ELSEVIER

Journal of Chromatography A, 795 (1998) 359–370

JOURNAL OF CHROMATOGRAPHY A

Characterization of multicapillary gas chromatography–microwave-induced plasma atomic emission spectrometry for the expeditious analysis for organometallic compounds

Isaac Rodriguez Pereiro[1,a], Andrzej Wasik[b], Ryszard Łobiński[a,*]

[a]*CNRS, URA 348, Université Bordeaux I, F-33405 Talence, France*

[b]*Politechnika Gdanska, Chemical Faculty, Department of Analytical Chemistry, ul. G. Narutowicza 11/12, 80-952 Gdańsk, Poland*

Received 3 July 1997; received in revised form 11 September 1997; accepted 12 September 1997

Abstract

Multicapillary column gas chromatography (MC-GC)–microwave-induced plasma atomic emission spectrometry (MIP-AES) is evaluated for fast speciation analysis of organometallic compounds. In situ derivatized organomercury, organotin and organolead compounds are separated isothermally within several seconds instead of several minutes required by the conventional procedures. Neither the resolution nor the sample capacity are sacrificed compared with conventional capillary GC with oven temperature gradient programming. Sub-picogram detection limits are obtained. Examples of applications of MC-GC–MIP-AES to speciation of butyltin and organomercury compounds in sediment, and of tetraalkyllead compounds in gasoline are given. © 1998 Elsevier Science B.V.

Keywords: Detection, GC; Microwave-induced plasma atomic emission spectrometry; Sediments; Gasoline; Gas chromatography, multicapillary; Organotin compounds; Organomercury compounds; Organolead compounds

1. Introduction

The recognition of the fact that the determination of the total level of a metal or of a metalloid is not sufficient to evaluate its impact on the environment, its bioavailability and its toxicity has stimulated the development of species-selective analytical methodology during the last decade [1–5]. The principal elements of interest include those released into the environment as organometallic species (e.g., alkyllead, alkyl- and aryltin) following an anthropogenic activity, or those (Hg, As, Ge, Se) of which the metabolism (e.g., detoxification) or transport mechanisms (e.g., volatilization from the ocean) involve the formation of a metal–carbon bond (e.g., by biomethylation).

The analytical problem consists of bringing the metal-containing species present in a sample to a sensitive (absolute detection limit at the pg level) element-specific detector in the time-resolved manner in a minimum of time. The commonly accepted

*Corresponding author. Present address: CNRS EP132, Hélioparc, 2 Avenue Pr. Angot, F-64000 Pau, France.

[1]Present address: CNRS EP132, Hélioparc, 2 Avenue Pr. Angot, F-64000 Pau, France.

PII S0021-9673(97)00954-0

approach has been a coupling of capillary gas chromatography (GC) with an atomic spectrometric (AS) technique because of the high-resolution and sensitivity, the latter due to the efficient (quasi-100%) sample introduction into a detector and virtually no energy losses for the desolvation and vaporization of the mobile phase [6–8]. The commercial availability of GC with microwave-induced plasma (MIP) atomic emission spectrometry (AES) detection since 1989 [9,10], and the rapidly growing availability of inductively coupled plasma (ICP) mass spectrometers in analytical laboratories have considerably contributed to the exponential growth of the number of applications of GC–AS to real-world analytical problems in recent years.

The analysis time and the sample throughput have long been controlled by the length of the sample preparation step which was traditionally complex, multistep and time-consuming [11]. However, a series of recently reported rapid 3-min-long microwave-assisted approaches integrating sample decomposition/leaching, extraction of the analytes into a non-polar solvent and their derivatization changed this situation [12,13]. It is the duration of a GC run that has now become the virtual bottleneck of an analytical procedure. Indeed, a GC run should be seldom shorter than 15 min. The additional time necessary to cool down the oven from the end-temperature (>250°C) to the starting temperature (ca. 60°C) limits further the sample throughput.

Fast GC pioneered by Desty [14] has been in the focus of interest for many years. The increase in efficiency has been achieved by reducing the column inner diameter (down to 10 μm) which allowed the use of shorter columns, and, consequently, separations within several seconds instead of several minutes, at the expense, however, of injection volume [15,16]. The latter is critical in trace environmental analysis. Only recently, a bundle of ca. 1000 1 m×40 μm I.D. wall-coated open-tubular capillaries denoted as a multicapillary (MC) column was reported to overcome this limitation [17].

The purpose of this paper is to optimize and evaluate the coupling of MC-GC with MIP-AES for species-selective analysis of volatile organomercury, -tin, and -lead and -mercury, down to the sub-picogram level.

2. Experimental

2.1. Apparatus

Chromatographic separations were carried out using an HP Model 6890 gas chromatograph (Hewlett-Packard, Wilmington, DE, USA) equipped with a capillary split/splitless injection port with electronic pressure control. Detection was achieved with an HP Model G2350A AES detector. Injections were made by means of an HP 6890 series automatic sampler. Data was handled using an HP Model D3398A ChemStation. Analyte species were separated on a MC column consisting of ca. 900 capillaries (1 m×40 μm I.D.) coated with 0.2 μm of SE-30 (Alltech Associates, PA, USA). It was connected at both ends to desactivated alumina tubes (ca. 0.3 m×0.53 mm I.D.). A piece (0.6 m×0.32 mm) of desactivated silica tubing (Alltech) served as a transfer line to the detector. The zero-dead volume feather-light connectors (Alltech) with associated ferrules were used. The column can work up to a maximum temperature of 200°C which is limited by the temperature resistance of the connectors between the MC column and desactivated alumina tubes, and not by the stability of the stationary phase.

