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Multicapillary column gas chromatography with element-selective detection

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Multicapillary column gas chromatography (MC GC) is presented as a novel technique for the time-resolved sample introduction of gaseous analytes in atomic spectrometry. The principles and the theory of MC GC, the coupling of MC GC with microwave-induced plasma atomic emission spectrometry and with inductively coupled plasma mass spectrometry, and features of the coupled techniques developed are discussed. Applications of MC GC with element-selective detection to species-selective analysis are reviewed. The possibility of incorporating MC columns into dedicated sample preparation accessories for elemental speciation by atomic spectrometry is evaluated.

Keywords: Multicapillary gas chromatography; Microwave-induced plasma atomic emission spectrometry; Inductively coupled plasma mass spectrometry; Environmental analysis; Element-selective detection

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1. Introduction

For the past three decades, there has been a surge of interest in species-selective analysis for organometallic compounds because of their impact on the environment and the quality of foodstuffs [1]. The notoriety of the Minamata accident in Japan raised concerns about the differentiation between methyl- and inorganic mercury in aquatic biota [2]. The extinction of oyster populations drew attention to the use of organotin compounds in antifouling paints [3]. The toxicity of tetraalkyllead [4], used as antiknock additives to petrol, stimulated studies of organolead environmental pollution. The recognition of these hazards has stimulated interest by regulatory agencies, quality control laboratories, and, consequently, manufacturers of analytical instrumentation, in speciation analysis [5].

The success of a speciation analysis depends on the speed of bringing metal-containing species present in a sample to a sensitive (absolute detection limit at the pg level) element-specific detector in a time-resolved manner. Usually, gas chromatography coupled with atomic absorption, fluorescence or inductively coupled plasma mass spectrometry (ICP-MS) has been used [6–9]. In the most common approach, the analytes are cryotrapped at the top of a packed column and released into a detector by heating the column. Alternatively, high resolution gas chromatography

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(GC) with long (15–50 m) capillary open tubular columns and precise oven temperature gradient programming was employed.

Both packed and capillary columns have a number of deficiencies and limitations. Packed columns can, by design, handle high flow rates and large sample sizes, but the efficiency and resolution properties are compromised because of the high dispersion of the analytes on the column. The large column volume negatively affects the sensitivity in the peak height mode and the detection limits. The packing itself is chemically active toward many organometallic species, which makes silanization necessary and worsens the reliability of results. These shortcomings are eliminated by the use of capillary columns; however, this is at the expense of small sample sizes and the low carrier gas flow rates allowed by such columns. The reduced sample size and the high dilution factor with the detector's makeup gas necessary to match the spectrometer's optimum flow rate result in considerable loss of sensitivity. A duration of a GC run of up to 20 min is not unusual. The need for a relatively large (and heavy) GC oven increases the cost of a dedicated speciation analyzer and prevents applications in the field. The importance of the hardware makes it difficult to consider a regular gas chromatograph as an inexpensive accessory for atomic spectrometry.

Recently, a number of papers have appeared on rapid (flash) gas chromatography employing columns that consist of a bundle of 900–2000 microcapillaries of a small (20–40 μm) internal diameter. These are referred to as polycapillary [10,11] or multicapillary [12–23] columns. Such a bundle allows one to eliminate the deficiencies associated with the use of capillary and packed columns while the advantages of both are preserved. At the same time a number of additional attractive features are offered. The critical evaluation of the state of the art of multicapillary chromatography as a novel and promising sample introduction technique for time-resolved analysis of gaseous species in atomic spectrometry is the topic of this article.

2. Requirements for gas chromatographic sample introduction in atomic spectrometry

In speciation analyses there is an increasing market demand for a compact accessory (of the hydride generation system type) offering the possibility of an automated and time-resolved introduction of gaseous analytes into an atomic spectrometer. An ideal sample introduction system for speciation analysis by atomic spectrometry faces several challenges that require considerable advances in our current knowledge, such as:

1. separation efficiency of at least 2000 theoretical plates, producing Gaussian-type signals with a half-width of 1 s (a trade-off between the maximum sensitivity in the peak height mode and the data acquisition capacity of the current element-specific detectors);
2. sample capacity of 5 μl of an organic solvent; or 50 ml of an aqueous sample to be purged;
3. interface-free coupling: the carrier gas should be the detector gas. Neither the addition of a makeup gas nor heating of the interface should be required;
4. speed of analysis: the separation of analyte species from one another should be possible within a time span characteristic of a signal from a flow injection hydride generation accessory (ca. 10–15 s);
5. miniaturization of the system: a future system should be a small-size accessory to an atomic spectrometer. Isothermal separations are required to simplify the hardware by eliminating the oven temperature gradient programming. Isothermal separations have the further advantage of increasing the throughput by eliminating the oven cooling time.

These requirements can be fulfilled neither in systems based on packed columns nor on capillary columns. The following discussion concerns the possibility of matching the above criteria by the use of multicapillary columns

3. Multicapillary chromatography

The idea of using a bundle of small-diameter capillaries is quite old [24]. At its roots there was the goal of increasing the speed of separation by increasing the separation efficiency and thus introducing the possibility of using shorter columns. The increase in efficiency can be achieved by a decrease in the inner diameter of the capillary while the reduced sample load should be compensated for by increasing the number of individual capillaries. The present-day multicapillary column consists of 900–2000 capillaries; for the convenience of fabrication a low-melting-point glass is used. Multicapillary columns offer a

number of interesting features resulting from their production technology. In particular, the development of a coating technology compensating for the inhomogeneities in the inner diameter of the individual columns has led to patenting [25] and commercialization [26] of the multicapillary columns. The basic and unique features of a multicapillary column are the high speed of separation of large sample volumes injected, and an exceptionally high range of volumetric velocities of the carrier gas at which the column retains its high efficiency.

