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Evaluation of gas chromatographic columns for the determination of methylmercury in aqueous head space extracts from biological samples

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ABSTRACT

Several gas chromatographic columns were evaluated for the determination of methylmercury in aqueous solution. The goal of the study was to further decrease the detection limit of the recently developed method of head space gas chromatography with microwave-induced plasma detection (HS-GC–MIP) for the determination of methylmercury in biological samples. The columns were first evaluated using gas chromatography with electron-capture detection (ECD). At the same time, the column efficiencies for the determination of ethyl- and phenylmercury were also studied. Of the packed columns the stationary phase used previously in HS-GC–MIP, AT-1000, yielded the best results. Better results were obtained with two wide-bore thick-film fused-silica open tubular (FSOT) columns, one of which was suitable for aqueous injections (Superox-FA) and the other for benzene or toluene (RSL-300). With these FSOT columns, absolute detection limits at the sub-picogram level were reached. A new HS-GC–MIP system was then constructed, which was adapted for the use of FSOT columns. As more sensitive measurements were obtained with a Superox-FA FSOT column than with an AT-1000 packed column using the GC–ECD system in the first part of this study, the FSOT column was evaluated in this HS-GC–MIP system for the determination of methylmercury in real tissue samples. It was demonstrated that the use of an FSOT column gives only a small decrease in the detection limit compared with a packed column; reconditioning of the FSOT column is, however, a disadvantage in routine measurements.

INTRODUCTION

Methylmercury (MeHg) is one of the most dangerous pollutants in the environment. It is highly toxic and is often found concentrated at the end of the food web. Fish especially tend to concentrate mercury in their tissues and analyses have shown that most of the mercury accumulated in their tissues is in the form of MeHg [1–5], despite the lack of obvious significant MeHg inputs to natural aquatic systems. The MeHg concentrations in natural waters and sediments are very low (pg kg^{-1}) [2,6]. Compared with this, the MeHg content in fish is usually in the range of micrograms per kilogram [2,6]. Concentration factors of 10^5–10^7 are commonly observed [6–9]. Most of the MeHg taken up by fish from the aquatic environment is accumulated in edible tissues [6]. MeHg uptake by fish is therefore the main route from the aquatic environment to humans. This has led to a

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considerable effort in the development of reliable, precise and sensitive analytical methods specific for the determination of this compound in fish and other aquatic organisms.

The most widely used analysis technique is gas chromatography with electron capture detection (GC–ECD) or microwave-induced plasma detection (GC–MIP) [1,10–18]. MIP has the advantage that it can be used as mercury-specific detection. In this method, usually referred to as the Westöo method, elaborate and time-consuming extractions have to be carried out prior to injection of the sample onto the GC column. One of the major problems in the determination is that organic mercury halides exhibit poor GC properties.

Most of the reported chromatography methods have used packed columns [10,12–16,19]. A variety of stationary phases has been recommended, but many of these columns have exhibited one or more of the following disadvantages [19]: (a) poor and often variable response to methyl- and ethylmercury chloride (MeHgCl and EtHgCl) because of apparent interactions with the column or their decomposition on it; (b) moderate to very severe tailing; and (c) poor column efficiency that can then lead to problems with interferences. Hence time-consuming and laborious column conditioning procedures are necessary [19]. The beneficial effects of the treatment are only temporary, as the presence of high-molecular-weight compounds in the sample often leads to degradation of the "column performance" [19].

Only a few methods have been reported in which capillary columns have been used [20–25]. Cappon and Toribara [26] and Olsen *et al.* [17] were the first to use wide-bore thick-film fused-silica open tubular (FSOT) columns (0.53 mm I.D., 1.2 μm film thickness) and they obtained very good results. However, they only used standard solutions in the evaluation. Wide-bore thick-film columns have the advantages that they accept large injections without the use of a splitter, are compatible with higher flow-rates and do not need a make up gas to be added after the column.

Petersen [27] evaluated FSOT columns with different internal diameters and film thicknesses coated with CP-Sil 8. These experiments suggested that it is important to use capillary columns with a thick film. This may be because the thick film reduces the contact between the volatilized mercury compound and a fused-silica column which is not entirely deactivated. Even with thick-film columns there was still a problem of high standard deviations on the results. Petersen [27] also tested several other capillary columns but most of these did not give any response for MeHgCl. The compound disappeared in the GC system if it was not primed with a mercury compound before analysis.

Lee and Mowrer [28] used a wide-bore thick-film FSOT column coated with OV 1701. Their chromatograms show a high number of peaks (sometimes interfering) and each sample analysis required about 30 min to elute all the peaks that could interfere with a subsequent injection.

A fast, accurate, precise and sensitive method for the determination of MeHg in biological samples has been developed at this laboratory [18,29,30]. In this method, the MeHg is cleaved from the biological tissue by sulphuric acid and by the addition of iodoacetic acid converted to the iodide form. These reaction steps take place in a closed head space vial. The MeHg iodide is then injected into the head space of a gas chromatograph and detected by MIP. This method has several advantages over the widely used Westöo method. By using direct headspace sampling (HS), the problem of "column performance" degradation is solved. Indeed, high-boiling compounds which often poison the stationary GC phase are no longer introduced into the column as occurs in direct injection chromatography. Another major advantage of this sampling procedure is its simplicity; all the reaction steps take place in the head space vial and the laborious isolation of the MeHg by multiple extraction with benzene or toluene is no longer required. The HS-GC–MIP method has a detection limit of 0.4 $\mu g\ l^{-1}$ or 20 $ng\ g^{-1}$ for MeHg in biological tissues.