Organotin and organomercury compounds were extracted from sediment samples in a 50-ml open vessel with a condenser made of borosilicate glass. A Microdigest Model A301 (2.45 GHz, maximum power 200 W) microwave digester (Prolabo, Fontenay-sous-Bois, France) equipped with a TX32 programmer was used.

2.2. Reagents

HPLC-grade solvents and analytical-grade chemicals, obtained from Aldrich (Milwaukee, WI, USA), and Milli-Q water (Millipore, Milford, MA, USA), were used throughout unless otherwise stated. The glassware used was cleaned with a common detergent, thoroughly rinsed with tap water, soaked for 12 h in a 10% nitric acid solution and finally rinsed with deionized water just before use.

Derivatization reagents, sodium tetraethylborate ($NaBEt_4$) and sodium borohydride ($NaBH_4$), were purchased from Strem (Bisscheim, France) and Al-

drich, respectively. Buffer solution was prepared by dissolving 2 *M* of sodium acetate in water followed by adjusting pH to 5 with conc. acetic acid.

2.3. Standards and samples

Standards of $BuSnCl_3$, Bu_2SnCl_2, Bu_3SnCl, $MeSnCl_3$, Me_2SnCl_2, Me_3SnCl, Me_4Sn were obtained from Aldrich. Individual stock solutions were prepared in methanol for polar compounds and in hexane for Me_4Sn. Dilute standards for each compound, and mixtures of butyl and methyl compounds were prepared weekly by dissolving concentrated standards in hexane (Me_4Sn) or methanol. Ethylated methyltin derivatives were prepared from the corresponding chloride compounds by extraction from 1 ml of a fresh 1% $NaBEt_4$ solution in water buffered to pH 5, into pentane. Butyltin hydrides were generated from ionic butyltin compounds using $NaBH_4$ and extracted into pentane [18].

Regarding mercury species, mercury(II) chloride $HgCl_2$ and methylmercury chloride (MeHgCl) were obtained from Aldrich. Individual stock solutions (1 mg/ml as Hg) were prepared by dissolving $HgCl_2$ and MeHgCl in a 1% solution of HNO_3 and in methanol, respectively. Dilute standards and mixtures of both species were made in methanol. Ethylated mercury species (MeEtHg and Et_2Hg) were prepared from the relevant ionic compounds by extraction from 1 ml of 0.1% aqueous $NaBEt_4$ fresh solution at pH 5 for 5 min into hexane.

Commercial solutions of Me_4Pb (39.3% Me_4Pb, 19% 1,2-dichloroethane, 18% 1,2-dibromoethane and 13% toluene) and Et_4Pb (99%) were obtained from Octel (Paris, France). Individual standards solutions and mixtures of both species were prepared in pentane. Concentrated standard solutions were manipulated in a separate room and stored in double glass containers to avoid cross-contamination problems. All organometallic standard solutions were protected from light and stored at 4°C.

The PACS-1 reference sediment containing butyltin compounds, issued by the National Research Council of Canada (NRCC), was purchased from Promochem (France). A certified reference material (CRM) sediment (CRM-580) was obtained from Community Bureau of Reference (BCR, Brussels, Belgium). Samples of leaded petrol were taken from local fuel stations.

2.4. Procedures

Determination of lead species in petrol samples were performed directly after the dilution of a sample in pentane (ca. 2000 times).

Extraction of tin and mercury compounds in sediments samples was performed using microwave-assisted procedures previously described in the literature [13,19]. In brief: for an extraction of organotin compounds, a sample of 0.1–0.2 g of sediment was leached with 10 ml of acetic acid solution (1+1) at a microwave power of 60 W for 2 min. The supernatant solution was separated from the sediment and extracted with ca. 0.2 g of $NaBH_4$ into 2 ml of hexane by shaking for 5 min. The organic phase was injected in the chromatographic system. For an extraction of mercury compounds a sample ca. 1 g of sediment was leached with 10 ml of 2 *M* HNO_3 at a microwave power of 60 W for 3 min. The supernatant solution was separated and neutralized with aqueous NH_3. After the adjustment of pH to 5, 1 ml of a 0.1% $NaBEt_4$ solution and 2 ml of hexane were added and the mixture was shaken for 5 min.

Optimum GC and AES conditions for the determination of organolead, tin and mercury species are summarized in Table 1.

3. Results and discussion

It is well known in GC that efficiency (number of theoretical plates per unit length) increases with the decreasing inner diameter of the capillary [20,21]. However, the lower the inner diameter, the lower also the injectable sample volume and, consequently, the higher the minimum detectable concentration of analyte. For these reasons capillaries with an internal diameter below 0.25 mm are seldom used. A way to overcome the above limitations is to increase the cross- section of the carrier flow-rate by assembling a large number of small-diameter capillaries into a bundle. This allows to combine the efficiency of a small diameter (ca. 0.04 mm) capillary with the sample capacity of a conventional capillary column.