3.1. Effect of the column length

The effect of the column length on its efficiency can be approached theoretically. The height (H) equivalent to the theoretical plate (HETP) for a multicapillary column is [11,12]:

$$H = H_0 + \Delta_s^2 L \quad (1)$$

where H_0 stands for the HETP for a capillary of $r = <r>$, where $<r>$ 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 $\Delta_s^2 = \sigma_s^2/S^2$, and L is the column length. H_0 describes the broadening of a chromatographic peak in an average capillary, whereas the second part is related to peak broadening being the consequence of the different velocities of the carrier gas in the different capillaries. Note that it is impossible to produce capillaries with *exactly* the same inner diameter. The second part of the expression takes into account the dispersion of the inner diameter of the capillaries which is multiplied by the length of the column.

Taking into account Eq. 1, the column efficiency (the number N of theoretical plates on the column of length L) can be calculated:

$$N = \frac{L}{H} = \frac{L}{(H_0 + \Delta_s^2 L)} \quad (2)$$

Thus, as the length of a multicapillary column increases, the number of theoretical plates reaches the limit:

$$N_{max} = \lim_{L \to \infty} N = \frac{1}{\Delta_s^2} \quad (3)$$

which is controlled only by the dispersion of the inner diameter of individual capillaries.

Above a certain column length, the number of theoretical plates (TP) will not increase any more, which is in obvious contrast to the other types of GC columns whose efficiency is directly proportional to the column length. In other words, the maximum efficiency of a multicapillary column is limited by the technological precision of manufacturing tubes with identical inner diameters. Currently, a dispersion of 3–4% can be attained. This, according to Eqs. 2 and 3, would allow one to manufacture columns with an efficiency of $<$ 600–1000 TP which is insufficient for the majority of analytical applications. In order to obtain a 20-cm multicapillary tube with an efficiency of 2500–3000 TP, the imprecision of the internal diameter of the individual capillaries should not exceed 1.5% which is impossible to attain with present technology. The efficiency of multicapillaries (MC), made of tubes with high I.D. dispersion values, can be improved by a suitable coating procedure [25].

3.2. Dispersion-reducing coating technology

The principle of improving the efficiency of a MC consists in 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, a column with insignificant retention time differences in the individual capillaries (and thus with improved efficiency) can be obtained.

If one considers that the film thickness in each capillary is proportional to its radius in the power of α,

$$d_f = C_A R^{\alpha} \quad (4)$$

where d_f denotes the thickness of the liquid phase and C_A and α are constants, it can be shown that the column efficiency, thickness of the stationary phase, radius, α and the capacity factor K are functionally dependent and depend on the coating procedure.

$$H = H_0 + \Delta_s^2 L \frac{1}{4} \frac{[2 + (3-\alpha)K]^2}{(1+K)^2} \quad (5)$$

Under the assumption that the efficiency of an MC is controlled by the different time of peak detection from individual capillaries rather than by the chromato-

graphic peak broadening in one capillary ($H_0 \ll \Delta_s^2 L$), we obtain:

$$N = \frac{L}{H} = \frac{4}{\Delta_s^2} \frac{(1+K)^2}{[2+(3-\alpha)K]^2} \quad (6)$$

where K is the capacity factor. Eq. 6 can be written as:

$$N = N_0 \frac{4(1+K)^2}{[2+(3-\alpha)K]^2} \quad (7)$$

where N_0 is the efficiency of an MC with respect to a non-retained component (dispersive broadening) and K corresponds to the capacity factor of the column.

The above considerations lead to the conclusion that the efficiency of an MC depends on the method of coating. It increases if the value of the coefficient $\alpha = \log d_f / \log R$ (cf. Eq. 4) is between 1 and 3. Then, the HETP decreases with the increasing capacity coefficient, thus the longer the retention time of the analyte the higher the efficiency of the column. In the ideal case (α=3) the column efficiency attains the maximum that equals the efficiency of the average capillary of the bundle.

The current technology enables different amounts of stationary phase to be deposited as a function of the cross-section of an individual capillary [25] and thus straight and short (> 22 cm) MCs with an efficiency of up to 14 000 TP/m can be obtained.

3.3. Van Deemter (Golay–Giddings) curves

Fig. 1 compares the Van Deemter (Golay–Giddings) curves obtained for selected alkyllead, alkylmercury and alkyltin compounds using a multicapillary and a capillary (BP-5: 30 m × 0.32 mm) column with a similar coating. Whereas the capillary column shows a narrow maximum of efficiency (minimum 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 multicapillary column shows two important peculiarities. Firstly, the minimum HETP value is smaller than that obtained with the conventional capillary column. Secondly, this minimum appears to be very broad (80–280 cm/s or 60–210 ml/min) which apparently allows the use of high flow rates to shorten chromatographic separations without sacrificing the resolution of the signals of interest. Note that the absence of the HETP growth with the linear carrier gas velocity may be due to the relatively large (approx. 0.5 s) response time of the detector used. Using an amplifier with a smaller

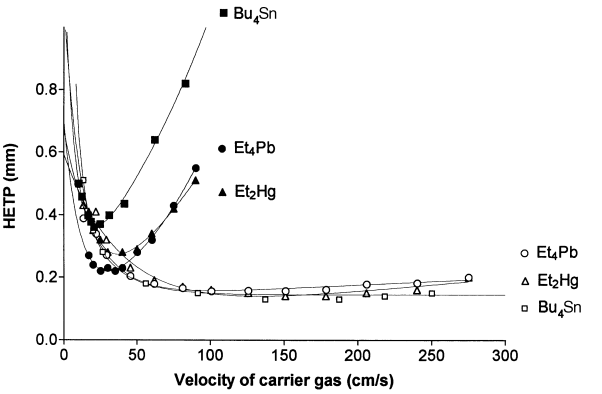

Fig. 1. Van Deemter curves for organometallic species. Filled symbols: conventional 0.32-mm capillary column; empty symbols: multicapillary column. Carrier gas: helium.

