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Species-Selective Analysis by Microcolumn Multicapillary Gas Chromatography with Inductively Coupled Plasma Mass Spectrometric Detection

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A glass rod (5−20 cm long, 2 mm o.d.) containing more than 1200 parallel microchannels (<40 μm i.d.) was converted into a high-resolution (>100 theoretical plates cm^{-1}) GC column by coating the inside of each channel in a way that compensated for the dispersion of the channel inner diameter. The columns were evaluated for the separation of mixtures of several organometallic (Hg, Sn, Pb) compounds prior to on-line sensitive metal-selective detection by ICPMS. Chromatographic separation conditions were optimized to enable a rapid (within a maximum 30 s) multielemental speciation analysis. Absolute detection limits were 0.1 pg for Hg, 0.05 pg for Sn, and 0.03 pg for Pb using the carrier gas flows of ∼200 mL min^{-1}. The microcolumn multicapillary GC/ICPMS developed was applied to the analysis of a number of environmental samples. The results were validated with certified reference materials for tin (BCR477, PACS-2) and mercury (DORM-1, TORT-1).

Because of the impact on the environment and the quality of foodstuffs, species-selective analysis for organometallic compounds has been attracting increasing popularity during the past two decades.[1] The notoriety of the Minamata accident raised concerns about the differentiation between methylmercury and inorganic mercury in aquatic biota.[2] Dying out of oysters drew attention to the use of organotin compounds in antifouling paints.[3] The toxicity of tetraalkyllead still in use as antiknock additives to gasoline in many countries stimulated studies of the environmental pollution by organic forms of lead.[4] The recognition of these hazards has stimulated the interest of regulatory agencies, quality control laboratories, and, consequently, of manufacturers of analytical instrumentation, in speciation analysis.[5]

The most widely used instrumental approach to speciation analysis has been based on the use of a coupled (hyphenated) technique combining a high-resolution separation technique with a sensitive element-selective detector.[6−9] The volatility and thermal stability of organometallic compounds (or ease of their conversion to volatile and thermally stable species) have favored gas chromatography as the separation technique. Plasma source techniques using excitation in a microwave-induced plasma (MIP AES) or ionization in an inductively coupled plasma (ICPMS) have been used as sensitive element-selective detectors.[6−9]

The state-of-the art knowledge implies the use of a packed or a capillary column housed in a regular GC oven with temperature gradient programming to carry out the separation of organometallic contaminants prior to element-selective detection.[7,8] The need for a fairly large column and the oven prevents the miniaturization of the separation unit and makes impossible the

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conception of a small-size sample introduction accessory dedicated to the environmental speciation analysis by atomic spectrometry. In addition, packed columns suffer from the poor separation efficiency; the sensitivity is compromised by the dispersion of the analytes on the column and often their degradation because of the interaction with the packing. Capillary columns offer improved efficiency, but runs are long and the need to cool the oven to the initial temperature limits the sample throughput to 2−3 samples/h.

Recently, a multicapillary (MC) column (a bundle of 919 40-μm capillaries) became commercially available (Alltech, Deerfield, IL) in the form of a 1-m helix.[10] The MC column was shown to preserve the advantages of both packed and capillary columns while eliminating their drawbacks[10,11] and turned out to be an attractive tool for GC analysis of organohalogen compounds[10,12,13] and for time-resolved introduction of organometallic compounds in atomic spectrometry.[14−16] Baseline separations could be achieved within a fraction (one-tenth) of the time required in capillary GC. They were reached in the isothermal mode that allowed some reduction of the oven size and increased the sample throughput. On the other hand, the elevated price, fragility, and still considerable size (a helix of 20-cm diameter) of such a column leave much area for improvement.

In terms of detectors, MIP AES has been the most widely used technique because of the commercial availability of the interface with GC and good compatibility of the carrier gas (60−200 mL^{-1}) with the gas flow rate required by the detector (50−300 mL^{-1}).[14−16] The basic problem is the isothermal separation of more volatile analytes from the tail of the solvent peak that perturbs the plasma.[15] This fact controls the minimum length of the multicapillary column which is 1 m for environmental applications.[15] The problem of the solvent effect can be apparently alleviated by the use of ICPMS detection, but the applications reported so far considered the purge-and-trap injection with no organic solvent present.[17,18]

The goal of this paper was to develop a multicapillary microcolumn dedicated to the separation of anthropogenic organometallic (Hg, Sn, Pb) compounds in environmental samples prior to their analysis by ICPMS. A new type of efficiently heated interface is evaluated for the introduction of GC effluents into an ICPMS with objectives of eliminating the postcolumn condensation and peak broadening, decreasing the detection limits, and improving calibration by the use of the xenon gas as internal standard.

EXPERIMENTAL SECTION

Apparatus. The GC used in this work was a HP model 5890 Series II Plus gas chromatograph (Hewlett-Packard, Wilmington, DE) equipped with a split−splitless injection port with electronic pressure control. Injections were made, usually in split mode, using a HP 6890 series autosampler. The ICPMS was a HP model 4500 ICPMS system (Hewlett-Packard, Palo Alto, CA). Chromatographic data were handled using specific software developed for the ICP system. The interface between GC and ICPMS and the connections are schematically shown in Figure 1.

The interface (Chemical Art Co., Tokyo, Japan)[19,20] was a deactivated fused-silica 1.5 m × 0.32 mm i.d. capillary tube that was threaded through a 1-m flexible heated transfer line and further through a 10-cm rigid transfer line up to the end of the central channel of the ICPMS torch.[19,20] The flexible part of the transfer line consisted of a $^1/_{16}$-in. stainless steel tube that was heated resistively and thermally insulated (inset A). Xenon gas (100 ppm in argon) was added at a constant mass flow rate (5 mL min^{-1}) to the argon nebulizer gas using a mass flow controller via a T piece. The makeup gas (argon with an admixture of xenon) was preheated by passing through a 1-m $^1/_{16}$-in. coil placed inside the chromatographic oven. It was made to flow between the internal wall of the heated transfer line and the external wall of the capillary tube and to merge with the GC carrier gas just before the plasma. The rigid part of the transfer line encapsulated an additional heater and a thermocouple to measure the temperature (inset B). The heaters extended to 5 cm from the end of the capillary (inset C). The end of the rigid part (inset D) was placed inside the ICPMS torch in place of the conventional injector. No special heating element was present in this part, but the stainless steel $^1/_{16}$-in. tube remained hot owing to its thermal conductivity.

Extraction of organotin and mercury species from sediments and biological materials were carried out in 22-mL open borosilicate glass vessels fitted with a 10-cm condenser using a Synthewave S402 microwave digester (2.45 GHz, maximum power 300 W) (Prolabo, Fontenay-sous-Bois, France).

Chromatographic Columns. A multicapillary column used was prepared by assembling ∼1200 individual capillaries (38 μm i.d.) made of low-melting-point glass. The rigid straight rod formed in this way was ∼20 cm long and had a cross section of a hexagon. The column was coated with SE-54. The SE-54 solution was pumped through one end of the multicapillary column at a constant volumetric flow (V_L) while the column was introduced into an oven kept at a constant temperature at a speed of V_C. At V_L largely exceeding V_C, the thickness of the coated phase should be proportional to the cube of the radius of the capillary. Shorter columns (5 and 10 cm) were obtained by cutting the 20-cm column. The rod was connected to a 0.32-mm fused-silica capillary by means of custom-designed and laboratory machined connectors. The column was connected to the injection port using a 15 cm × 0.32 mm i.d. deactivated silica tube. Comparative experiments were performed using a conventional capillary column (BP-5, 30 m × 0.32 mm i.d., 0.25 μm film thickness) purchased from Hewlett-Packard.