Table 1
GC–MIP-AES conditions for the separation of organometallic compounds, using a MC column

	Mercury	Lead	Tin (methyltin species)	Tin (butytin species)
GC parameters				
Injection port	Split/splitless	Split/splitless	Split/splitless	Split/splitless
Injection mode	Split	Split	Split	Split
Injection port temperature (°C)	280	250	280	280
Injected volume (μl)	1	1	1	1
Column flow (ml/min)	65	95	65	65
Split relation	2:1	6:1	1:1	2:1
Oven program	A. Isothermal 70°C B. 70°C (0.1 min) 100°C/min 120°C	Isothermal 130°C	A. Isothermal 70°C B. 60°C (0.1 min) 100°C/min 120°C	60°C (0.1 min) 100°C/min 180°C
AES parameters				
Transfer line temperature (°C)	280	250	280	280
Cavity block temperature (°C)	280	250	280	280
Wavelength (nm)	253.65	405.78	303.42	303.42
Helium make-up flow (ml/min)	140	285	260	260
Spectrometer purge flow (l/min)	2	2	2	2
Solvent vent (min)	0.19	0.07	0.10	0.20
H_2 pressure (p.s.i.)	50	25	25	25
O_2 pressure (p.s.i.)	10	30	35	35

The high linear flow-rates (up to 3 m/s) through a MC column set strong requirements in terms of injection time to avoid peak broadening, and in terms of the detector's time constant to allow the acquisition of a representative number of data points for a short transient signal. The fast injection needed can be ensured by using a split injector; this causes a loss in sensitivity which should be compensated by the low absolute detection limit of the detector. An MIP-AES system matches the above characteristics in a close to ideal way. Absolute detection limits for many elements are at the 0.1 pg level and the response time is fast [6,9]. Another advantage is the small dead volume of the detector which does not distort the sharp (half-width down to 0.3 s) chromatographic peaks.

3.1. Van Deemter (Golay–Giddings) curves

Fig. 1 compares the Van Deemter (Golay–Giddings) curves obtained for representative compounds of each of the investigated elements using a MC and a conventional capillary column with a similar coating. Whereas a conventional (BP-5 30 m×0.32 mm) capillary shows a narrow maximum of efficiency, defined as the minimum value of the height of a theoretical plate (HETP), with a gas velocity range of 20 cm/s of He, corresponding to a column flow of about 1 ml/min, the shape of the curve for the MC column shows two important peculiarities. Firstly, the minimum HETP value is smaller than that obtained with the conventional capillary column. Secondly, this minimum is very broad (80–280 cm/s or 60–210 ml/min) which allows the use of high flow-rates to shorten chromatographic separations without sacrificing peak resolution. Consequently, efficient separations can be achieved in a considerably shorter time.

3.2. Isothermal separations

Isothermal separation was optimized in the first place because (1) it offers a possibility to work with simpler hardware, and (2) the post-run cool-down phase can be avoided thus increasing the sample throughput.

The objective of the optimization was to achieve the shortest possible duration of a run which would assure both the separation of the most volatile analyte from the solvent peak and the baseline

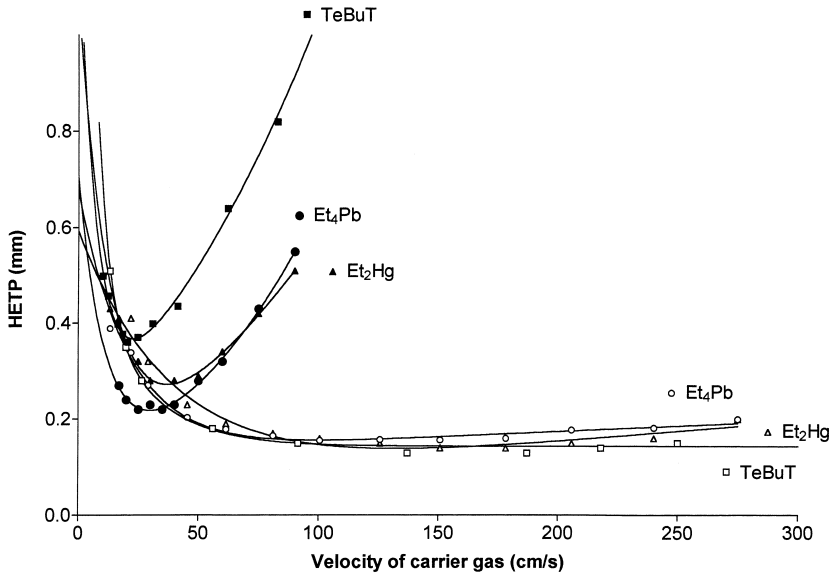

Fig. 1. Van Deemter curves for the organometallic compounds studied. (a) Et_2Hg (b.p.=159°C, t=70°C); (b) Bu_4Sn (b.p.=285°C, t=175°C); (c) Et_4Pb (b.p.=200°C, t=120°C). Closed symbols: BP-5 column; open symbols: MC column.

separation between the analytes. Fig. 2 presents example chromatograms using a MC column (each one obtained in a different run) for the three groups of organometallic species studied: tetramethyl and tetraethyl lead, ethylated mercury species and ethylated methyl tin compounds. A Gaussian shape with peak symmetry around 0.90 is always observed. In each case the duration of the run (15–30 s) is much shorter than that (8–15 min) obtained using a conventional capillary column with a gradient temperature oven programming mode, Fig. 3.

Fig. 2 shows a very good resolution between all the chromatographic peaks, which suggests the possibility of even faster separations if one worked at higher temperatures or at higher column flows. A more dramatic reduction of the duration of a GC run is prevented, however, by the necessity of separating the solvent band from the most volatile analyte of each group; otherwise the plasma is disturbed and deposits are formed in the discharge tube. Even working with pentane (b.p. 36.5°C), it turned out to be impossible to vent the solvent off the plasma in less than 0.06–0.07 min, even when split ratios up to 6:1 were used. Higher split ratios were not attempted because of the enormous high-purity helium consumption. A possible solution to this problem is to eliminate the organic solvent on the level of sample preparation by replacing the extraction of analytes into an organic phase by an extraction into a gas phase, followed by preconcentration of the analytes by cryogenic trapping and injection by flash heating of the trap. Another possibility to shorten the duration of a GC run is to increase the flow-rate or temperature after the solvent peak has passed. This was evaluated further.