Table 1
Comparison of different chromatographic parameters of different column types

Criterion/parameter	Column				
	Packed	Micropacked	Capillary	Multicapillary	Minimulticapillary
Dimensions[a] (L × n × D)	2 m × 1 × 2 mm	0.3 m × 1 × 0.5 mm	30 m × 1 × 0.2 mm	1 m × 900 × 0.040 mm	0.22 m × 1200 × 0.030 mm
Pressure (bar)	1–2	1–100	0.1–1	0.5–10	0.5–2
Carrier gas flow rate (ml/min)	30–60	1–5	1–2	20–200	20–300
Number of theoretical plates (N_{PT})	2000	3000	100 000	up to 5000	2500
N_{PT} (m^{-1})	1000	10 000	3000	> 5000	> 9000
Loading (mg)	1000	2–3	0.2	2	3
Separation speed (N_{PT} s^{-1})	4	100	70	> 250	> 500

[a]Column length × number of capillaries × internal diameter.

response time, e.g. 0.01 s, the shape of the curve would approach more that of the conventional capillary.

In conclusion, a multicapillary column allows us to achieve efficient separations faster, using volumetric flow rates higher than in conventional capillary chromatography.

3.4. Multicapillary column vs. packed and capillary column

Table 1 compares key characteristics of the different types of chromatographic columns. The salient features are the high volumetric flow, which is readily compatible with the flows required by an MIP or ICP, the highest number of theoretical plates per column unit length, which makes relatively short columns (22 cm) sufficient for reaching efficient isothermal separations of organometallic compounds, and the highest separation speed (N_{TP} s^{-1}) of all the columns available on the market. The total efficiency is inferior to that of conventional capillary columns but the use of an element-specific detector simplifies the chromatograms and makes this parameter much less critical than in the case of conventional chromatography. In terms of allowable column load, MCs are intermediate between the capillary and the packed column, the difference being a factor 10 from each side. The above feature makes MCs potentially capable of fulfilling the criteria listed in Section 2. Two columns – a straight 22 cm long MC with ca. 1200 individual capillaries and a helix 1-m MC with 919 individual capillaries – were investigated in our laboratory in view of their utility for time-resolved sample introduction into microwave-induced plasma atomic emission spectrometry (MIP-AES) and inductively coupled plasma mass spectrometry (ICP-MS).

4. Multicapillary chromatography of organometallic species

Two principal separation modes are possible. The isothermal separation mode offers the possibility of working with simpler hardware and avoiding the post-run cooling step, thus increasing the sample throughput. The temperature-programmed separation mode enables us to reduce the duration of a run and the separation efficiency but requires additional equipment. The attractiveness of MC GC is the possibility of rapid isothermal separations using compact-size columns.

4.1. Isothermal separations

Fig. 2A presents example chromatograms using a multicapillary column (each one obtained in a different run) for the three mixtures of organometallic species that are important for environmental speciation analysis: tetraalkyllead compounds, ethylated butyltin compounds and ethylated mercury species obtained with a 1-m column. A Gaussian shape with peak symmetry around 0.90 is always observed. In each case the duration of the run (30–45 s) is much shorter than that (6–8 min) obtained using a conventional capillary column with a gradient temperature oven programming mode (Fig. 2B). Note that in the case of mercury compounds it is difficult to separate Me_2Hg from the solvent. Therefore purge-and-trap injection (no solvent) was used for the separations in Fig. 2A whereas in Fig. 2B no signal for Me_2Hg can be seen.

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 (bp. 36.5°C), it turned out to be impossible to vent the solvent off the plasma in less than 0.06–0.07 min. A possible solution to this problem is to eliminate the organic solvent at the sample preparation stage 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, which results in temperature-programmed separations. The problem can also be alleviated by using a detector less vulnerable to solvent vapor than MIP-AES, e.g. ICP-MS with high oxygen load in the plasma.

4.2. Temperature-programmed separations

The basic limitation of the isothermal elution mode is rapid peak broadening with the decreasing volatility of the analyte compound [17]. Whereas it is not a problem for volatile (bp. <150°C) species as shown in Fig. 2, it may become one for compounds with large differences in their boiling points.