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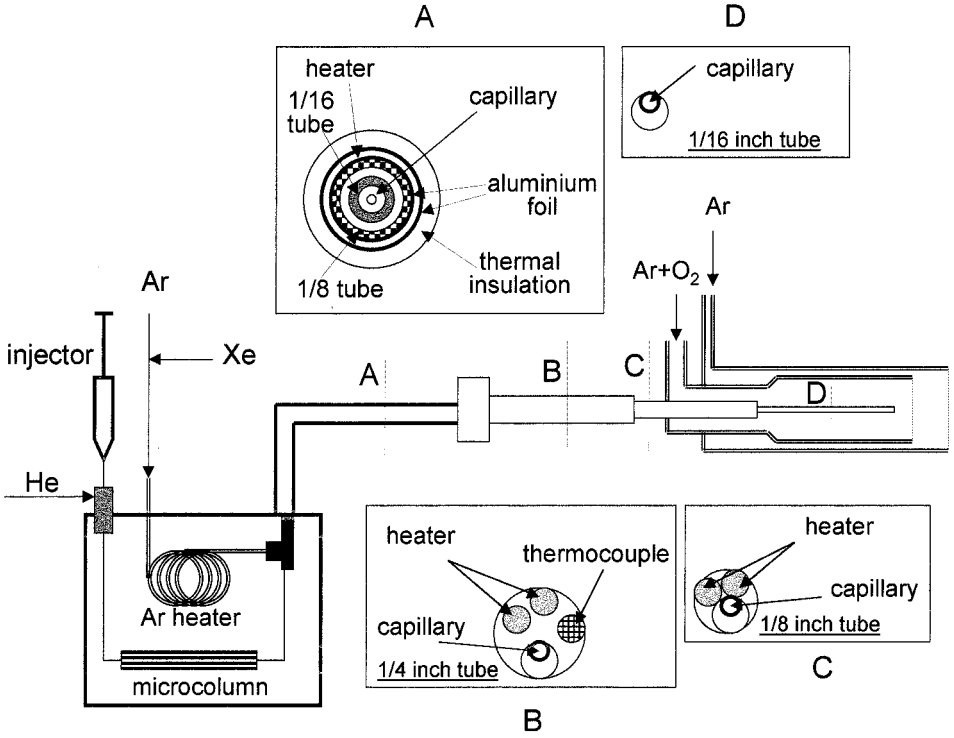

Figure 1. A scheme of the interface between GC and ICPMS used in this work. Insets A−D represent cross sections of the interface at various locations.

Reagents, Standards, and Solutions. HPLC grade solvents and analytical grade chemicals obtained from Aldrich (Milwaukee, WI) and Milli-Q water (Millipore, Milford, MA) were used throughout unless otherwise stated. Glassware was cleaned using a common detergent, throughly rinsed with tap and Milli-Q water, soaked for 12 h in a 10% nitric acid solution, and finally rinsed with Milli-Q water just before use. Helium, 99.995%, was used as a carrier gas. The plasma gas was argon, 99.996%. The xenon gas was 100 ppm (v/v) Xe in argon. All the gases were from Air Liquide.

Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemicals (Bisscheim, France). The reagent was manipulated under dry nitrogen to prevent its degradation. Fresh 1% (w/v) aqueous solutions were prepared every 8 h. Acetate buffer solutions of 1 and 0.1 M were prepared by dissolving sodium acetate in water and pH adjusting to 5 and 4, respectively, using acetic acid. Tetramethylammonium hydroxide (TMAH), 25% aqueous solution, and glacial acetic acid were obtained from Aldrich.

Standards of $BuSnCl_3$ (MBT), Bu_2SnCl_2 (DBT), Bu_3SnCl (TBT), $PhSnCl_3$ (MPhT), Ph_2SnCl_2 (DPhT), and $PhSnCl_3$ (TPhT) were obtained from Aldrich. Individual stock solutions (1 mg mL^{-1}) were prepared in methanol. Dilute standards for each compound and mixtures of them were also made in methanol. Ethylated derivatives were prepared from the corresponding chloride compounds by extraction into isooctane from 1 mL of a fresh 1% $NaBEt_4$ solution in water buffered to pH 5. Mercury chloride and methylmercury chloride (MeHgCl) were also obtained from Aldrich. Individual stock solutions were prepared in a 1% nitric acid solution 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 ionic compounds by extraction from a 1-mL fresh solution of 0.1% aqueous $NaBEt_4$ at pH 4 for 5 min into hexane. Et_4Pb (99%) was obtained from Octel (Paris, France). Stock and diluted solutions were made in pentane. ***Safety note*:** organometallic compounds are highly toxic and readily absorbed through skin. They should be manipulated under a fume hood. Automatic micropipets should be used to prepare dilute solutions, and the amount of the concentrated standard taken to prepare a working solution should be minimal (5 μL).

The vent of the GC injector should be connected to an exhaust. Concentrated standards should be oxidized with HNO_3 prior to disposal.

The reference materials, DORM-1 (Dogfish muscle) and TORT-1 (Lobster hepatopancreas), with certified contents of methylmercury and total mercury, and PACS-2 (marine sediment), with certified amounts of DBT and TBT, were obtained from the National Research Council of Canada (NRCC). The BCR 477 reference material (Mussel tissue) was obtained from the Community Bureau of Reference (BCR, Brussels, Belgium). Samples of leaded gasoline were collected at a local fuel station.

Sample Preparation Procedures. Determination of lead species in gasoline samples was performed directly after 1000-fold dilution of the original sample in pentane. The quantification of alkyllead compounds (Me_4Pb, Me_3EtPb, Me_2Et_2Pb, $MeEt_3Pb$, Et_4Pb) was done using the response obtained for Et_4Pb (peak area vs concentration given as lead), assuming that the ICP response for lead was independent of its organic form.

Extraction of tin and mercury species from biological materials (DORM-1, TORT-1, BCR 477) was performed with a TMAH solution under the action of a microwave field according to the

Table 1. Optimum Chromatographic Conditions for the Separation of Organometallic Compounds Using Microcolumn Multicapillary Chromatography

parameter	organometallic species of Sn	Pb	Hg
injection mode	split	split	split
injection vol (μL)	1	1	2
injector temp (°C)	280	200	200
column head pressure, psi			
22-cm microcolumn	25	25	25
5-cm microcolumn	20	20	20
split flow (mL/min)	240	220	80
oven temperature (°C)			
isothermal separations			
22-cm multicapillary microcolumn	135 °C for 1 min	80 °C for 1 min	50 °C for 1 min
5-cm multicapillary microcolumn	100 °C, 1 min	45 °C, 1 min	23 °C, 1 min
temperature-programmed separations			
BP-5 capillary column	80 (1 min) to 250 °C (5 min) at 20 °C/min		
22-cm multicapillary microcolumn	135 (0.2 min) to 220 °C (1 min) at 70 °C/min		
5-cm multicapillary microcolumn	100 (0.2 min) to 220 °C (1 min) at 70 °C/min		
transfer line temp (°C)	280	200	200

previously reported conditions.[18,21] Organotin compounds were extracted from PACS-2 sediment, using acetic acid and microwave leaching as described elsewhere.[21] Extracts were adjusted to pH 5 (in the case of the tin compounds) or to pH 4 (mercury species), derivatized with $NaBEt_4$. The resultant ethylated compounds were extracted into isooctane or hexane, respectively. Organotin compounds in the PACS-2 and BCR477 materials were quantified using a calibration curve; tripropyltin (TPT) was used as an internal standard. Methylmercury and inorganic mercury species in the TORT-1 and DORM-1 materials were quantified using the standard addition procedure at three concentration levels.