3.3. Temperature programmed separations

The basic limitation of the isothermal elution mode is rapid peak broadening with the decreasing volatility of the analyte compound (Table 2). Whereas it is not of a big problem for volatile (b.p.< 150°C) species it is becoming one for compounds of which the boiling point is above the maximum working temperature of the column and large differences of individual analytes exist. Attempts to achieve an isothermal separation of $BuSnH_3$ (b.p. 100°C), Bu_2SnH_2 (b.p. 190°C) and Bu_3SnH (b.p. 260 C) within a reasonably short time (under 2 min) failed, in part because of the impossibility of resolving the $BuSnH_3$ peak from the solvent band at high oven temperatures and column flows.

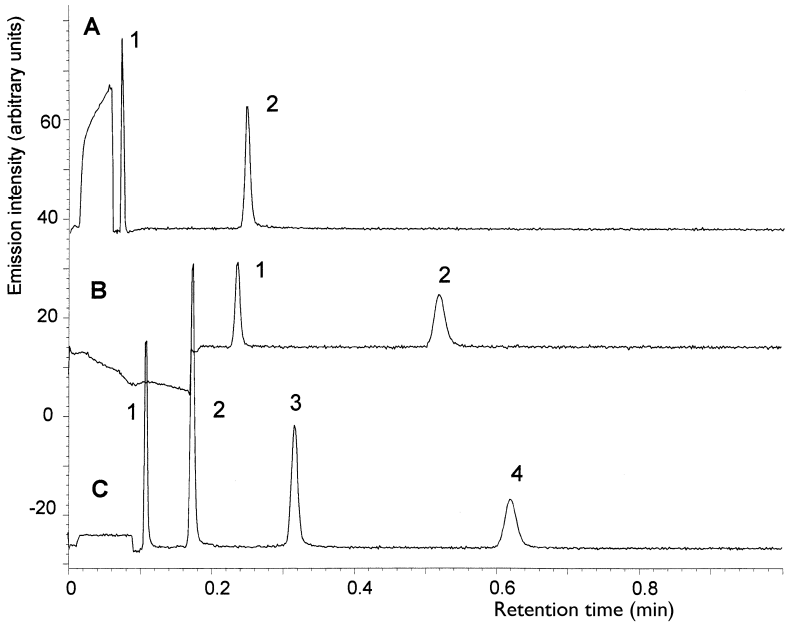

Fig. 2. Chromatograms obtained by MC-GC–MIP-AES for different mixtures of organometallic species in the isothermal mode. (A) 1=Me_4Pb (6.0 ng/ml), 2=Et_4Pb (10.4 ng/ml); Pb channel (406 nm); (B) 1=HgMeEt (14.0 ng/l), 2=$HgEt_2$ (14.0 ng/ml), Hg channel (254 nm); (C) 1=Me_4Sn (28.0 ng/ml), 2=Me_3SnEt (22.8 ng/ml), 3=Me_2SnEt_2 (15.8 ng/ml), 4=$MeSnEt_3$ (26.7 ng/ml), Sn channel (303 nm). Concentrations given as the metal.

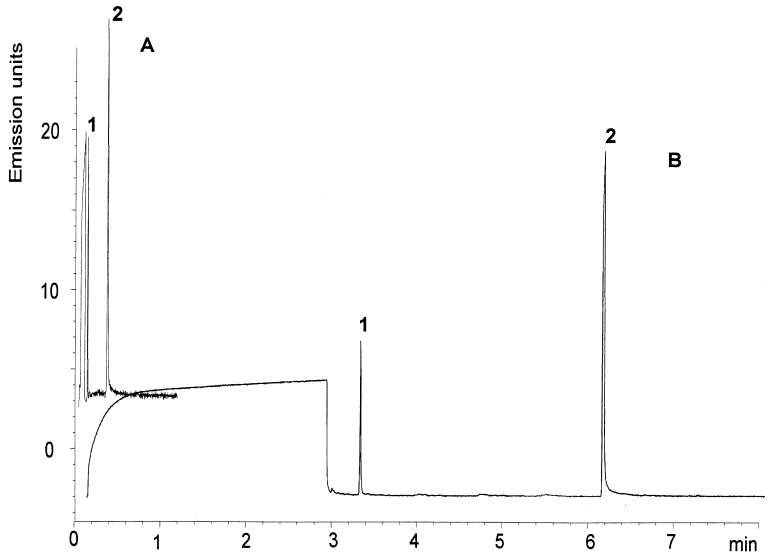

Fig. 3. Chromatogram for a standard mixture of organolead compounds in pentane: 1=Me_4Pb (6.0 ng/ml), 2 =Et_4Pb (10.4 ng/ml). (A) MC column (isothermal separation at 70°C); (B) conventional BP-5 column, 30 m×0.32 mm I.D., 0.25 μm [60°C (1 min), 20°C/min, 200°C].

Table 2
Typical peak width for studied compounds under conditions given in Table 1

Compound	Boiling point (°C)	Peak width ($min \cdot 10^{-3}$)	
		Isothermal	Temperature programmed
$BuSnH_3$	100		6
Bu_2SnH_2	190		13
Bu_3SnH	260		15
Me_4Sn	78	5	4
Me_3SnEt	105	7	7
Me_2SnEt_2	145	10	9
$MeSnEt_3$	163	19	10
HgMeEt		8	7
$HgEt_2$	159	16	9
Me_4Pb	110	1	
Et_4Pb	200	8	

Ramping the oven temperature at the maximum allowable rate of 100°C/min was thus attempted. Fig. 4 shows temperature programmed separations of organomercury species, ethylated methyltin compounds and butyltin hydrides. Whereas the resulting gain in retention time of 2–3 s for organomercury and methylethyltin compounds does not justify the extra time necessary to cool down the oven to the