Head space analysis above an aqueous solution provides a considerable enrichment of MeHg in the vapour phase compared with the analysis above a benzene solution [18]. Therefore aqueous solutions will give a more sensitive determination, but a water-resistant chromatographic column must be used. Very few stationary phases are suitable for aqueous injections; only Talmi [15] has mentioned the use of a column packing suitable for aqueous solutions. He used a 1% free fatty acid phase (FFAP) liquid phase on graphitized carbon beads.

In the HS-GC–MIP method [29–31], AT-1000 was used as the stationary phase. This stationary phase is well suited to aqueous injections. The water is completely eluted from the column within 30 s and quantitative peaks are obtained for the MeHgX (X = Cl, Br, I) eluted thereafter. No special column conditioning procedures are required. The column efficiency, however, is very low (200–250 plates per meter for MeHgCl).

In this work, the efficiencies of several columns (packed and capillary) were studied for the determination of MeHgCl in aqueous solution. The objective of this work was to further decrease the detection limit of this HS-GC–MIP method.

The columns were first evaluated by injecting aqueous MeHgCl standard solutions. At the same time, the column properties for the determination of EtHgCl and phenylmercury chloride (PhHgCl) were studied. An electron-capture detector was used for this study as its non-specificity, a disadvantage compared with the MIP detector when analysing real samples, does not play a role when only organomercury standard solutions are injected into the gas chromatograph.

A new HS-GC–MIP system was then constructed, which was adapted for the use of capillary columns. More sensitive measurements were obtained using a GC–ECD system with a Superox-FA FSOT column than with the AT-1000-packed column, so the FSOT column was evaluated in this HS-GC–MIP system for the determination of MeHg in real tissue samples.

EXPERIMENTAL

GC–ECD study

All the columns were evaluated on an HP 5730A gas chromatograph with an electron-capture detector (^{63}Ni radioactive source). Standard solutions were injected with Hamilton microliter syringes into the injector at 200°C. A glass liner was placed in this injector to avoid possible interactions of the organomercury compounds with the hot metal surface. For the same reason, glass was used for the packed columns. The detector temperature was 300°C. Argon was used as the carrier gas.

The columns evaluated are listed in Table I. The AT-1000 column was also tested in this system so that the results obtained with the other columns could be compared with those obtained with the stationary phase used earlier in the HS-GC–MIP system. Chromosorb 101 to 108 of the Chromosorb Century Series (Alltech Assoc.) were chosen because they are known to be hydrophobic. They are porous, polyaromatic, cross-linked resins with a uniform rigid structure of a distinct pore size. They do not have to be coated before use (this is in fact gas–solid chromatography). Two FSOT columns were tested: Superox-FA and RSL-300 (both from Alltech Assoc.). These are wide-bore thick-film columns.

TABLE I

COLUMNS TESTED USING THE GC–ECD SYSTEM

Column	Type and chemical name	Dimensions [length (m) × I.D. (mm)]
10% AT-1000 on Chromosorb W AW	Packed, polyethylene glycol ester	2 × 2
Chromosorb 101	Packed, styrene-divinylbenzene	2 × 2
Chromosorb 102	Packed, styrene-divinylbenzene	2 × 2
Chromosorb 103	Packed, cross-linked polystyrene	2 × 2
Chromosorb 104	Packed, acrylonitrile-divinylbenzene	2 × 2
Chromosorb 105	Packed, polyaromatic	2 × 2
Chromosorb 106	Packed, cross-linked polystyrene	2 × 2
Chromosorb 107	Packed, cross-linked acrylic ester	2 × 2
Chromosorb 108	Packed, cross-linked acrylic ester	2 × 2
Supcrox-FA	FSOT, polyethylene glycol ester	10 × 0.53
RSL-300	FSOT, polyphenylmethylsiloxane	10 × 0.53 (both 1.2 μm film)

The RSL-300 column is not suitable for aqueous injections, but this column was evaluated to compare the results with those obtained with the water-resistant Superox-FA column. It was chosen because it has a similar stationary phase to the DB-5 column used very successfully by Olsen *et al.* [17].

HS-GC–MIP study

The HS-GC–MIP system for the determination of MeHg using the AT-1000-packed column and the head space extraction method used to determine MeHg in biological samples have been described previously [29–31]. A typical chromatogram obtained with this system is given in Fig. 1.