Instrumental Conditions. The optimal chromatographic conditions for all the studied compounds and columns are given in Table 1. ICPMS conditions were optimized using the continual signal of the ^{126}Xe isotope. This signal served (1) to tune the MS spectrometer, (2) to adjust the position of the transfer line (fused-silica capillary) in the torch, and (3) to optimize ICP operating parameters such as the *XYZ* position, rf power, rf matching voltage, lense voltages, and auxiliary, plasma, and carrier gas flow rates. These parameters were optimized daily with the objective to reach the maximum sensitivity for the ^{126}Xe isotope. Dwell time was optimized, for each group of organometallic compounds, in a way that intensity data for at least 10 points could be acquired for the narrowest peak in the chromatogram. Oxygen was added to the auxiliary argon gas at 20 mL min^{-1} in order to minimize the carbon deposition (due to the organic solvent injected on the chromatographic column) on the ICP cones. Operational ICPMS optimum conditions are given in Table 2. Slight variations of these values where observed from day to day.

Table 2. Optimum ICPMS Parameters for the Detection of Metals in Microcolumn Multicapillary GC Effluents

parameter	value
ICP rf power	1300 W
rf matching voltage	2.24 V
sampling depth	7−8 mm
sampler and skimmer cones material	nickel
gas flows	
argon plasma gas	15 L/min
argon carrier gas	0.70−0.75 L/min
argon auxiliary gas	1 L/min
oxygen (added to the auxiliary flow)	20 mL/min
xenon (100 ppm v/v in argon) gas	5 mL/min
isotopes monitored (dwell time)	^{202}Hg (140 ms), ^{208}Pb (80 ms), ^{120}Sn (140 ms), ^{126}Xe

RESULTS AND DISCUSSION

Preparation of Multicapillary Microcolumns. The column efficiency N_{TP} m^{-1} decreases linearly with a decrease in the column diameter.[22] However, the accompanied decrease in the sample load and the consequent loss of analytical sensitivity sets the compromise value for the diameter of a capillary at 250−320 μm. The idea of multicapillary chromatography consists of increasing the separation efficiency by decreasing the inner diameter of the capillary while the reduced sample load should be compensated by the large number of individual capillaries. This results in the high speed of separation of large sample volumes injected and a high range of volumetric velocities of the carrier gas at which the column maintains its high efficiency.

The practical realization of this idea is hampered by the virtual impossibility of manufacturing small inner diameter capillary columns with exactly the same diameter (the i.d. dispersion currently achieved is 3−4%). The differences in the diameter of individual capillaries in a bundle result in a somewhat different (at the same applied column head pressure) migration rate of the analyte in each of the individual capillaries and, consequently, in the peak broadening and the loss of the column efficiency.[23]

It was shown[24,25] that in order to obtain a multicapillary column with an efficiency of 100−200 theoretical plates (TP) cm^{-1}, the

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standard deviation of the inner diameter of the capillaries should not exceed 1.5%, which is impossible to attain by the currently available technology. Therefore, to produce a working multicapillary column, a process to correct for the inhomogeneity of the inner diameter of the capillaries in the bundle should be developed.

The principle of improving the efficiency of an MC consists of depositing a larger quantity of stationary phase in capillaries with the larger cross section while a smaller quantity is deposited in capillaries with the smaller cross section. The relative increase in the analyte's velocity in larger capillaries would thus be compensated by its stronger retention by the larger amount of stationary phase. At a particular correlation between the capillary cross section and the quantity of stationary liquid phase in the capillary, an MC column with insignificant retention time differences in the individual capillaries (and thus with improved efficiency) can be obtained.

It was shown recently[16] that the height of a theoretical plate in multicapillary chromatography can be expressed as

$$H = H_0 + \Delta_s^2 L \frac{1}{4} \frac{[2 + (3 - \alpha)K]^2}{(1 + K)^2} \qquad (1)$$

where H_0 stands for the HETP for a capillary of $r = \langle r \rangle$, where $\langle r \rangle$ is the average inner diameter value for the bundle of capillaries, Δ_s^2 is the relative variance of the cross section of individual capillaries with regard to the average capillary cross section $\Delta_s^2 = \sigma_s^2/S^2$, L is the column length, and K is the capacity factor. The coefficient correlates the internal diameter of the capillary with the thickness of the coating liquid-phase d_f according to the expression $d_f = C_A R\alpha$ (C_A is a constant).[16,23−25] The coefficient α depends on the method used to coat the capillary.

Equation 1 is composed of three parts. The first part, H_0, describes then the broadening of a chromatographic peak in an average capillary, the second part, $\Delta_S^2 L$, is related to the peak broadening resulting from the difference in the diameter of the individual capillaries, and the third part, $[[2 + (3 - \alpha)K]/(1 + K)]^2$, represents the correcting effect of the coating.

Assuming that the efficiency of an MC is controlled by the differences in the retention times in the individual capillaries rather than by the chromatographic peak broadening in one capillary ($H_0 <<< \Delta_S^2 L$), we obtain

$$N = N_0 \frac{4(1 + K)^2}{[2 + (3 - \alpha)K]^2} \qquad (2)$$

where N_0 is the efficiency of a multicapillary column obtained by simply assembling a number of capillaries in a bundle. Hence, the increase in efficiency of the produced multicapillary column with respect to N_0 will depend on the procedure used to coat the column with the stationary phase (SE-54 in the case studied).

If a static coating procedure is used (the column filled with a stationary-phase solution which is then evaporated at a constant temperature), the film thickness obtained is proportional to the radius of the capillary ($\alpha = 1$).[24,25] The efficiency of such a column is then equal to that of a column obtained by assembling a number of short capillary columns in one multicapillary column.

In the case of the dynamic coating procedure (a plug of the coating solution is pushed through the column due to a constant pressure drop set between the column ends), the film thickness will be proportional to the product of the capillary radius and the square root of the plug velocity. Since the latter is proportional to the radius of the column, the film thickness will be proportional to the radius of the capillary at the power of 1.5.[24,25] With $\alpha = 1.5$, the efficiency of the multicapillary column dynamically coated is increased by a factor of 1.8 with respect to N_0 (for well-retained compounds $K \gg 1$).