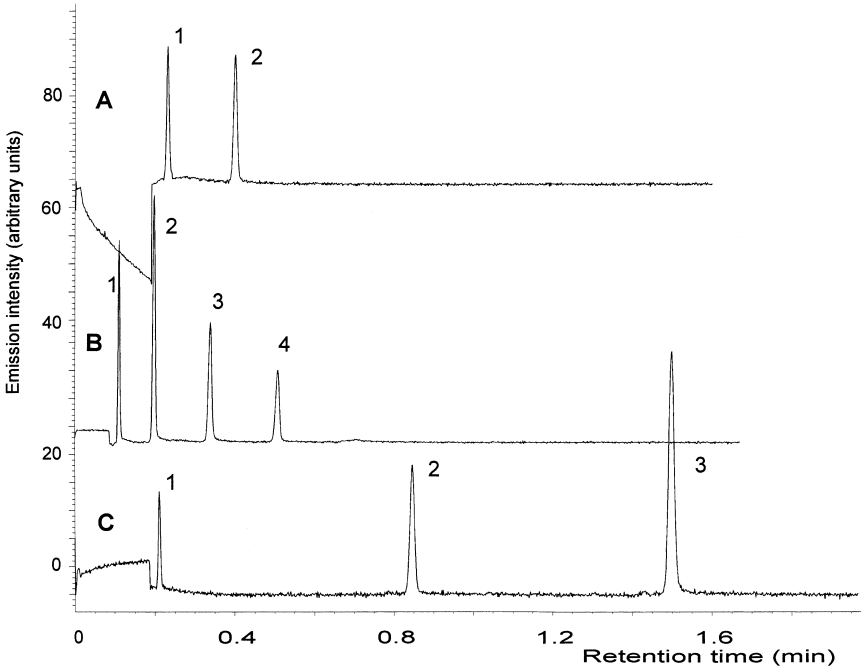

Fig. 4. Chromatograms obtained by MC-GC–MIP-AES for different mixtures of organometallic species in the oven temperature programmed mode (cf. Table 1). (A) 1=HgMeEt (14.0 ng/l), 2=$HgEt_2$ (14.0 ng/ml), Hg channel (254 nm); (B) 1=Me_4Sn (28.0 ng/ml), 2=Me_3SnEt (22.8 ng/ml), 3=Me_2SnEt_2 (15.8 ng/ml), 4=$MeSnEt_3$ (26.7 ng/ml), Sn channel (303 nm); (C) 1=$BuSnH_3$ (24.1 ng/ml), 2=Bu_2SnH_2 (19.7 ng/ml), 3=Bu_3SnH (35.6 ng/ml), Sn channel (303 nm). Concentrations given as the metal.

initial temperature, the temperature programmed mode allows to obtain an analytically useful chromatogram of butyltin hydrides.

Table 2 compares typical peak widths obtained with the MC column for isothermal and temperature programmed separations. The latter mode allows a significative decrease of the peak width for less volatile compounds. Smaller peak widths also result in increased sensitivity in the peak height mode.

Chromatographic separations on a MC column can also be accelerated by programming the carrier gas flow-rate. However, because the flow-rate changes the response of the detector a method to compensate it before the analytes reach the detector must be developed.

3.4. Data acquisition with MC columns

The high efficiency of MC columns sets particular requirements regarding the speed of detectors response. The maximum data acquisition rate of the instrument used is 10 Hz. Taking into account the minimum number of points (6) to allow for a precise definition of a chromatographic peak, it seems evident that peaks with half-widths below ca. 10^{-3} min (0.06 s) cannot be acquired. The need for fast separation makes splitless injection impossible; the split injection affects negatively the detection limits of the procedure which may be critical in trace analysis.

3.5. Optimization of the detection conditions

The Model G2350A detector used for this study differs a little from its predecessor (HP 5921A) in terms of configuration of the discharge tube and of the purge gas flow system. A re-optimization of the detector conditions was then judged necessary. The most critical parameter in terms of detection conditions is the helium plasma gas flow. It is measured at the cavity vent and is composed of the column flow, the normal make-up flow (which also carries the reagent gases), and the extra make-up flow (a fixed amount of 110 ml/min added by a make-up valve). Fig. 5 shows the effect of helium plasma gas and of the reagent gases for the three elements studied.

For tin and lead a maximum sensitivity is observed at high cavity flows (260 and 285 ml/min), whereas for mercury the optimum flow is lower (about 60 ml/min) (Fig. 5A). The optimum make-up flows are compatible with the optimum carrier gas