The HS-GC–MIP system used here consists of four commercially available components: an HS-6 semi-automated head space sampler (Perkin-Elmer), an Intersmat 120 gas chromatograph, a heated four-way valve for solvent ventilation (Valco GC-T) and an MPD 850 microwave plasma instrument (Applied Chromatography Systems). The HS-6 semi-automated head space sampler is mounted on the Intersmat gas chromatograph. The HS-6 sampler was first modified so that the sample com-

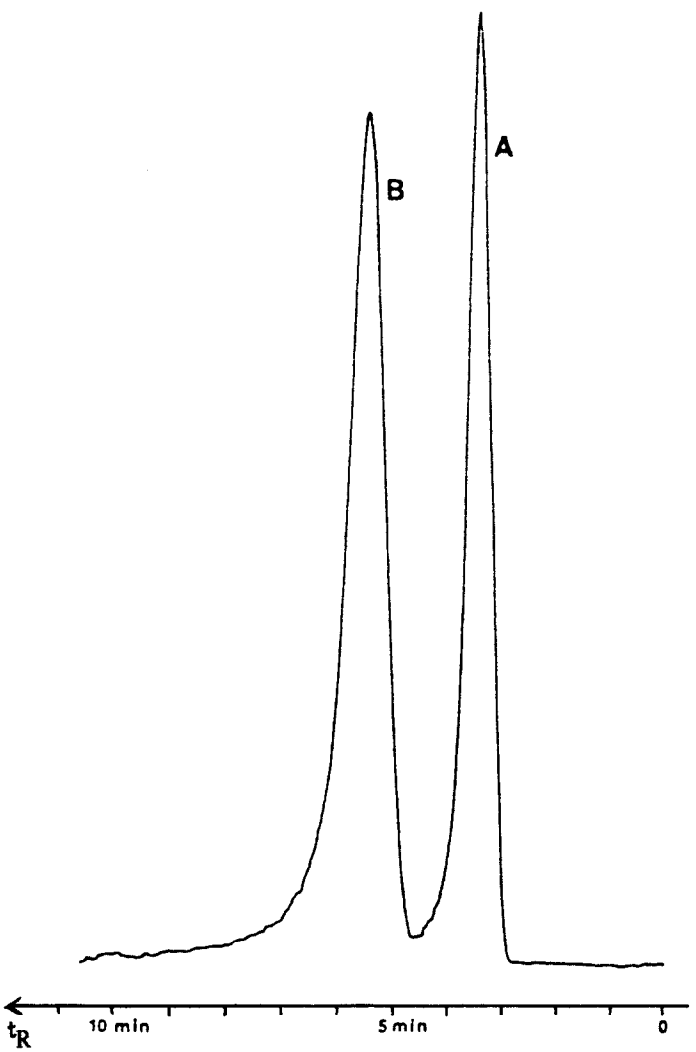

Fig. 1. Chromatogram obtained with the HS-GC–MIP system using an AT-1000-packed column. Peaks: A = MeHgCl; B = EtHgCl.

pounds make contact only with a PTFE surface [32].

The GC analyses were carried out with a 15 m × 0.53 mm I.D. (1.2 μm film thickness) FSOT column coated with Superox-FA (Alltech Assoc.). The outlet of the column is connected to the heated four-way valve. This valve is used when it is necessary for the column effluent to by-pass the plasma during the elution of the solvent peak. The four-way valve also allows a continuous argon flow to the plasma tube at all times. A second length of fused-silica capillary column (about 75 cm long, 0.53 mm I.D., no coating, deactivated) is used to connect the valve outlet to the plasma tube. Outside the GC oven, this second piece of column is enclosed in a 5 mm I.D. insulated copper tube that is heated to the maximum column temperature with a heating tape. The argon plasma is sustained in a 1 mm I.D. quartz tube. As on the packed column system, this tube is centered in a quarter-wave Evenson-type cavity (Electro Medical Supplies, Model 214L). The cavity is connected to the microwave generator via a 50-Ω coaxial cable. The plasma tube is aligned before the entrance split of the spectrometer.

The MPD 850 incorporates a 0.75 m Rowland spectrometer with six phototubes and associated slits above which are mounted a control unit, an amplifier and power supply unit and a microwave generator. A reciprocal linear UV dispersion of 0.695 nm mm^{-1} is achieved using a 960 groove mm^{-1} holographic grating fitted into a Paschen-Runge mounting.

Reagents

GC–ECD study. All chemicals were of analytical-reagent grade. Analytical standard solutions of MeHgCl, EtHgCl and PhHgCl (all from Merck) with a concentration of 10 ng μl^{-1} were prepared daily from a stock solution of 200 ng μl^{-1}. For PhHg benzene solutions were used because of the very low solubility of that compound in water. Generally, 1.0 μl of working standard was injected onto the packed columns and 0.2 μl onto the FSOT columns.

HS-GC–MIP study. Iodoacetic acid was of analytical-reagent grade and the sulphuric acid of Suprapur quality (Merck). The standard MeHgCl solutions in the range 0–100 ng ml^{-1} were prepared daily from a stock solution of 10 μg ml^{-1}, which was stored in a refrigerator [33].

All solutions were prepared in distilled, deionized water obtained with a Milli-Q apparatus (Millipore).

RESULTS AND DISCUSSION

GC–ECD study

For each column, the optimum GC conditions (optimum oven temperature and carrier gas flow-rate) were determined first. The analysis time, resolution, reproducibility (relative standard deviation on the MeHg peak heights obtained in six replicate measurements) and detection limit were also evaluated.