A much better efficiency can be obtained by a modified dynamic coating procedure in which a multicapillary is filled with the coating solution first (as in the static method), but the removal of the unretained liquid phase is performed by applying a pressure drop between the column ends. This leads to the proportionality of the liquid-phase amount in every capillary to R in the power of 2.5[24,25] and consequently to a 16-fold increase in the efficiency of such a column in comparison with a column obtained by simple assembling of individual capillaries in a bundle (N_0).

A further improvement could be obtained by modifying the coating method in a way that for a multicapillary column the SE-54 liquid was pumped through one end of the multicapillary column at a constant volumetric flow (V_L) while the column was introduced into an oven kept at a constant temperature at a speed of V_C. At V_L largely exceeding V_C, the thickness of the coated phase should be proportional to the cube of the radius of the capillary, which would mean the full compensation of the dispersion of the radius of the individual capillaries.[26]

The last method was used in this work to produce 20-cm multicapillary microcolumns of which shorter columns (5 and 10 cm) were obtained for the purpose of the study described below.

Separation of Organometallic Compounds on Multicapillary Microcolumns. The mixtures of organometallic compounds investigated included the following: (1) ethylated methylmercury and Hg^{2+} species (MeEtHg, Et_2Hg), (2) alkyllead compounds (Me_4Pb, Me_3EtPb, Me_2Et_2Pb, $MeEt_3Pb$, Et_4Pb), (3) ethylated butyltin compounds ($BuEt_3Sn$, Bu_2Et_2Sn, Bu_3EtSn), and (4) ethylated butyl- and phenyltin compounds ($Bu_nEt_{3-n}Sn$, $Ph_nEt_{3-n}Sn$). Tripropyltin (Pr_3EtSn) used often as an internal standard in organotin environmental speciation analysis was sometimes included in the array of organotin standards. Three principal chromatographic parameters were taken into account during the optimization of the separation conditions for the above organometallic compounds: baseline resolution between the adjacent peaks, effect of the baseline perturbation due to the arrival of solvent at the plasma on the signal of the most volatile species, and the duration of the analytical run. Mixtures of compounds with similar boiling points (butyltin, organomercury, and alkyllead species) were separated by chromatography in the isothermal mode. Oven temperature programming was necessary when phenyltin compounds were present in an analyzed solution. The maximum heating rate (70 °C min^{-1}) allowable by the chromatographic oven was used in order to minimize the duration of a run. Split injections were performed using an autosampler to avoid broadening of the injection band unavoidable in the case of a manual injection on a multicapillary microcolumn.

Separations on 20-cm Microcolumns. Figure 2A−C shows that baseline resolution can be achieved readily in the isothermal

(26) Chromatographic column, Russian patent 2060498; *Bull. Otkryti i Izobreteni* **1995**, *18* (in Russian).

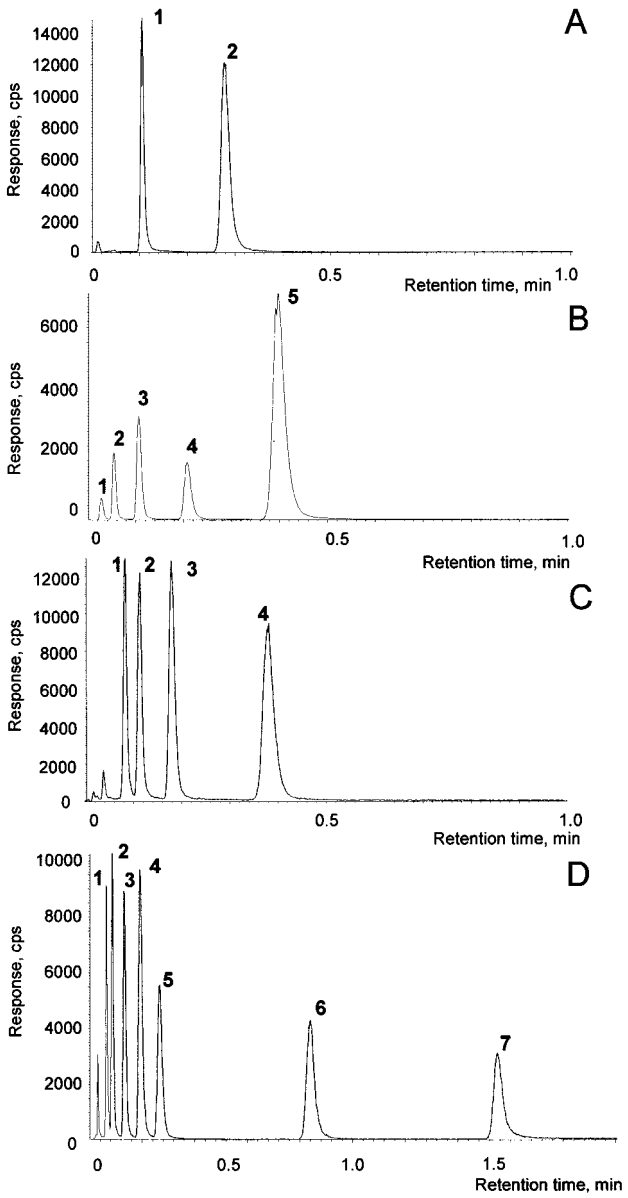

Figure 2. Separation of organometallic compounds using a 20-cm microcolumn. Each chromatogram corresponds to an independent run. See Tables 1 and 2 for conditions. Concentrations in parentheses are given as metal. (A) organomercury standards: (1) MeEtHg (60 ng mL^{-1}) and (2) Et_2Hg (94 ng mL^{-1}) in hexane. Isothermal separation. (B) Alkyllead in gasoline diluted with pentane (1:1000): (1) Me_4Pb, (2) Me_3EtPb, (3) Me_2Et_2Pb, (4) $MeEt_3Pb$, and (5) Et_4Pb. Isothermal separation. (C) Organotin standards in isooctane: (1) $BuSn_3Et$ (19.2 ng mL^{-1}), (2) Pr_3SnEt (25 ng mL^{-1}), (3) Bu_2SnEt_2 (33.3 ng mL^{-1}), and (4) Bu_3SnEt (40.77 ng mL^{-1}). Isothermal separation. (D) Organotin standards in isooctane: (1) $BuSn_3Et$ (11.4 ng mL^{-1}), (2) Pr_3SnEt (25 ng mL^{-1}), (3) Bu_2SnEt_2 (19.6 ng mL^{-1}), (4) $PhSnEt_3$ (37.6 ng mL^{-1}), (5) Bu_3SnEt (23.6 ng mL^{-1}), (6) Ph_2SnEt_2 (31.0 ng mL^{-1}), and (7) Ph_3SnEt (28.2 ng mL^{-1}). Temperature-programmed separation.

separation mode for organomercury, alkyllead, and ethylated butyltin species, respectively, using a 20-cm microcolumn. In all cases, a column head pressure of 25 psi corresponding to a carrier gas flow of 120 mL min^{-1} at 30 °C was used. Chromatographic separations were achieved within less than 30 s which is similar to the case of a 1-m helix multicapillary column and 5−10 times less than with a conventional 25-m capillary.[15] The reproducibility (peak area) of five consecutives injections was better than 5%.