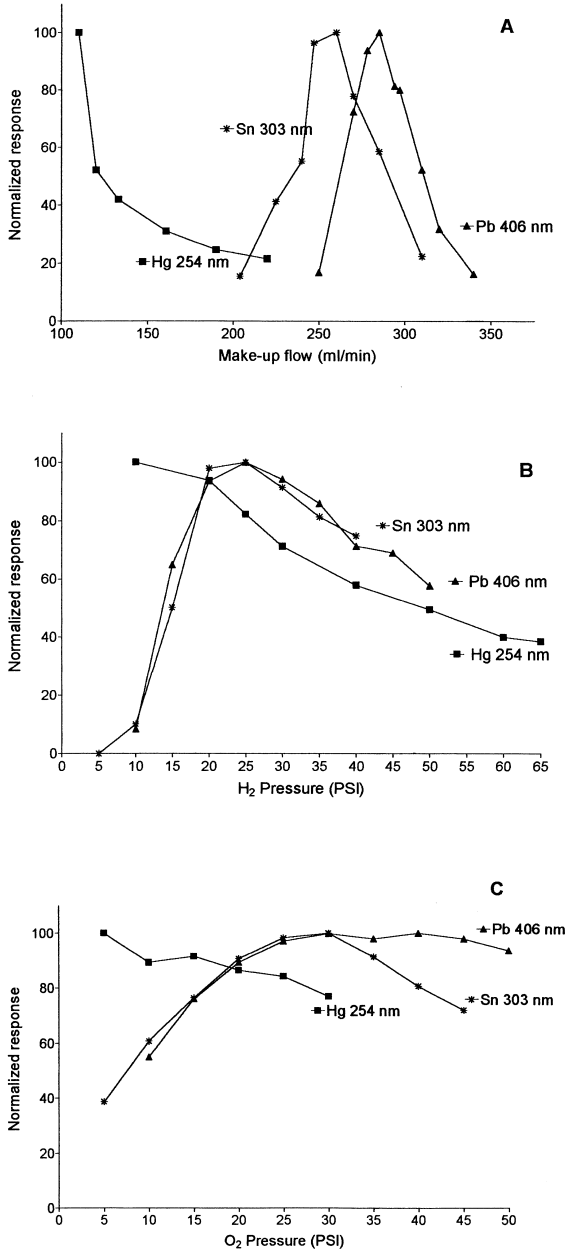

Fig. 5. Influence of the make-up and reagent gases on sensitivity of mercury, tin and lead. (A) Helium make-up flow (measured at the cavity vent); (B) hydrogen pressure; (C) oxygen pressure.

flow-rates for Sn and Pb compounds but not for mercury. In the latter case it is advantageous to work with the lowest column flow within the minimum of the Van Deemter curve) of 65 ml/min. At these conditions a minimum cavity flow ca. 100 ml/min was found necessary to provide enough hydrogen and oxygen to obtain a stable plasma. Higher flows resulted in a further loss of sensitivity but also improved the stability of the baseline. A make-up flow of 140 ml/min was adopted as a compromise value.

Influence of auxiliary gases, H_2 and O_2 on the detector response is shown in Fig. 5B and Fig. 5C, respectively. Tin and lead show curves with very similar optimum values. The response for mercury decreases when H_2 and O_2 pressures increase. It was observed that the stability of the baseline for Hg improves at high (50 p.s.i.) hydrogen supply pressures (Fig. 6) (1 p.s.i.=6894.76 Pa). For oxygen a minimum pressure of 10 p.s.i. was set to avoid the formation of deposits on the wall of the discharge tube.

3.6. Analytical figures of merit

Calibration curves were obtained by analyzing all the species under study at five levels of concentration between 2–3 ng/ml and ca. 200 ng/ml in isothermal and temperature programmed mode (cf. Table 1). Standards corresponding to each level were injected in duplicate. In all cases correlation coefficients (r^2) between 0.998 and 1.000 were obtained within the range investigated. Data are summarized in Table 3.

Table 3 also summarizes detection limits estimated as a minimum amount of analyte producing a signal-to-noise (S/N) ratio of 3. For the Hg and Sn species, low split ratios have been used so detection limits shown in Table 3 are close to the instrumental absolute detection limits (ADLs). For lead species a higher split ratio (6:1) needed to be used in other to alleviate the solvent interference which makes the values of detection limits higher that the instrumental ADLs. When a split ratio of 1:1 is used, a peak height of around 10 units per injected pg of lead is obtained for Me_4Pb which corresponds to a detection limit under 50 fg for lead; an ADL of 25 fg was reported in the literature [22].

Good precision of retention times, peak area and peak height was obtained for organometallic species using MC-GC as demonstrated by repeated injections of standard solutions in Table 4. The precision of the analysis for butyltin hydrides using a rapid oven temperature gradient (100°C/min) is similar to that obtained in isothermal separations. This suggests that in spite of the considerable diameter of the MC column the heat transfer and the temperature gradient

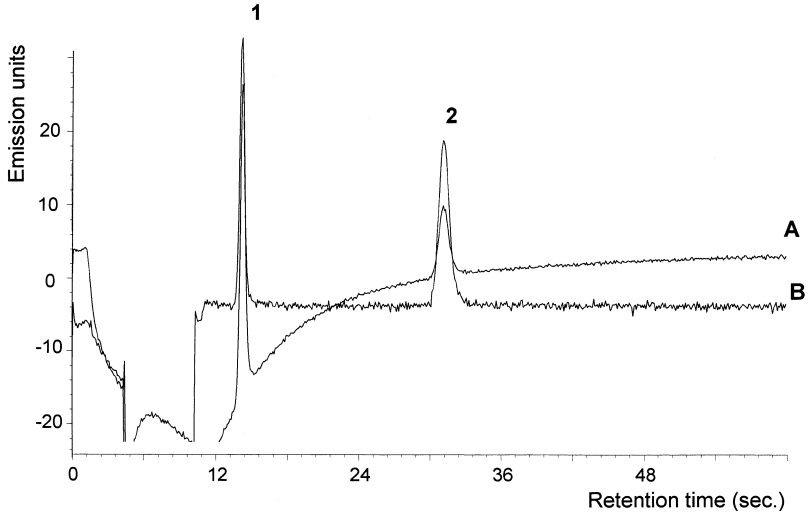

Fig. 6. Effect of hydrogen on the baseline stability during GC of organomercury species with MIP-AES detection. (A) 10 p.s.i., (B) 50 p.s.i.; 1=HgMeEt, 2=$HgEt_2$.