With the AT-1000 column, sharp peaks were observed not only for MeHgCl but also for EtHgCl. The height equivalent to a theoretical plate (HETP) was considerably lower here (for MeHgCl, HETP = 0.36 cm, for EtHgCl, HETP = 0.28 cm) than with the HS-GC–MIP system (for MeHgCl, HETP = 0.77 cm, for EtHgCl, HETP = 0.38 cm). This is possibly due to dilution taking place at the interface of this GC–MIP system between the outlet of the column and the quartz capillary plasma tube. Olsen *et al.* [17] avoided this problem by using a piece of their working column incorporated inside a heated nickel tube at the temperature of the GC oven, between the GC outlet and the plasma tube. As with the HS-GC–MIP system, no PhHg peak was observed.

Of the eight Chromosorb column packings tested, Chromosorb 101 gave the best results for the determination of MeHgCl and EtHgCl (Table II). The HETP was even lower than the plate height obtained with AT-1000. The sensitivity for MeHgCl was, however, fourteen times lower with the Chromosorb 101 column. In addition, when injecting MeHgCl and EtHgCl two small by-peaks were observed. When only MeHgCl was injected, one much smaller by-peak was observed. These results suggest an interaction between the mercury compounds and the stationary phase. Of the other Chromosorbs, 103, 106, 107 and 108 yielded a high number of theoretical plates but the sensitivity was much lower than with AT-1000 and a gradual decrease of the peak height with successive injections was observed due to interactions between the solvent (water), the mercury compounds and the stationary phase. After a certain time of reconditioning, the maximum peak height obtained for the first injection was again reached. In all instances the solvent (water) probably changed the polarity of the stationary phase.

TABLE II

GC SEPARATION EFFICIENCIES OBTAINED WITH THE GC CONDITIONS OF TABLE III

Column	MeHgCl HETP (cm)	MeHgCl relative sensitivity[a]	EtHgCl HETP (cm)	MeHgCl–EtHgCl resolution	PhHgCl HETP (cm)	PhHgCl relative sensitivity[b]
AT-1000	0.36	1	0.28	3.41	n.d.[c]	–
Chromosorb 101	0.19	14	0.16	6.55	n.d.	–
Chromosorb 102	1.00	45	1.00	0	0.61	19
Chromosorb 103	0.25	40	0.26	5.28	0.83	27
Chromosorb 104	n.d.	–	n.d.	–	n.d.	–
Chromosorb 105	2.22	25	2.67	0	n.d.	–
Chromosorb 106	0.56	60	0.36	0	0.50	56
Chromosorb 107	0.15	75	n.d.	–	0.11	49
Chromosorb 108	0.71	190	0.16	0	n.d.	–
Superox-FA	3.79	0.23	3.60	2.30	3.01	0.93
RSL-300	2.18	0.23	1.28	5.23	2.07	0.32

[a] Relative sensitivity: height of the MeHg peak obtained on the AT-1000 column divided by the MeHg peak height obtained on the tested column.

[b] MeHg peak height obtained on the AT-1000 column divided by the PhHg peak height obtained on the tested column.

[c] n.d. = not detectable.

PhHg peaks could only be observed on Chromosorb 102, 103, 106 and 107. Good peak shapes and reproducibility were obtained especially with Chromosorb 102, but the sensitivity was nineteen times lower than the MeHgCl peak on AT-1000 and interactions of the solvent with the stationary phase were also observed. In the Chromosorb series the best stationary phase for MeHgCl and EtHgCl was non-polar (Chromosorb 101) and for PhHgCl it was weakly polar (Chromosorb 102). For MeHgCl and EtHgCl, the AT-1000 column showed a much higher sensitivity.

Better results were obtained with the two FSOT columns. The best efficiency with these columns would be obtained in the capillary mode (2–4 ml min^{-1}) and using hydrogen as the carrier gas. Unfortunately, the operating parameters used (they are summarized and compared with the AT-1000 column conditions in Table III) are not optimum, as with the HS-GC–MIP system argon has to be used

TABLE III

GC CONDITIONS USED WITH THE GC–ECD SYSTEM

Column	Temperature	Carrier flow-rate (ml min^{-1})	Solvent
AT-1000	Isothermal: 150°C (MeHgCl, EtHgCl)	100	Water
Chromosorb 101–108	Isothermal: 155°C (MeHgCl, EtHgCl)	20	Water
	155°C (PhHgCl)		Benzene
Superox-FA	Isothermal: 150°C (MeHgCl, EtHgCl)	25	Water
	150°C (PhMeCl)		Benzene
RSL-300	Isothermal: 100°C (MeHgCl, EtHgCl)	25	Benzene
	150°C (PhHgCl)		Benzene
	Programme: 90°C, 16°C min^{-1} to 180°C (separation of all three components)		Benzene

(hydrogen cannot be used because it is unsuitable as a plasma support gas for the MIP). In addition, to benefit the advantage of adding no make up gas after the column (in fact the "capillary mode" is not used) requires much higher flow-rates than optimum.