When phenyltin compounds were present in addition to the butyltin compounds in a sample (often the case with biological materials), no successful separation could be achieved in the isothermal mode because of a large difference between the boiling points of Ph_2SnEt_2 and Ph_3SnEt and those of the ethylated butyltin compounds. A increase in the column temperature after an initial isothermal period is necessary in order to elute the di- and triphenyltin species (Figure 2D). When the heating rate of 70 °C min^{-1} was applied (maximum available with the oven used), elution of the full range of organotins could be achieved within ∼90 s. The good thermal conductivity of the glass of which the column was made suggests the possibility of even a faster elution if hardware allowing a faster increase in temperature is available.

The results obtained indicate the possibility of eliminating the regular chromatographic oven and replacing it with a small tubular oven housing the microcolumn. This opens the way to the conception of a small sample introduction accessory for speciation analysis by ICPMS.

It should be noted that the separation efficiency obtained for mercury species is much better and runs are shorter than in former studies[17,18] using the PTV injection onto a 1-m helix multicapillary column. The reasons are the faster injection and the use of an optimized heated GC/ICPMS interface avoiding the condensation of the analytes in the transfer line.

Decreasing the Column Length. The successful separations obtained with the 20-cm microcolumn suggest the possibility of using even shorter columns for the separation of the organometallic compounds studied. Use of shorter columns means a decrease in terms of the unit price of the column and also creates the possibility of a further miniaturization of the instrumentation. The column size of a 5−10 cm is comparable to that of a liner in a programmable temperature vaporization injector.

The major problem to be circumvented is the elimination of the effect of the plasma instability in the beginning of the chromatogram on the signal of the most volatile compound(s). As was shown in Figure 3, this is not a critical issue for relatively large amounts (several picograms) of an analyte injected (Figure 3A). Indeed, the analysis time for the isothermal speciation of mercury can then be decreased to ∼5 s on a 10-cm column (Figure 3A). However, when ultratrace amounts (below 500 fg) are chromatographed, the baseline instability due to the coelution of the tail of the solvent peak makes reliable quantification impossible (Figure 3B).

Note that reducing the column length not only reduces the separation efficiency because the column is shorter by half but also because the carrier gas flow rate is at the same column head pressure and oven temperature, twice as high. As demonstrated in Figure 3C and D, the careful optimization of the oven temperature and column head pressure allows the alleviation of the effect of the solvent in the plasma on the most volatile compound even for analyte concentrations close to the detection limit. No gain in the duration of the chromatographic run is then (Figure 3D), however, obtained in comparison with a 20-cm microcolumn (cf. Figure 2A).

The high quality of separations on a 10-cm microcolumn for all the organometallic species studied in the optimized conditions (data not shown) indicates the possibility of a further reduction

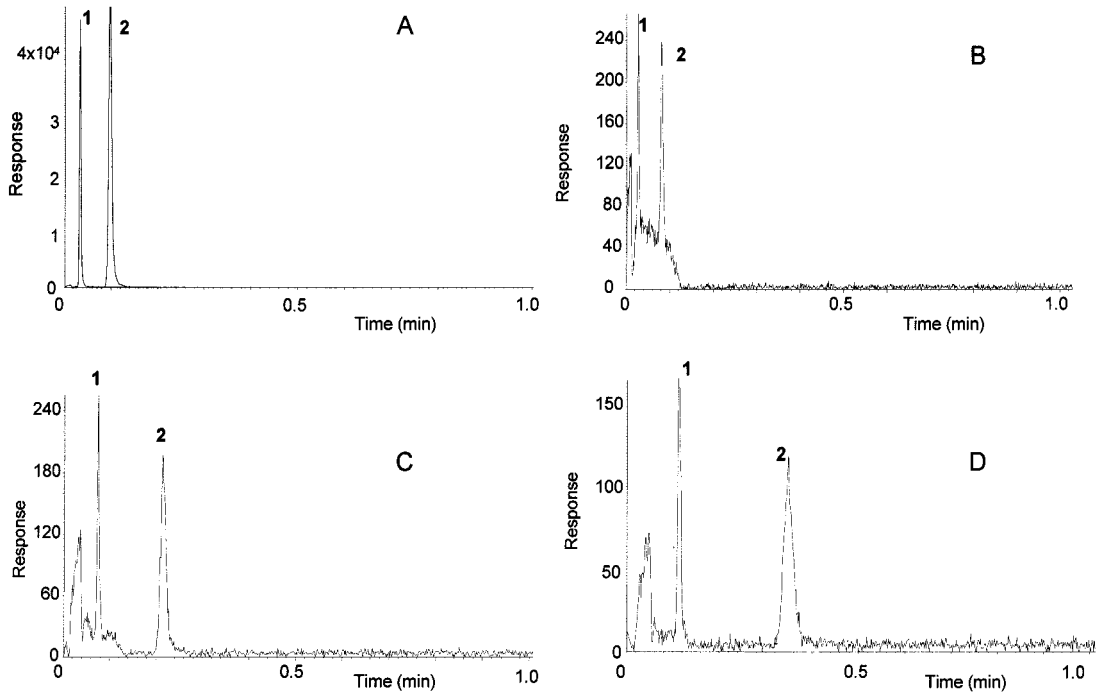

Figure 3. Effect of the optimization of the separation conditions on the solvent background. Separation of MeHgEt and Et_2Hg on a 10-cm microcolumn. Isothermal separations. (A) (1) MeEtHg (60 ng mL^{-1}) and (2) Et_2Hg (94 ng mL^{-1}). $T = 50$ °C, column head pressure 25 psi. (B–D) (1) MeEtHg (0.60 ng mL^{-1}) and (2) Et_2Hg (0.94 ng mL^{-1}). (B) $T = 50$ °C, column head pressure 25 psi. (C) $T = 40$ °C, column head pressure 25 psi. (D) $T = 30$ °C, column head pressure 20 psi.

of the column length provided that the oven and column head pressure values are reoptimized.

Separations on 5-cm Microcolumns. Figure 4 shows a set of chromatograms similar to that shown in Figure 2 but obtained using a 5-cm microcolumn. The dotted line represents the signal of ^{126}Xe that is used as an indicator of the plasma stability and as an internal standard. The optimization of the chromatographic separation conditions on the 5-cm column aimed at the compensation of the smaller column length by an increased retention of the analytes achieved by decreasing the column temperature and the column head pressure. It can be seen that separation conditions can be found in which the solvent responsible for the plasma instability elutes sufficiently before the most volatile analyte compound.

The optimum separation temperature is about half that for a 20-cm column with comparable quality of separation obtained. No gain in the duration of the chromatographic run is achieved, but the system is attractive owing to the high degree of miniaturization. The organomercury species are separated virtually at the ambient temperature. As demonstrated in Figure 4D, efficient temperature-programmed separations can be performed using a 5-cm microcolumn as well. The limitation of the hardware used in terms of the insufficient heating rate (maximum of 70 °C min^{-1} was possible) did not allow the reduction of the duration of the chromatographic run in comparison with a 22-cm column (cf. Figure 2D).

Figures of Merit. Once the plasma ionization conditions are optimized detection limits (calculated in the peak height mode) depend on the injection conditions (split value) and the chromatographic separation conditions (peak width). For comparison, a series of chromatograms (Figure 5) was run using a capillary column. Separation conditions optimized earlier for MIP AES detection were adopted.[15] Table 3 compares the detection limits obtained with 20- and 5-cm multicapillary microcolumns with those obtained using a conventional capillary column. Values for peak widths are also given.