Table 3
Evaluation of system sensitivity and linearity, with the MC column, under conditions described in Table 1

Compound	Isothermal separations					Temperature programmed separations				
	Peak height units per injected pg.	Detection limit ($S/N=3$)	Slope	S.E.	Correlation coefficient (r^2)	Peak height units per injected pg.	Detection limit ($S/N=3$)	Slope	S.E.	Correlation coefficient (r^2)
HgMeEt	2.8	0.1	2.82	0.07	0.9980	2.6	0.1	2.62	0.07	0.9980
$HgEt_2$	1.8	0.2	1.80	0.04	0.9984	2.5	0.1	2.47	0.05	0.9986
Me_4Pb	3.4	0.07	3.38	0.05	0.9992					
Et_4Pb	1.4	0.18	1.36	0.01	0.9994					
$SnMe_4$	1.2	0.2	1.19	0.04	0.9985	1.5	0.2	1.53	0.03	0.9992
$SnMe_3Et$	0.9	0.3	0.87	0.01	0.9998	1.0	0.3	1.02	0.02	0.9995
$SnMe_2Et_2$	0.9	0.3	0.95	0.02	0.9993	1.1	0.2	1.07	0.01	0.9998
$SnMeEt_3$	0.3	1.0	0.26	0.01	0.9995	0.5	0.5	0.48	0.02	0.9993
$SnBuH_3$						0.4	0.8	0.37	0.005	0.9990
$SnBu_2H_2$						0.6	0.5	0.63	0.009	0.9986
$SnBu_3H$						0.6	0.5	0.64	0.004	0.9998

S.E.=Standard error.

between the internal capillaries and those close to the surface is very reproducible from one injection to another.

3.7. Analysis of real samples

MC-GC–MIP-AES was applied to the analysis of gasoline for alkyllead species and of two extracts of reference sediments for organomercury and organotin.

Fig. 7A shows a chromatogram of butyltin species, derivatized as hydrides and extracted into hexane. Analysis was carried out without a clean-up step. A 10-fold gain in the analysis time is achieved in comparison with the literature reports [18,23].

Fig. 7B shows a chromatogram for a sample of

Table 4
Repeatibility of the GC–MIP-AES system, using a MC column, for tin mercury and lead species

Compound	Concentration (ng/ml as metal)	Isothermal separation			Temperature programmed separation		
		Retention time (min)	Peak height (emission units)	Peak area (arbitary units)	Retention time (min)	Peak height (emission units)	Peak area (arbitary units)
$SnBuH_3$	24.1				0.215±0.4%	8.5±3%	3.3±2%
$SnBu_2H_2$	19.7				0.859±0.2%	11.7±1%	9.8±2%
$SnBu_3H$	35.6				1.522±0.3%	21.5±3%	22.1±2%
$SnMe_4$	28.0	0.110±0.1%	43.6±3%	12.9±3%	0.125±0.2%	49.1±3%	14.0±3%
$SnMe_3Et$	22.8	0.175±0.3%	57.7±2%	22.6±2%	0.213±0.2%	59.5±2%	25.1±2%
$SnMe_2Et_2$	15.8	0.318±0.2%	24.9±2%	17.7±3%	0.355±0.1%	28.0±2%	16.9±4%
$SnMeEt_3$	26.7	0.621±0.1%	9.8±1%	12.5±4%	0.526±0.2%	16.9±3%	12.3±4%
HgMeEt	50.0	0.237±0.2%	138.3±2%	69.3±2%	0.206±0.2%	117.8±6%	46.3±6%
$HgEt_2$	51.2	0.518±0.1%	103.6±2%	120.2±1%	0.345±0.2%	116.7±4%	67.6±5%
Me_4Pb	20.1	0.073±0.7%	64.1±4%	18.1±4%			
Et_4Pb	22.4	0.247±0.3%	33.1±1%	17.9±1%			

$n=10$ injections.