With the Superox-FA column sharp and fairly symmetrical peaks were observed for the three mercury compounds (Fig. 2). The sensitivity was much higher than with the AT-1000 column (peak heights about four times higher, detection limit about six times lower) and PhHg also eluted from the column. It was not possible to obtain baseline separation between the PhHg and MeHg peak on the Superox-FA column, even with temperature programming. In contrast, this was possible on the RSL-300 column. This column gave the best results: increased baseline stability, sharp peaks (Fig. 3), low retention times, lower detection limits (Table IV) and excellent baseline resolution for the three selected organomercury chlorides. With temperature programming, more than 2000 plates were obtained for EtHg and PhHg (Fig. 4). A disadvantage for our purposes (working with aqueous mercury solutions in an HS sampler) is that aqueous solutions cannot be used.

Each of the two FSOT columns has advantages and disadvantages when used in the HS-GC–MIP system. The RSL-300 column allows the determination of the three mercury compounds but leads to a serious loss in sensitivity at the level of the HS sampler as water cannot be used with this column. With the Superox-FA column water can be used as the solvent, providing a vapour phase enrichment in the head space vial compared with a benzene solution, but the analysis then suffers from an incomplete separation of MeHgCl and PhHgCl. However, the presence of PhHg is very rare in most environmental samples.

HS-GC–MIP study

The only column that might give an improvement in sensitivity for the determination of MeHg with the HS-GC–MIP system using the AT-1000 column is the Superox-FA column. However, it is very likely that a smaller volume of sample will be injected into the head space of the FSOT column than into the packed column. Band broadening will also occur more easily with an open tubular column, therefore there can be a loss in sensitivity. Head space sampling into open tubular columns is more critical than into packed columns due to the low flow resistance of the former. Also, lower inlet pressures are generally applied to open tubular columns. The sample volume injected depends on this pressure and the flow resistance of the column. For reproducible sampling it is essential that the column head pressure is higher than the vapour pressure in the sample vial, otherwise phenomena such as double peaking and broad peaks with excessive tailing may occur. Moreover, the lower detection limit attained with the FSOT column in the GC–ECD system was partly due to an increased baseline stability. With another type of detector this effect can be totally different.

The MPD-850 detector was first evaluated and compared with the detector used in the packed column system, the Perkin-Elmer AAS-403 [29–31]. The only correct way for comparison is to use the same head space and gas chromatography system coupled to each of the detectors. The Perkin-Elmer AAS-403 detector coupled to the packed-column system was already evaluated. The AAS detector in this system was therefore replaced by the MPD-850. The HS-GC system was maintained at the normal optimum working conditions. It was shown that the best detection limit that could be attained using the MPD-850 detector was twice as high as the detection limit attained when using the AAS-403. The MeHg signal was almost three times higher with the MPD-850, but unfortunately the noise level was approximately six times higher.

Finally, the Superox-FA FSOT column was tested on the HS-GC–MIP system. Before sharp, symmetrical and reproducible peaks could be obtained for the lower MeHg concentrations (0–100 $\mu g\ l^{-1}$, the normal range for the working standards used with standard additions) it was necessary to "activate" the Superox-FA column by injecting a large concentration of MeHgCl several times (10 mg l^{-1}). It was necessary to repeat this activation every 5–10 days, depending on the number of analyses performed.

A stable plasma could be obtained at all the carrier gas flow-rates evaluated (15–35 ml min^{-1}). It was not therefore necessary to add a make up gas. The MeHg signal was almost doubled when the internal diameter of the plasma tube was reduced from 2 mm (that used on the packed column system)