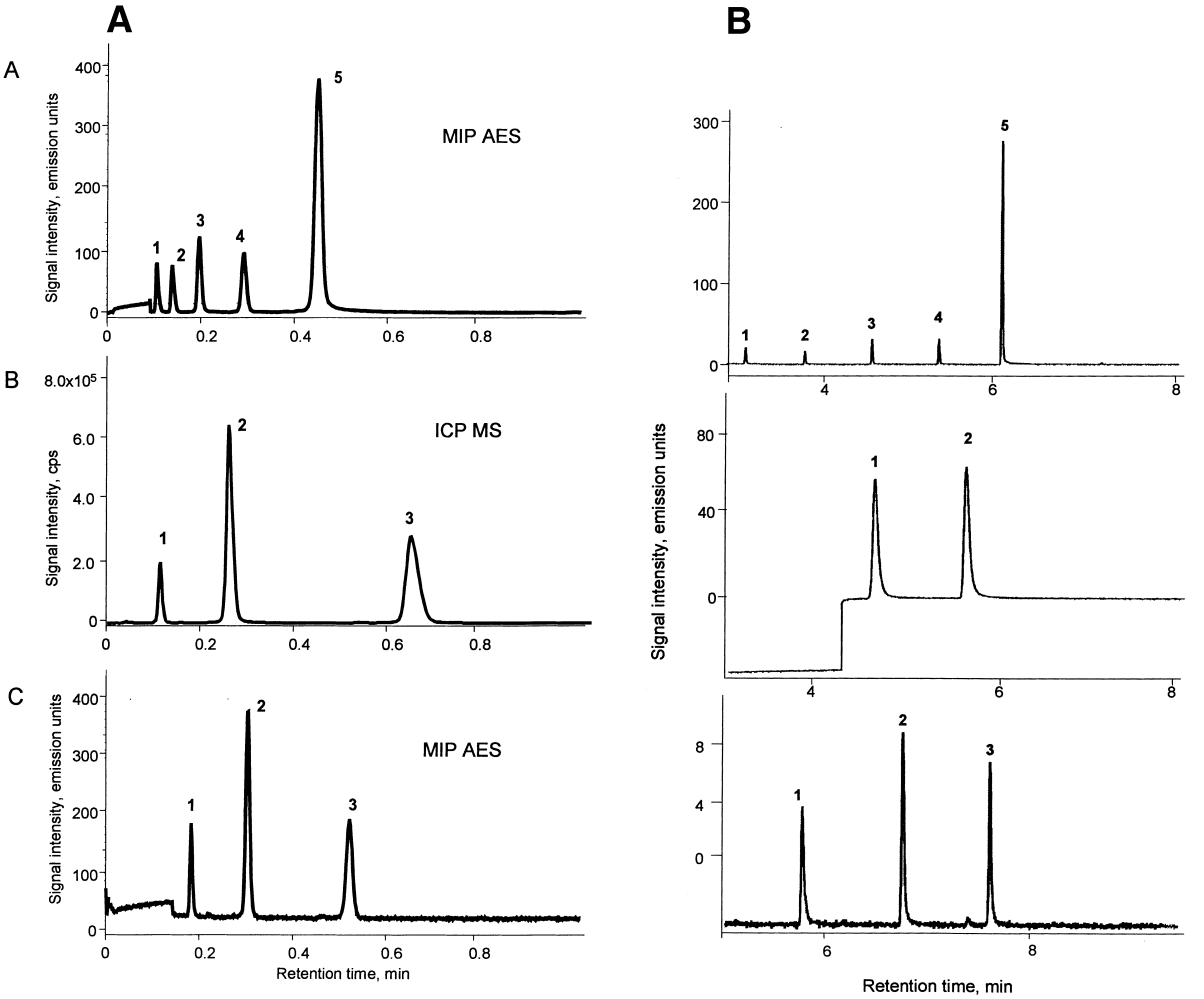

Fig. 2. (A) Isothermal multicapillary GC separations of organometallic species (1-m column). Top panel: Split injection, 120°C, column flow 85 ml/min. 1. Me_4Pb (11.5 ng/ml), 2. Me_3EtPb (6.8 ng/ml), 3. Me_2Et_2Pb (6.7 ng/ml), 4. $MeEt_3Pb$ (5.5 ng/ml), 5. Et_4Pb (130 ng/ml). MIP-AES detection. 1 μl injected. Middle panel: Purge-and-trap injection, oven 70°C, column flow 70 ml/min (argon). 1. Me_2Hg (200 pg), 2. MeEtHg (400 pg), 3. Et_2Hg (400 pg). ICP-MS detection ^{202}Hg. Bottom panel: Split injection, 155°C, column flow 65 ml/min. 1. MBT (29.2 ng/ml), 2. DBT (89.4 ng/ml), 3. TBT (64.2 ng/ml). MIP-AES detection. 1 μl injected. (B) Temperature-programmed separations (capillary column 30 m × 0.32 mm i.d., 0.25 μm film thickness). 1 μl injected. Top panel: Splitless injection (1 min), 60°C (1 min), 20°C/min, 200°C (5 min). 1. Me_4Pb, 2. Me_3EtPb, 3. Me_2Et2Pb, 4. $MeEt_3Pb$, 5. Et_4Pb. Concentrations are the same as in A. MIP-AES detection. Middle panel: Splitless injection (1 min), 45°C (1 min), 20°C/min, 200°C (3 min). 1. MeEtHg (100 ng/ml), 2. Et_2Hg (100 ng/ml). MIP-AES detection. Bottom panel: Splitless injection (1 min), 80°C (1 min), 20°C/min, 280°C (5 min). 1. MBT (29.2 ng/ml), 2. DBT (89.4 ng/ml), 3. TBT (64.2 ng/ml). MIP–AES detection. 1 μl injected.

One of the best known cases is speciation of butyltin: $BuSnEt_3$ (bp. 208°C), Bu_2SnEt_2 (bp. 245°C) and Bu_3SnEt (bp. 265°C), and phenyltin: $PhSnEt_3$ (bp. 254°C), Ph_2SnEt_2 (bp. 285°C) and Ph_3SnEt (bp. 363°C) compounds. Fig. 3 shows chromatograms for such a mixture (derivatized extract of fish tissue prepared according to Rodriguez et al. [15]) using the following columns: a conventional capillary column (Fig. 3, top), a commercially available column composed of 919 capillaries of 0.043 mm (Fig. 3, middle) and a custom-made column composed of 1200 capillaries of 0.038 mm representing a straight 22-cm long tube (Fig. 3, bottom).