Since capillary GC of organometallic compounds is performed in the oven temperature-programmed elution mode, the peak width and the detection limits expressed as the metal concentration are practically independent of the boiling point of the analyte. In the splitless injection mode used in capillary GC, the concentration detection limits correspond to the absolute detection limits.

The issue of detection limits is much more complex in multicapillary GC. Most of the separations developed are isothermal. The peak width increases with increasing boiling point of the analyte, which means a decrease in detection limit. On the other hand, peaks in microcolumn multicapillary GC may be narrower than in capillary GC, which improves the sensitivity in the peak height mode. The peak width is critically dependent on the column temperature and may vary by 1 order of magnitude from the most to the least volatile compound as, for example, in the case of Me_4Pb and Et_4Pb. The minimum peak width is limited by the acquisition rate of the quadrupole mass analyzer used in this work.

A multicapillary column, especially a 5-cm microcolumn, requires a rapid injection. The split mode is preferred, which means that some of the analyte is diverted off the column during the injection, thus negatively affecting the detection limits. This effect is compensated by the decreased postcolumn dilution with the makeup gas in MC GC in comparison with capillary GC. This factor is ~500-fold with a 0.32-mm capillary and ~10-fold with a multicapillary column.

The comparison in Table 3 shows that for compounds with lower boiling points the decreased peak width compensates well

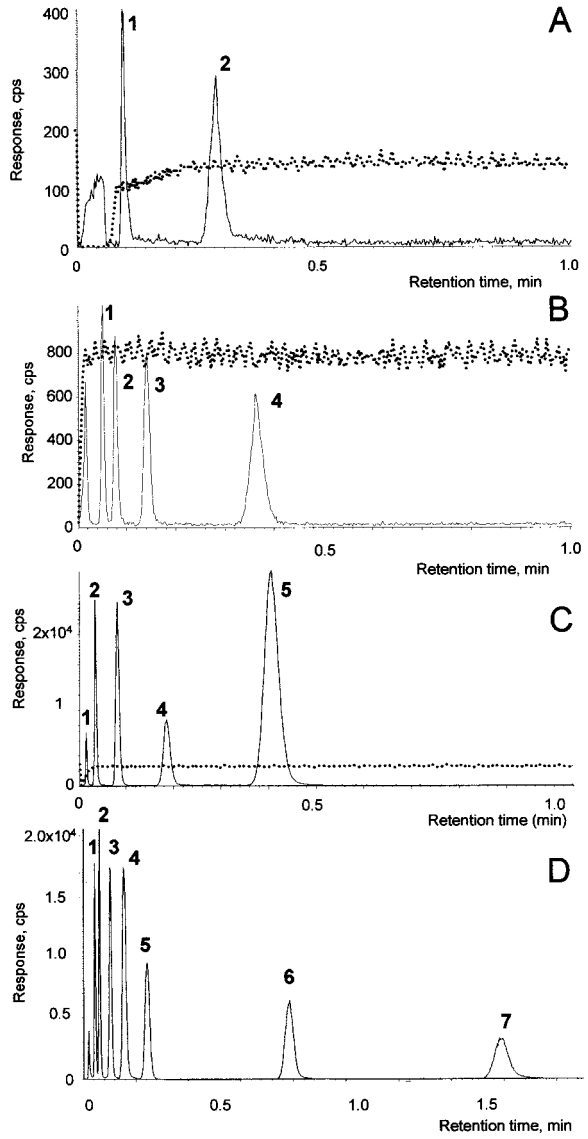

Figure 4. Separation of organometallic compounds using a 5-cm microcolumn. Each chromatogram corresponds to an independent run. See Tables 1 and 2 for conditions. Compounds were injected in isooctane. The dotted line represents the intensity of the ^{126}Xe signal. (A) (1) MeEtHg (0.60 ng mL^{-1}) and (2) Et_2Hg (0.94 ng mL^{-1}). Isothermal separation. (B) Organotin standards: (1) $BuSn_3Et$ (0.96 ng mL^{-1}), (2) Pr_3SnEt (1.25 ng mL^{-1}), (3) Bu_2SnEt_2 (1.66 ng mL^{-1}), and (4) Bu_3SnEt (2.04 ng mL^{-1}). Isothermal separation. (C) Alkyllead species in gasoline diluted with pentane (1:1000): (1) Me_4Pb, (2) Me_3EtPb, (3) Me_2Et_2Pb, (4) $MeEt_3Pb$, and (5) Et_4Pb. Isothermal separation. (D) Organotin standards: (1) $BuSnEt_3$ (11.4 ng mL^{-1}), (2) Pr_3SnEt (25 ng mL^{-1}), (3) Bu_2SnEt_2 (19.6 ng mL^{-1}), (4) $PhSnEt_3$ (37.6 ng mL^{-1}), (5) Bu_3SnEt (23.6 ng mL^{-1}), (6) Ph_2SnEt (31.0 ng mL^{-1}), and (7) Ph_3SnEt (28.2 ng mL^{-1}). Temperature-programmed separation.