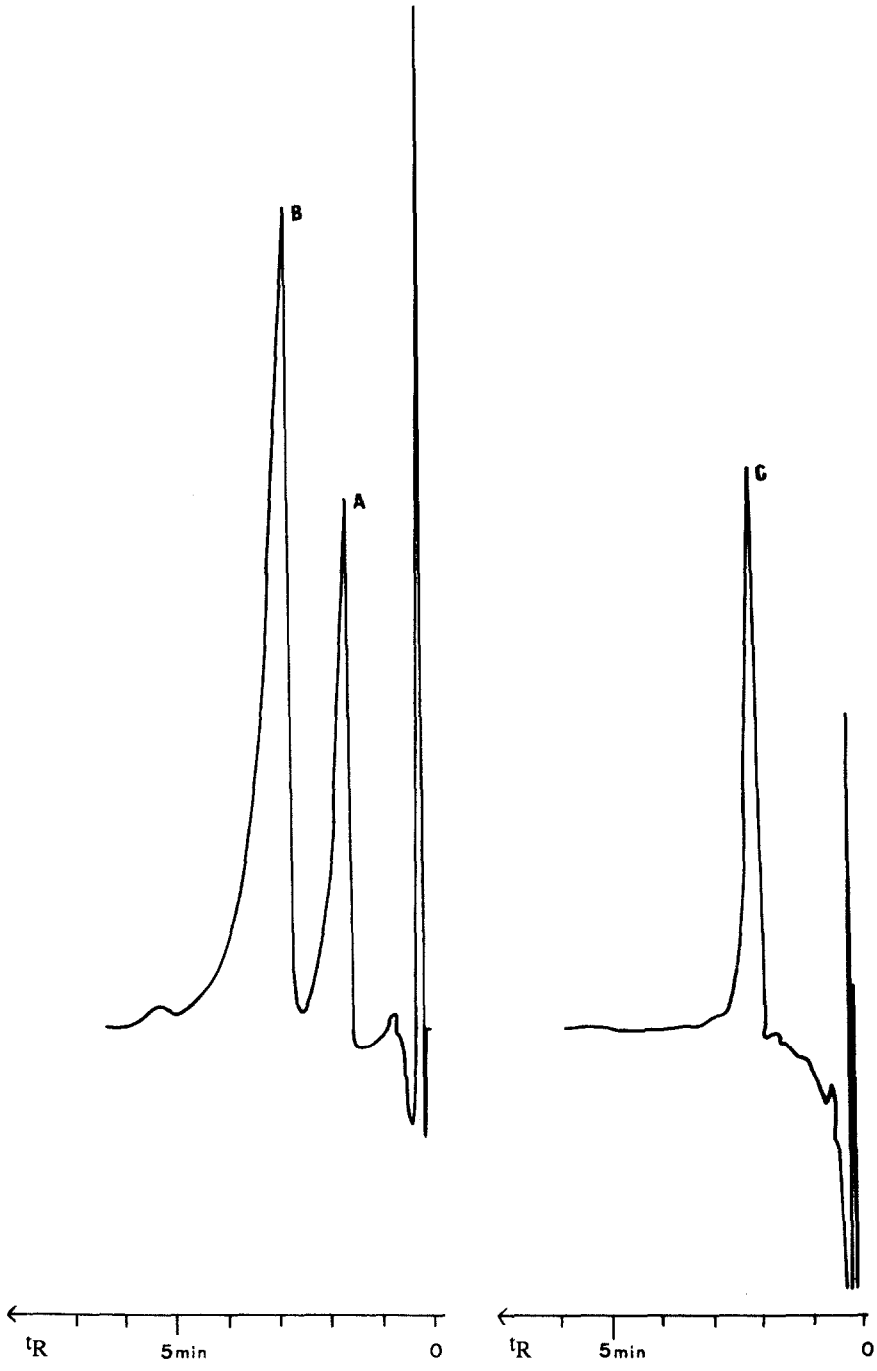

Fig. 2. Chromatograms (isothermal) obtained with the GC–ECD system using a Superox-FA FSOT column. Peaks: A = MeHgCl; B = EtHgCl; C = PhHgCl.

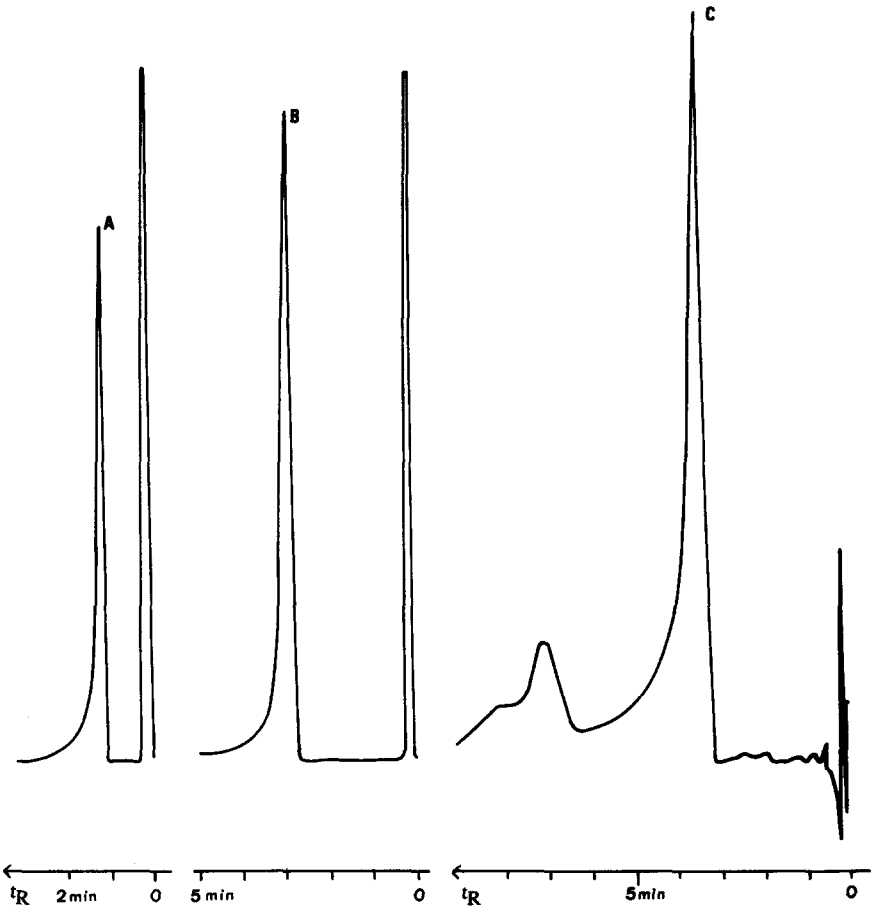

Fig. 3. Chromatograms (isothermal) obtained with the GC–ECD system using an RSL-300 FSOT column. Peaks: A = MeHgCl; B = EtHgCl; C = PhHgCl.

to 1 mm, whereas the noise level remained constant. It was also revealed that an adequate heating of the interface tube from the column to the plasma tube is essential to avoid tailing of the peaks. Cold spots in the interface have to be avoided, otherwise condensation will occur.