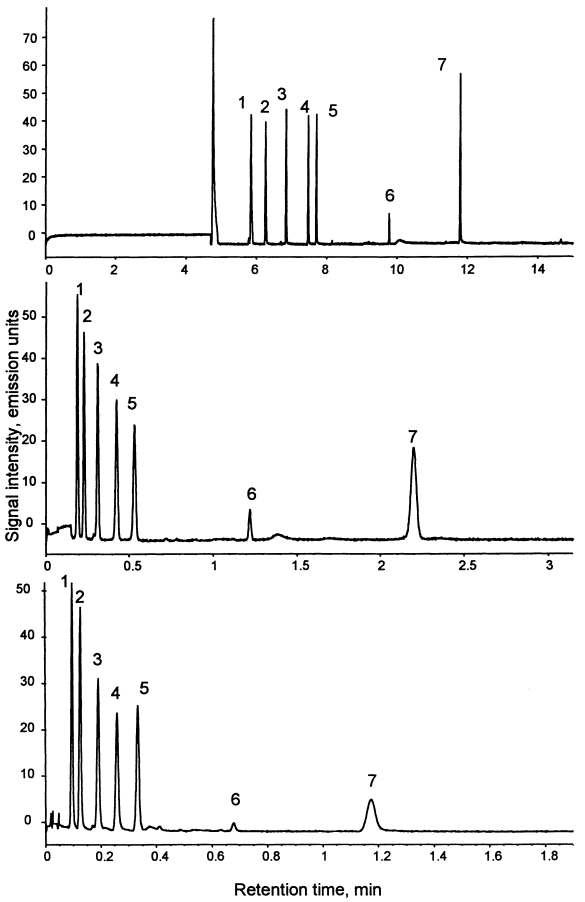

Fig. 3. Organotin compounds in the reference material BCR 477. 1. MBT, 2. TPT (I.S. 88 ng/ml), 3. DBT, 4. MPhT, 5. TBT, 6. DPhT, 7. TPhT. MIP–AES detection. Top panel: Capillary column (BP-5, 30 m × 0.32 mm, 0.25 μm film thickness). Splitless injection, 80°C (1 min), 20°C/min, 280°C (4 min). Middle panel: Multicapillary column (1 m). Split injection, 165°C (0.6 min), 100°C/min, 220°C (1.5 min). Column flow 65 ml/min. Bottom panel: Multicapillary column (22 cm). Split injection, 120°C (0.1 min), 100°C/min, 200°C (1 min). Column flow 50 ml/min. 1 μl injected.

Temperature-programmed separations of the mixtures as dealt with in Fig. 2 result in gain in the duration of a few seconds which does not justify the extra equipment and time necessary to cool the oven to the initial temperature. Chromatographic separations on a multicapillary 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 for this before the analytes reach the detector must be developed.

4.3. Effect of the column length

Fig. 3 shows that the use of the short straight 22-cm columns allowed a 10-fold decrease of the duration of a run for a full GC analysis compared with a 0.32 capillary, and for a two-fold decrease compared with a commercially available 1-m multicapillary column. Note that despite the five times shorter length the loss in the number of theoretical plates using the custom-designed multicapillary column is only two-fold in comparison with the 1-m column because of a better compensation of the dispersion of the cross-section of individual capillaries by the coating on shorter columns as indicated above. The 22-cm straight columns also proved to be efficient for the separation of ethylmercury species [22].

The dimensions of the short column used in this work (220 mm × 2.1 mm o.d.) allow a tremendous miniaturization of the oven and the development of a compact GC sample introduction accessory for atomic spectrometry. The detection limits are similar in all cases; the higher allowable load on an MC is compensated by the need of using the split injection mode.

5. Interfacing multicapillary chromatography with plasma source spectrometry

5.1. Detection by MIP-AES

Interfacing a multicapillary column with an MIP atomic emission detector requires the column diameter to be reduced to 0.32 mm to fit the discharge tube. This is realized with a custom-designed (or commercial) reducing union. The optimum makeup flows are compatible with the optimum carrier gas flow rates for Sn (260 ml/min) and Pb (285 ml/min) compounds but not for mercury (60 ml/min). 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 total flow of 140 ml/min was adopted as a compromise value. It was observed that the stability of the baseline for Hg improves at relatively high (50 psi) hydrogen supply pressures.