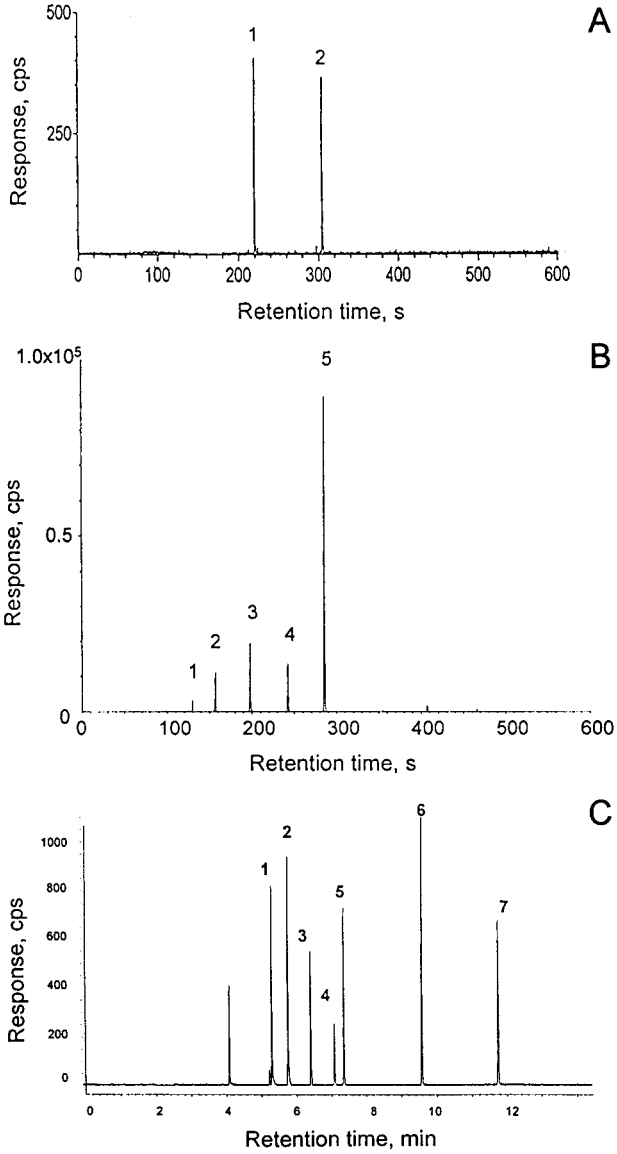

Figure 5. Reference GC/ICPMS chromatograms obtained for organometallic cotaminants on a conventional (BP-5, 30 m × 0.32 mm i.d., $d_f = 25$ μm) capillary column. Temperature-programmed separations. (A) Organomercury standards: (1) MeHgBu (2.0 ng mL^{-1}) and (2) $HgBu_2$ (2.0 ng mL^{-1}). (B) Alkyllead in gasoline diluted with pentane (1:1000): (1) Me_4Pb, (2) Me_3EtPb, (3) Me_2Et_2Pb, (4) $MeEt_3Pb$, and (5) Et_4Pb. (C) Organotin standards: (1) $BuSnEt_3$ (1.06 ng mL^{-1}), (2) Pr_3SnEt (1.0 ng mL^{-1}), (3) Bu_2SnEt_2 (0.75 ng mL^{-1}), (4) $PhSnEt_3$ (0.72 ng mL^{-1}), (5) Bu_3SnEt (0.87 ng mL^{-1}), (6) Ph_2SnEt (1.13 ng mL^{-1}), and (7) Ph_3SnEt (1.03 ng mL^{-1}). Splitless injection, 1 μL, oven 80 °C (1 min), 20 °C min^{-1}, 280 °C.

for the loss of compound during injection. Consequently, the detection limits obtained with a capillary column and with a multicapillary microcolumn are similar. For the less volatile compounds, multicapillary chromatography turns out to be a few times less sensitive. The detection limits found are among the lowest ever reported for a GC/ICPMS or a GC/MIP AED coupling.[8]

Reproducibility in the peak area mode for five consecutive injections of 1 pg of analytes in a standard solution was better than 2−5%. Calibration curves were linear over 3 orders of magnitude (the range investigated).

Analysis of Certified Reference Materials. The analytical method developed was applied to speciation analysis of lead in gasoline, organotin compounds in sediments and biological materials, and organomercury in biological materials and validated with certified reference materials (CRMs). For sample preparation, procedures described in detail elsewhere were used.[18,21] Chromatograms obtained for the PACS-2, BCR 477, and TORT-1 materials are shown in Figure 6. Results of the quantification of the organometallic species in the analyzed materials and the

Table 3. Comparison of the Peak Width and Detection Limits Obtained by Capillary GC and Multicapillary Microcolumn GC with ICPMS Detection

	30-m capillary column[a]		multicapillary microcolumn[b] 20 cm		5 cm	
compd	peak width[c]	ADL[d] (fg)	peak width[c]	ADL (fg)	peak width[c]	ADL (fg)
$BuSn^{3+}$	1140	56	480	31	420	27
Pr_3Sn^+	1260	60	600	41	540	34
Bu_2Sn^{2+}	1080	50	840	77	840	76
Bu_3Sn^+	1140	52	1640	100	1980	111
$PhSn^{3+}$	1320	80	960	68	960	70
$PhSn^{2+}$	1380	62	2160	160	1740	133
Ph_3Sn^+	1500	75	2340	180	3600	210
$MeHg^+$	1100	150	540	160	540	120
Hg^{2+}	1120	150	1260	300	1620	280
Me_4Pb	1120	30	240	30	180	26
Me_3EtPb	1140		260	39	240	33
Me_2Et_2Pb	1140		520	67	480	63
$MeEt_3Pb$	1160		1140	152	1020	150
Et_4Pb	1180	30	1800	280	1860	320

[a] 1 μL splitless injection. [b] 1 μL split injection. [c] Measured at half the maximum peak height, in milliseconds. [d] Absolute detection limits, measured as three times standard deviation of the noise.

certified (or indicative values) available are summarized in Tables 4 and 5.

For the PACS-2 and BCR 477 materials, a good agreement was found between the measured and certified levels of $BuSn^{3+}$, Bu_2Sn^{2+}, and Bu_3Sn^+. Phenyltin compounds are absent in the sediment, and no certified values are available for the biomaterial. Nevertheless, the values obtained for the phenyltin compounds are of an order of magnitude similar to the indicative values available as the result of an intercomparison exercise.[27] The methylmercury concentrations found in the DORM-1 and TORT-1 materials matched well the reference values. In addition, the sum of the concentrations of $MeHg^+$ and Hg^{2+} in the sample was in agreement with the value for the total mercury content available. Organolead compounds in a leaded gasoline sample were quantified using the response (peak area) for a standard of Et_4Pb. The concentrations found (μg g^{-1}, for five independent measurements) were Me_4Pb (5.3 ± 0.3), $EtMe_3Pb$ (19.4 ± 0.4), Et_2Me_2Pb (37.6 ± 0.6), Et_3MePb (30.8 ± 0.3), and Et_4Pb (211.1 ± 0.7) (cf. the chromatograms in Figures 2B and 4C).

Multielemental Speciation Analysis. The elemental selectivity of the ICPMS system in combination with the high resolution of a multicapillary microcolumn allows simultaneous multielemental speciation analysis provided that the chromatographic separation conditions are carefully optimized. Because of the large discrepancies between the boiling points of the anthropogenic organometallic contaminants, no isothermal separation conditions could be found for the simultaneous environmental speciation analysis. However, when column temperature gradient programming is used, simultaneous analysis becomes possible.

Figure 7 shows a chromatogram acquired simultaneously on ^{120}Sn, ^{202}Hg, and ^{208}Pb channels for an extract of the TORT-1 material prepared in the conditions optimum for mercury (100 mg of sample was extracted with 2 mL of hexane). At these conditions, organotin and organolead (including Pb^{2+}) compounds are quantitatively recovered. The dwell time needed to be decreased to 60 ms to enable simultaneous monitoring of three elemental channels. Eleven different species of tin, mercury, and