TABLE IV

ABSOLUTE DETECTION LIMITS (GC–ECD SYSTEM)

Defined as the signal level corresponding to twice the standard deviation of the background signal.

Column	MeHgCl (pg)	EtHgCl (pg)	PhHgCl (pg)
AT-1000	4.1	4.1	–
Superox-FA	0.7	0.5	3.1
RSL-300	0.4	0.3	0.5

The HETP attained was very high (6.8 cm). The retention time was very short (1 min) and was close to the time necessary for the column effluent to by-pass the plasma (30 s), the time necessary for complete elution of the solvent peak. A typical chromatogram (at 170°C and 30 ml min^{-1}, the optimum conditions) is shown in Fig. 5. Compared with the MeHg peak obtained with the packed column system (Fig. 1) a narrower peak showing less tailing is obtained.

When the pure solvent (water) was injected after the injection of a standard solution, a small memory peak was observed. As a modified head space

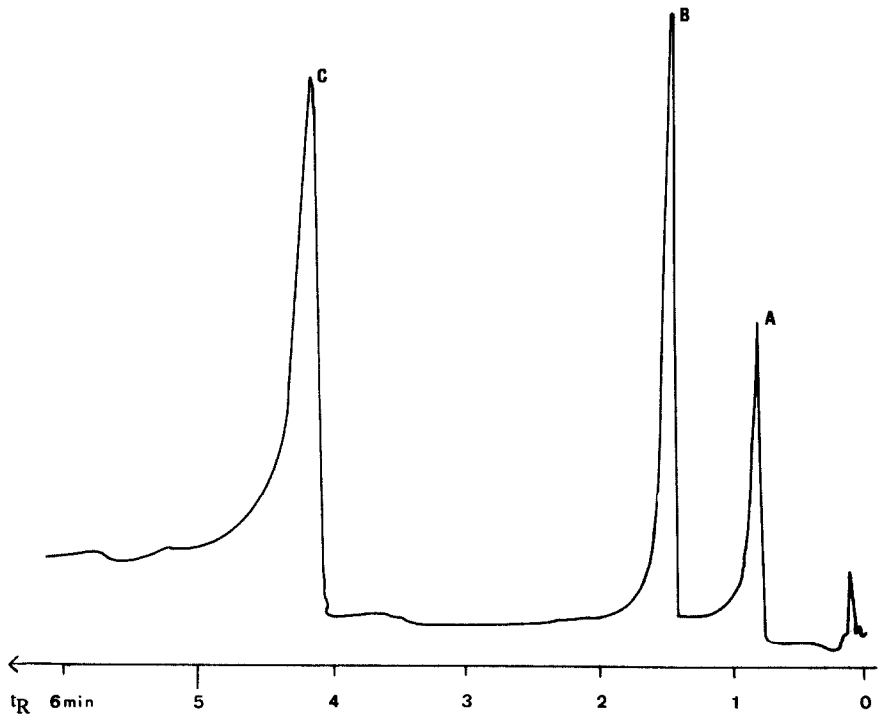

Fig. 4. Chromatogram (temperature programming) obtained with the GC–ECD system using an RSL-300 FSOT column. Peaks: A = MeHgCl; B = EtHgCl; C = PhHgCl.

sampler was used it seems that head space sampling into the FSOT column is more critical to avoid memory peaks than head space sampling into the packed column. This memory effect was dependent on the concentration of the standard: the memory peak was higher for a standard with a higher concentration. Despite this small memory effect, the reproducibility for the measurement of MeHgCl standard solutions on the capillary HS-GC–MIP system was very good. The relative standard deviation of the peak heights of six replicate measurements was typically 4%, which is slightly higher than that typically obtained with the packed column system (3%). The correlation coefficient of the linear regression for the calibration graph was 0.999 (seven concentrations, each concentration injected three times to give a total of 21 injections). The detection limit, expressed as the signal level corresponding to twice the standard deviation of the background signal, was 0.5 $\mu g\ l^{-1}$. The detection limit obtained with the packed column system using the MPD-850 was 0.8 $\mu g\ l^{-1}$, or 1.6 times higher. If the AAS-403 was used as the detector in the capillary system, it was possible to obtain a detection limit of about 0.25 $\mu g\ l^{-1}$.