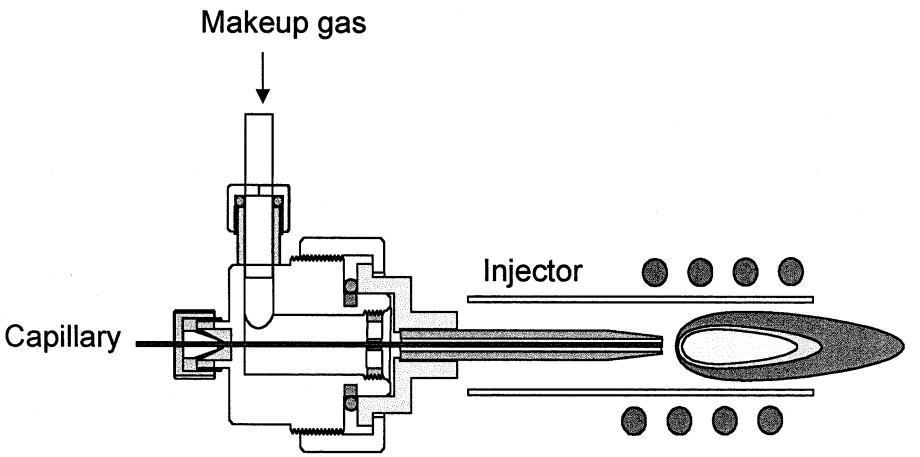

Fig. 4. Interface of multicapillary GC with ICP-MS,

5.2. Detection by ICP-MS

The interface with ICP-MS is not commercially available; the one used in our laboratory is shown in Fig. 4 [23]. In order to interface MC GC with ICP-MS the multicapillary column was prolonged with a piece of 20 cm of 0.32 mm fused-silica capillary using a reducing union as above. The capillary was drawn (the connection was made gas-tight with a ferrule and a nut) through a piece of Teflon that was screwed in the place of the nebulization chamber. The capillary was further drawn through a 0.8 mm i.d. ceramic injector and positioned ca. 1 mm from its end. Another opening in the Teflon interface allowed the introduction of the makeup (nebulizer) argon gas, concentrically with regard to the capillary, in such a way that it flowed between the capillary outer wall and the injector inner wall to enter the plasma.

This design allows the use of He and Ar as carrier gases and negligible peak broadening in the interface as with the MIP-AED design no heating of the interface was required for the ethylated mercury species.

6. Data acquisition with multicapillary columns

The duration of the run can be further reduced by increasing the column flow rate. However, at a 10-Hz data acquisition rate the 6–10 points per second necessary to produce a reproducible signal are impossible to acquire with flow rates higher than those used. The use of a detector with a faster acquisition rate is necessary to allow for a further reduction of the duration of a chromatographic run. The rapidity of the separations on multicapillary columns sets requirements in terms of sample introduction and detection.

It should be emphasized that the relatively slow response time of the detectors used, MIP-AED and, especially, ICP-MS, results in an efficiency loss of the MCs. When the limiting factors such as the solvent co-eluting with the most volatile analyte, the insufficient speed of injection and the insufficient speed of data acquisition are eliminated, extremely rapid separations can be carried out. The chromatogram shown in Fig. 5 obtained for a mixture of hydrocarbons with a fast dedicated injector and with a 250 Hz data acquisition flame ionization detector allows one to calculate the number of 2400 TP. Multicapillary GC may therefore be an attractive sample introduction

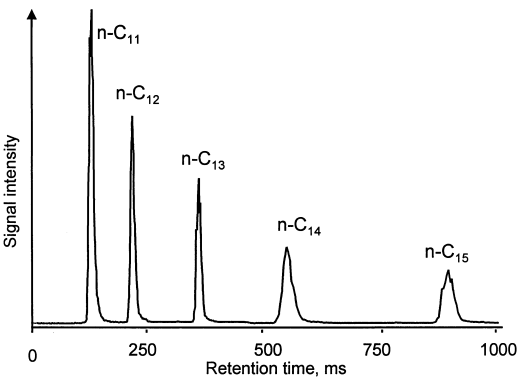

Fig. 5. MC GC separation of a mixture of hydrocarbons. 22-cm MC column. Detection by FID. Data acquisition rate: 250 Hz. Separation conditions: isothermal at 140°C. Head pressure 1.5 bar. Carrier gas: nitrogen at 50 ml/min.

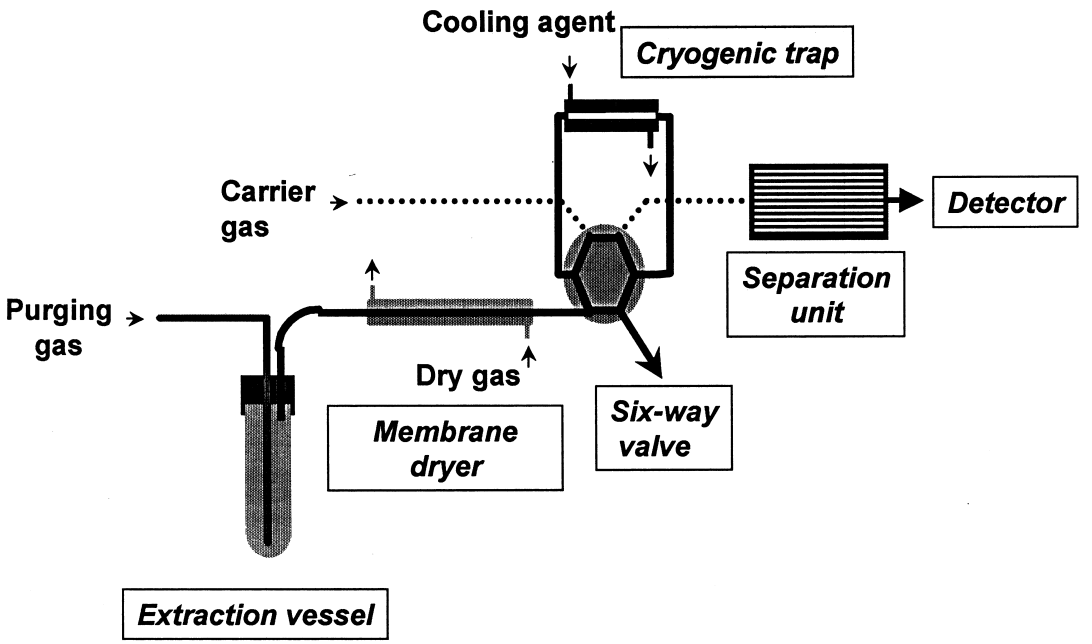

Fig. 6. Scheme of the accessory for time-resolved introduction of gaseous samples into a plasma source atomic spectrometer.

technique for ultrarapid element selective detectors such as ICP-TOF-MS.

