P.S. Maxwell and S.S. Berman, *J. Chromatogr.*, 475 (1989) 373.
33 M.O. Stallard, S.Y. Cola and C.A. Dooley, *J. Organomet. Chem.*, 3 (1989) 105.
34 I.S. Krull, K.W. Panaro, J. Noonan and D. Erickson, *J. Organomet. Chem.*, 3 (1989) 295.
35 G.B. Jiang, P.S. Maxwell, K.W.M. Siu, X.T. Loung and S.S. Berman, *Anal. Chem.*, 63 (1991) 1506.
36 Y.K. Chau, P.T.S. Wong, G.A. Bengert and J. Yaromich, *Chem. Speciation Bioavailability*, 1 (1989) 151.
37 V. Desauziers, F. Leguille, M. Astruc and R. Pinel, *J. Organomet. Chem.*, 3 (1989) 469.
38 H. Suyani, J. Creed and J.A. Caruso, *J. Anal. At. Spectrom.*, 4 (1989) 777.
39 E.J. Parks, F.E. Brinckman, K.L. Jewett, W.R. Blair and C.S. Weiss, *Appl. Organomet. Chem.*, 2 (1988) 441.
40 A.P. Walton, G.T. Wei, Z. Liang, R. Michel and J.B. Morris, *Anal. Chem.*, 63 (1991) 232.
41 H. Suyani, J. Creed, T. Davidson and J.A. Caruso, *J. Chromatogr. Sci.*, 27 (1989) 139.
42 H. Suyani, D. Heitkemper, J. Creed and J.A. Caruso, *Appl. Spectrosc.*, 43 (1989) 962.