In a final step, a real sample was analysed using the capillary column system. The mussel sample (*mytilus edulis*), was obtained from the Community Bureau of Reference for an intercomparison exercise on the determination of MeHg in biological tissues. Ten other laboratories also analysed this sample. It was analysed in this laboratory with both systems, the packed column and capillary HS-GC–MIP systems. Fig. 6 shows the calibration graph obtained with the capillary system using the standard additions method [29,30]. As can be seen, a correction for the memory effect is very important. Without correction, a value of $0.189 \pm 0.005\ \mu g\ g^{-1}$ MeHgCl (result $\pm$ S.D.) is found for MeHg in mussel tissue. With correction (the signal is the sum of the major MeHg peak and the small memory peak), a value of $0.170 \pm 0.011\ \mu g\ g^{-1}$ MeHgCl is found. Fig. 7 compares this result with that obtained with the packed column system and those obtained

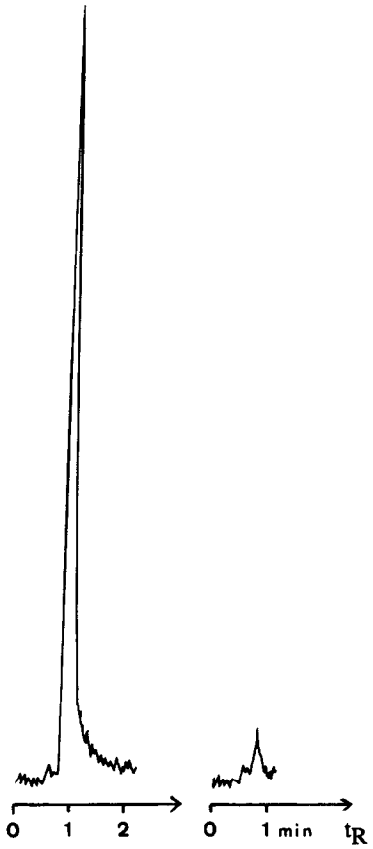

Fig. 5. Chromatogram (isothermal) obtained with the new HS-GC–MIP system using a Superox-FA FSOT column. The small peak is a typical memory peak obtained for this MeHg peak.

by the other laboratories participating in the intercalibration exercise.

In conclusion, the capillary column system yields only a limited success in terms of attaining a better sensitivity. With the Superox-FA column, a factor of 1.6 in the detection limit can be gained, compared with a packed column, but a factor 6 was obtained with a capillary column and the GC–ECD system. It should be noted that this factor 6 was partly due to an increased baseline stability for the capillary column. With the MIP detector, the difference in noise level for both columns was minimal.

It is also clear from this study that it is impossible to compare only the packed and the capillary columns when using the HS-GC–MIP system. The HS-GC and the GC–MIP interfaces have to be

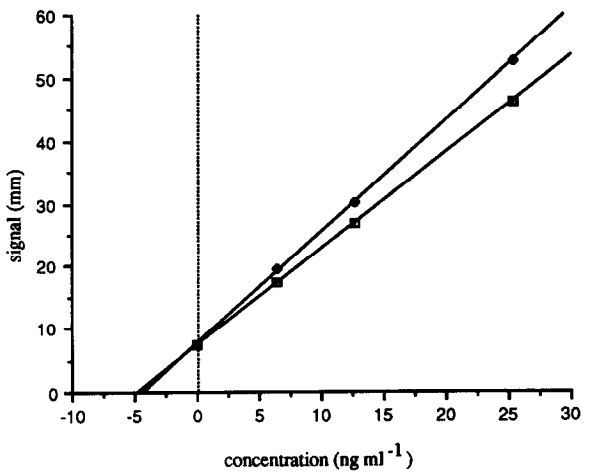

Fig. 6. Calibration graph obtained for the mussel sample using the HS-GC–MIP system with Superox-FA FSOT column. (⊡) Without correction for the memory effect; (◆) with correction. (⊡) $y = 7.28 + 1.53x$, $r^2 = 1.000$; (◆) $y = 7.60 + 1.78x$, $r^2 = 1.000$.

optimized for each specific column (*e.g.* the amount of sample which can be injected onto the capillary column is smaller than onto the packed column; the internal diameter of the interface tube from the capillary column to the plasma tube is smaller than with a packed column and the plasma tube itself has

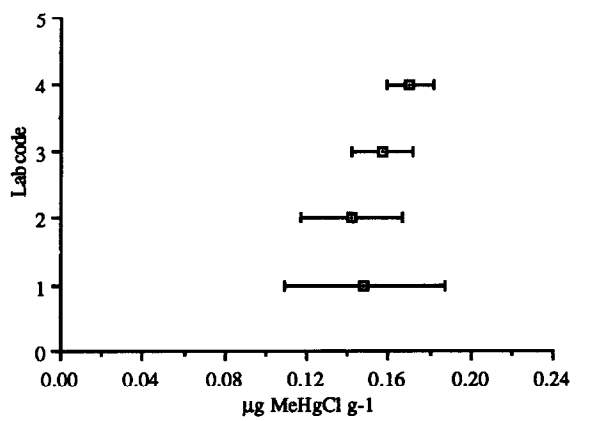

Fig. 7. Intercomparison of the results found for the mussel sample. Lab code 1, mean of all individual values ±S.D. reported by the ten different laboratories participating in the intercalibration exercise; lab code 2, mean of mean values ±S.D. reported by the same labs; lab code 3, result ±S.D. found by this laboratory using packed HS-GC–MIP; lab code 4, result ±S.D. found by this laboratory using capillary HS-GC–MIP.

a smaller internal diameter), so that more than the column parameters differ for the two systems.

The capillary column has some important disadvantages compared with the packed column: the capillary column has to be activated regularly and there is a limited memory effect. As packed columns are also cheaper and more easy to handle than capillary columns, it seems obvious to continue working with a packed column.

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