7. Integrated accessory for species-selective analysis by atomic spectrometry

The ultimate goal of much research has been the incorporation of an MC in a device that allows the transfer of the analyte compounds from a sample to a detector in a time-resolved manner. For GC the analytes need to be presented in a volatile organic solvent or in gas phase. Liquid–gas extraction of analytes from a sample offers a considerable advantage over liquid–liquid extraction because of the possibility of the quantitative transfer of analytes from the sample onto the column, and ease of automation.

The scheme of the accessory developed for time-resolved introduction of analytes into an atomic spectrometer is shown in Fig. 6. Organometallic compounds (alkyllead, butyltin, methylmercury) and some ions [Pb^{2+}, Hg^{2+}, Se(IV), As(III)] are in situ volatilized by means of a suitable derivatization reaction (hydride generation or ethylation with $NaBEt_4$). The derivatives formed are purged from the vessel and pass through a water scrubber (Nafion dryer) to a wide-bore (0.53 mm) capillary trap where they are cryofocussed at −100°C. Then the trap is heated to release the species on a multicapillary column. The analysis cycle takes less than 5 min.

The system developed shows two major advantages over the commercial and the literature described purge-and-trap systems. It is a free-standing accessory including the separation step and there is no need for a gas chromatographic oven because of the application of a multicapillary column. The second advantage consists of using a 30-cm Nafion tube dryer which allows the elimination of the external chiller for removal of water from the purge-gas stream. The compact accessory for an MIP or ICP spectrometer allows species-selective analysis of liquid and solid (with optional microwave cavity) samples.

8. Applications

Multicapillary GC and the accessory developed have been applied to the analysis of a variety of environmental samples using atomic spectrometry (MIP-AES and ICP-MS). Example chromatograms are shown in Fig. 7. Results obtained by the methods developed elsewhere for certified reference materials are summarized in Table 2. The concentrations obtained are in agreement with the certified or indicative values. The only exception is the MBT concentration in sediment samples; the higher values obtained are probably due to the novel, more efficient