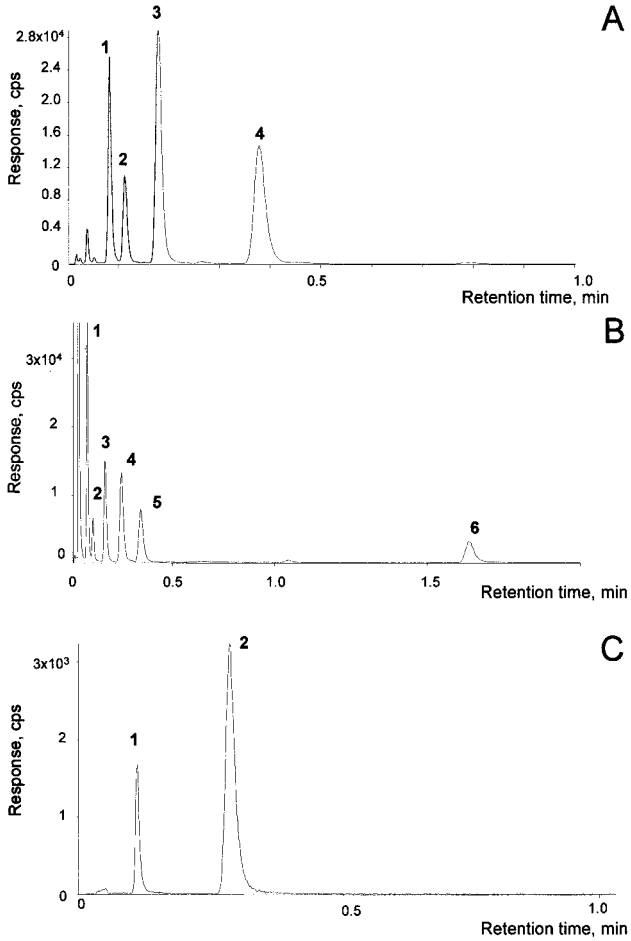

Figure 6. Analysis of certified reference materials. See Experimental Section for a description of the extract preparation. (A) Organotin compounds in the PACS-2 sediment: (1) $BuSn_3Et$, (2) Pr_3SnEt (IS, 25 ng mL^{-1}), (3) Bu_2SnEt_2, and (4) Bu_3SnEt. Isothermal separation. (B) Organotin compounds in the BCR 477 Mussel tissue: (1) $BuSnEt_3$, (2) Pr_3SnEt (IS, 25 ng mL^{-1}), (3) Bu_2SnEt_2, (4) $PhSnEt_3$, (5) Bu_3SnEt, and (6) Ph_3SnEt. Temperature-programed separation. (C) Mercury species in the TORT-1 material: (1) MeEtHg and (2) Et_2Hg. Isothermal separation.

Table 4. Results for the Determination of Organotin Compounds by Multicapillary Microcolumn GC with ICPMS Detection in Certified Reference Materials[a]

	material analyzed: PACS-2 (μg g^{-1} as Sn)		BCR-477 (μg g^{-1} as cation)	
compd	found	certified	found	certified
$BuSn^{3+}$	0.51 ± 0.02	0.30[a]	1.67 ± 0.07	1.50 ± 0.28
Bu_2Sn^{2+}	1.21 ± 0.01	1.09 ± 0.15	1.61 ± 0.01	1.54 ± 0.12
Bu_3Sn^+	0.94 ± 0.02	0.98 ± 0.13	1.91 ± 0.20	2.20 ± 0.19
$PhSn^{3+}$			1.72 ± 0.12	0.98 ± 0.66[b]
Ph_3Sn^+			1.81 ± 0.20	1.42 ± 0.58[b]

[a] Five independent analyses. Indicative values. [b] Noncertified values. Mean of results obtained from all laboratories taking part in the intercomparison exercise.[27]

(27) Quevauviller, Ph.; Morabito, R.; Ebdon, L.; Cofino, W.; Muntau, H.; Campbell, M. J. European Commission, BCR, Report EUR 17921 EN, 1997.

Table 5. Results for the Determination of Mercury Species by Multicapillary Microcolumn GC with ICPMS Detection in Certified Reference Materials[a]

	found (μg g^{-1} as Hg)			certified (μg g^{-1} as Hg)	
sample	$MeHg^+$	Hg^{2+}	$MeHg^+ + Hg^{2+}$	$MeHg^+$	total Hg
DORM-1	0.71 ± 0.01	0.17 ± 0.03	0.88 ± 0.03	0.730 ± 0.06	0.80 ± 0.07
TORT-1[b]	0.124 ± 0.007	0.242 ± 0.008	0.366 ± 0.008	0.130 ± 0.01	0.330 ± 0.06
TORT-1[c]	0.111 ± 0.010	0.257 ± 0.020	0.368 ± 0.020	0.130 ± 0.01	0.330 ± 0.06

[a] Five independent analyses. [b] Results obtained with a 20-cm microcolumn. [c] Results obtained with a 5-cm microcolumn.

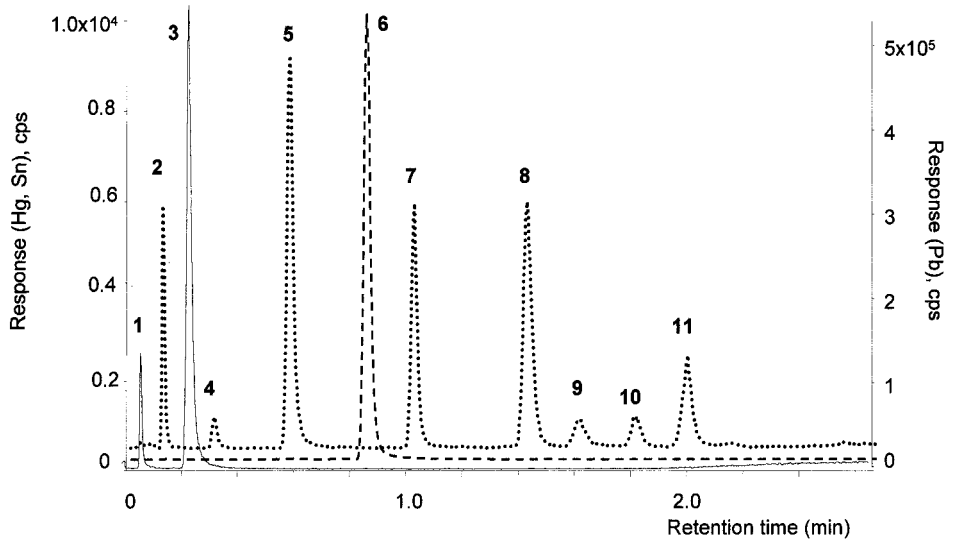

Figure 7. Simultaneous multielemental speciation analysis by microcolumn multicapillary GC/ICPMS in an extract of the TORT-1 material. Solid line, ^{202}Hg signal; dashed line, ^{208}Pb signal; dotted line, ^{120}Sn signal. Peak identification: (1) MeEtHg, (2) unidentified, (3) Et_2Hg, (4) unidentified, (5) Et_4Sn, (6) Et_4Pb, (7) $BuSnEt_3$, (8) Bu_2SnEt_2, (9, 10) unidentified, and (11) Bu_3SnEt. Oven program: 50 °C (0.1 min), 70 °C min^{-1}, 200 °C.

lead, some of them not identified, were separated and selectively detected with an acceptable signal/noise ratio within less than 2 min.

The maximum column heating rate (70 °C min^{-1}) allowed by the hardware available did not allow simultaneous speciation analysis using a 5-cm column. For this a heating rate of ~200 °C min^{-1} would be necessary in order to keep the peak width in the range of ~0.5 s.

CONCLUSIONS

The multicapillary 5-cm microcolumn developed with an efficiency of 100−200 TP cm^{-1} enables the isothermal separation within several seconds of all the anthropogenic organometallic compounds (Sn, Hg, Pb) studied in environmental speciation research so far. The exception is a full speciation analysis of organotin compounds in biomaterials that requires 90 s and temperature gradient programming because of the presence of high-boiling phenyltin compounds. Microcolumn multicapillary chromatography opens the way to the elimination of the regular oven in gas chromatography of anthropogenic organometallic environmental contaminants and to a conception of a miniature accessory for time-resolved introduction of gaseous analytes into an ICPMS for environmental speciation analysis.

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