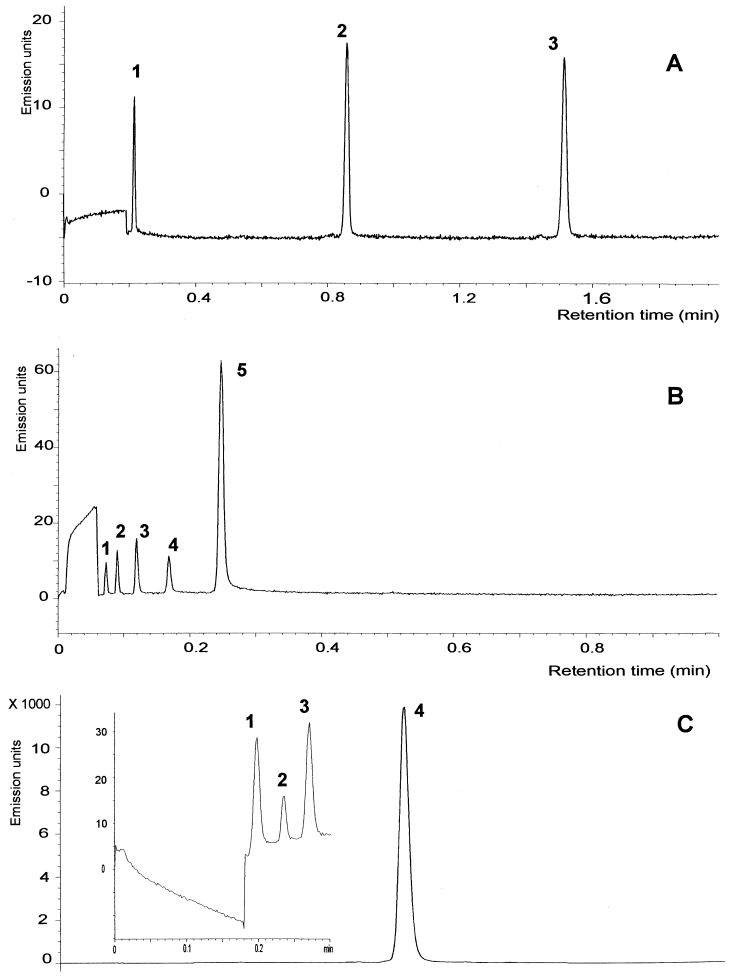

Fig. 7. Chromatograms obtained for real world samples by MC-GC–MIP-AES. (A) PACS-1 sediment (100 mg). 1=$BuSnH_3$, 2=Bu_2SnH_2, 3=Bu_3SnH; (B) leaded gasoline (diluted 1:2000 in pentane). 1=Me_4Pb, 2=Me_3PbEt, 3=Me_2PbEt_2, 4=$MePbEt_3$, 5=Et_4Pb. (C) CRM-580 sediment (500 mg). 1=Unknown, 2=HgMeEt, 3=unknown, 4=$HgEt_2$.

leaded gasoline diluted with pentane to alleviate the interference from heavier hydrocarbons. In a time of only 15 s, the MC column in isothermal mode is able to resolve five organolead species ($Me_nEt_{4-n}Pb$, $n=1\div4$). Upon dilution with pentane the baseline is stable and no ghost peaks are observed.

Fig. 7C shows a Hg-specific chromatogram obtained for a CRM-580 sediment. Apart from Et_2Hg and MeEtHg two other peaks appear. They remain unidentified, but their emission spectra contain three emission lines characteristic for mercury: 194.2, 253.7 and 184.9 nm. The large linear range allows one to quantify the ionic mercury and organomercury species within one run.

The method was validated for organotin compounds with two CRMs from different sources. For tributyltin the concentration found in the PACS-1 sediment (1.27 ± 0.04 μg/g as Sn) matches perfectly the certified value 1.27 ± 0.22 μg/g. An agreement between the found value of 1.00 ± 0.05 μg/g and the certified value of 1.16 ± 0.18 μg/g (as Sn) is also observed for dibutyltin. For biological tissues the only certified value in the NIES-11 Fish tissue available is that for tributyltin: 1.3 ± 0.1 μg/g as

chloride. The obtained 1.19 ± 0.02 μg/g remains in good agreement with the certified value.

4. Conclusions

MC chromatography which offers an over 10-fold reduction of the duration of chromatographic run without loss of efficiency and without loss of sample capacity is shown to be a promising tool for time-resolved sample introduction for atomic spectroscopy. The fact that separation can be carried in the isothermal mode offers further advantage in terms of increasing sample throughput owing to the elimination of the post-run cooling of the oven. Column flow-rates in the minimum of the Van Deemter curve are compatible with MIP-AES. MC-GC–MIP-AES is an attractive tool for rapid screening and quantitative analysis of volatile and thermally stable metallocompounds in organic solvents and in environmental matrices.

Acknowledgements

The study was financially supported by the European Union (Contract: SMT4-CT96-2044 Automated Speciation Analyser). I.R.P. acknowledges a post-doctoral fellowship of the Spanish government.

References

[1] R.M. Harrison, S. Rapsomanikis (Eds.), Environmental Analysis Using Chromatography Interfaced with Atomic Spectroscopy, Ellis Horwood, Chichester, 1989.
[2] I.K. Krull (Ed.), Trace Metal Analysis and Speciation, Elsevier, Amsterdam, 1991.
[3] P. Uden (Ed.), Element-specific Chromatographic Detection by Atomic Emission Spectroscopy, American Chemical Society, Washington DC, 1992.
[4] N.P. Vela, L.K. Olson, J.A. Caruso, Anal. Chem. 65 (1993) 585A.
[5] P.C. Uden, J. Chromatogr. A 703 (1995) 393.
[6] R. Lobinski, F.C. Adams, Trends Anal. Chem. 12 (1993) 41.
[7] R. Lobinski, Analusis 22 (1994) 37.
[8] R. Lobinski, F.C. Adams, Spectrochim. Acta Rev., (1997) in press.
[9] B.D. Quimby, J.J. Sullivan, Anal. Chem. 62 (1990) 1027.
[10] J.J. Sullivan, B.D. Quimby, Anal. Chem. 62 (1990) 1034.
[11] D.E. Wells, Mikrochim. Acta 109 (1992) 13.
[12] J. Szpunar, V.O. Schmitt, O.F.X. Donard, R. Łobiński, Trends Anal. Chem. 15 (1996) 181.
[13] I. Rodriguez Pereiro, V.O. Schmitt, J. Szpunar, O.F.X. Donard, R. Łobiński, Anal. Chem. 66 (1996) 4135.
[14] D.H. Desty, Adv. Chromatogr. 1 (1965) 199.
[15] R. Tijssen, N. van den Hoed, M.E. van Kreveld, Anal. Chem. 59 (1987) 1007.
[16] R. Annino, J. High Resolut. Chromatogr. 19 (1996) 285.
[17] V.O. Schmitt, I. Rodriguez Pereiro, R. Lobinski, Anal. Commun. 34 (1997) 141.
[18] M.J. Waldock, M.E. Waite, Appl. Organom. Chem. 8 (1994) 649–658.
[19] C.M. Tseng, A. de Diego, F. Martin, O.F.X. Donard, J. Anal. Atom. Spectrom., (1997) in press.
[20] D.W. Grant, Capillary Gas Chromatography, Wiley, Chichester, 1995.
[21] R.L. Grob, Modern Practice of Gas Chromatography, Wiley, Chichester, 3rd ed., 1995.
[22] R. Lobinski, F.C. Adams, Anal. Chim. Acta 262 (1992) 285.
[23] T.M. Dowling, P.C. Uden, J. Chromatogr. 644 (1993) 153.