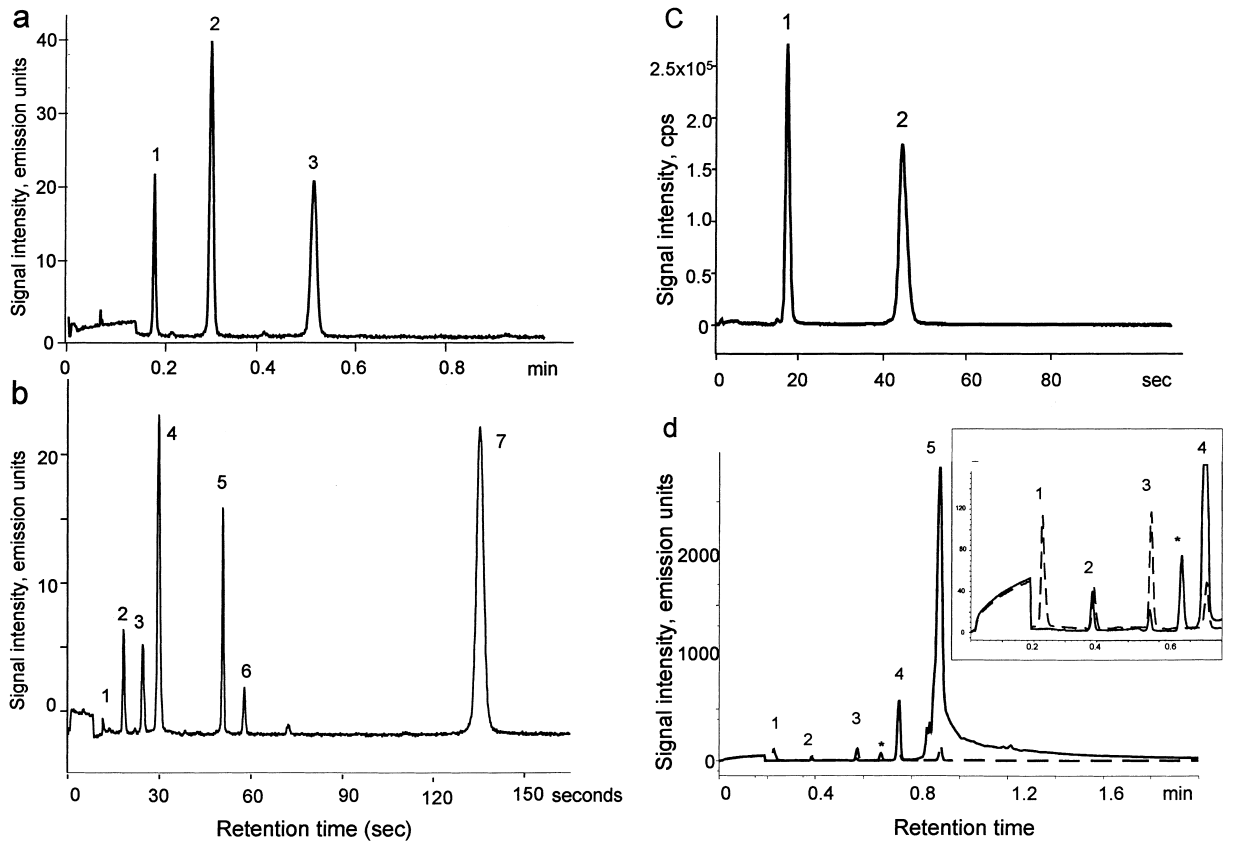

Fig. 7. Applications of multicapillary GC (22-cm column) for the analysis of certified reference materials. (a) PACS-2 material. Split injection, isothermal at 155°C, column flow 65 ml/min. 1. MBT, 2. DBT, 3. TBT. MIP-AES detection. (b) NIES-11 material. Split injection, temperature gradient 120°C (0.1 min), 100°C/min, 200°C (1 min). Column flow 50 ml/min. 1. MBT, 2. TPT (I.S. 88 ng/ml), 3. DBT, 4. MPhT, 5. TBT, 6. DPhT, 7. TPhT. (c) DORM-1 material. Purge-and-trap injection, 70°C (2 min), column flow 70 ml/min. 1. MeEtHg, 2. Et_2Hg. ICP-MS detection ^{202}Hg. (d) Road dust CRM. Purge-and-trap injection, temperature gradient: 70°C (0.2 min), 100°C/min, 150°C (1 min), column flow 85 ml/min. 1. Me_4Pb, 2. Me_3EtPb, 3. Me_2Et_2Pb, 4. $MeEt_3Pb$, 5. Et_4Pb, * unidentified compound. Solid line, sample; dashed line, standards.

microwave-assisted leaching procedure used [27]. Isothermal separations can be used for butyltin and alkylmercury speciation. Especially interesting in terms of experimental detection limits is the possibility of speciation of mercury by purge-and-trap multicapillary GC–ICP-MS where the theoretical detection limits down to 5–10 fg/ml for a 10-ml water sample are controlled by the blank value.

Fig. 7a shows a chromatogram of butyltin species, leached from a sediment under conditions described elsewhere [27], derivatized by ethylation using $NaBEt_4$ and extracted into iso-octane. A 10-fold decrease of the analysis time was achieved. In Fig. 7b butyltin and phenyltin compounds were extracted from a biological tissue as ethyl derivatives into nonane and chromatographed on a short column with GC–AED (Fig. 7b). Again a 10–15-fold gain in speed in comparison with capillary columns was reached. The chromatogram (Fig. 7c) obtained for a fish tissue sample with the detection of Hg by ICP-MS shows two peaks corresponding to the ethylated derivatives of methylmercury and of Hg(II), respectively.

The chromatogram obtained for a sample of tunnel dust (Fig. 7d) using detection of lead emission at 406 nm shows the presence of a huge peak of $PbEt_4$ corresponding to the derivatized Pb^{2+} present in the sample (and Et_3Pb^+ and Et_2Pb^{2+} compounds). Two peaks corresponding to the derivatized Me_3Pb^+ and Me_2Pb^+ species can be identified on the basis of their retention times. The chromatogram also reveals the presence of a $MeEt_3Pb$ signal, which may be an artefact of the derivatization procedure. There is also one peak with

Table 2
Determination of organometallic compounds in different standard reference materials using MC GC–MIP-AED after microwave-assisted sample preparation

Methylmercury

Sample	Found (μg/g)	Certified (μg/g)	Separation of $MeHg^+$ from the matrix	Comments	Ref.
CRM 464 tuna fish	5.52 ± 0.24	5.50 ± 0.177	solvent extraction	as MeHg, MIP-AES	[20]
CRM 463 tuna fish	2.73 ± 0.17	3.04 ± 0.16	solvent extraction	as MeHg, MIP-AES	[20]
DORM-1 dogfish	0.685 ± 0.04	0.731 ± 0.06	solvent extraction	as Hg, MIP-AES	[20]
DORM-1 dogfish	0.714 ± 0.01	0.731 ± 0.06	purge-and-trap	as Hg, MIP-AES	[21]
TORT-1 lobster hepatopancreas	0.131 ± 0.01	0.128 ± 0.014	purge-and-trap	as Hg, MIP-AES	[21]
DORM-1 dogfish	0.74 ± 0.05	0.731 ± 0.06	purge-and-trap	as Hg, ICP-MS	[28]
TORT-1 lobster hepatopancreas	0.12 ± 0.003	0.128 ± 0.014	purge-and-trap	as Hg, ICP-MS	[28]

Organotin compounds

Sample	Found				Certified				
	MBT	DBT	TBT	TPhT	MBT	DBT	TBT	TPhT	Ref.
[1]NIES-11			1.19 ± 0.02	5.80 ± 0.81			1.30 ± 0.1	6.3*	[15]
[2]PACS-1	1.18 ± 0.01	1.03 ± 0.05	1.27 ± 0.04		0.28 ± 0.17	1.16 ± 0.18	1.27 ± 0.22		[15]
[2]PACS-2	0.46 ± 0.02	1.05 ± 0.04	0.97 ± 0.06		0.3*	1.09 ± 0.15	0.98 ± 0.13		[22]

*Indicative value (non-certified); [1]Conc. μg/g as chloride; [2]Conc. μg/g as tin; [3]Conc. μg/g as cation.

a retention time between Me_2Et_2Pb and Me_3EtPb, the origin of which remains unknown. This peak corresponds, nevertheless, to an organolead compound since the emission spectrum taken at its apex was found to contain the lines characteristic of this element.

9. Conclusions and perspectives

Multicapillary GC offers an attractive approach to time-resolved introduction of gaseous analytes into a plasma-source spectrometer. It combines the advantages of the packed and capillary GC and eliminates their drawbacks. The separations achieved are fast at carrier gas flow rates similar to those required by atomic spectrometers. Isothermal separations are usually sufficient but oven temperature or carrier gas flow programming may be required in some cases. The separation efficiency of multicapillary columns, including straight 22-cm columns, is sufficient to ensure the baseline resolution for the most widely analyzed organometallic compounds in environmental matrices.

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