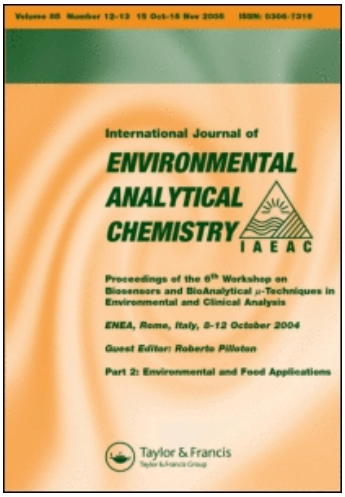

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A VERSATILE CAPILLARY GAS CHROMATOGRAPHY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER INTERFACE

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A versatile, inexpensive, easily made interface for capillary GC-ICPMS (HRGC-ICPMS) on line coupling has been constructed. The interface does not require any changes of the ICP, and can be done in less than a minute. Optimizing of the ICP-MS and the interface can be performed on-line under GC conditions. The capability of the hyphenated system are demonstrated by analyzing standards of non-polar organometallic compounds of P, As, Sn and Sb, as well as organotins in an environmental sediment sample.

KEY WORDS: ICP-MS, GC-ICP-MS, organometals, speciation, organotin partitioning.

INTRODUCTION

Because of the great differences in toxicity and physico-chemical properties between different chemical forms of elements, speciation analysis has become an inevitable part of elemental environmental chemistry[1,2]. The last decades have brought a rapidly increasing number of papers concerning speciation methodologies, but elemental speciation analyses are still one of the challenges of modern environmental analytical chemistry.

This remains especially true when analyzing at ultra trace levels for organometallic species in complex environmental samples (e.g. sediments). Either one has to go through some extensive clean-up procedures, to isolate to some extent the substances of interest, or one has to use a selective detector, in both cases combined with some sort of chromatographic system.

Partly because of the tradition in elemental laboratories for extensive series of samples and partly because the organometals display a great variation in critical physico-chemical parameters like volatility and stability, most efforts have been made in the direction of using selective detectors, mainly different AAS[2–6] and MS[6–8] systems.

MS systems offer true real time multielement and—isotope detection, and thereby offer excellent possibilities for quick screening of samples for various organometallic compounds with a high degree of precision. Very often analyses of complex samples (e.g. sediments) with GC-MS give high background levels, calling for extensive clean-up

procedures. This problem may to some extent be overcome by using ICP-MS as a chromatographic detector.

This is clearly demonstrated by the coupling of ICP-MS with HPLC[9] for analyzing of primarily polar organometallic compounds, in food[10], drugs[11], water[12] and biota[13].

For non-polar organometallic compounds, GC-ICP-MS correspondingly seems to be an excellent detector, as pointed out already in 1986–87[14,15], but all the same, only few papers have dealt with this hyphenation since then[16–22]. Most of them deal with coupling of low-resolution GC (LRGC) (with packed columns) and ICP-MS. This might be adequate for separation of hydrides or even methylated species, but looking for heavier substituted species raises the number of species in question, and thus requires higher resolving power than achievable by packed columns. Only a few groups[16,21] to our knowledge have demonstrated such a hyphenation. But these couplings require, like the majority of the LRGC ones, modifications of the torch box or/and injector geometry, thus losing something in flexibility. Facing the needs for speciation of some aromatic organometallic compounds at ultratrace levels consequently led us to construct our own HRGC-ICP-MS interface. We required a versatile, low-cost, easily made construction, that could be coupled to the ICP-MS in a short time without any changes in the construction, allowing a rapid change to other ICP-MS configurations.

The major problems connected with interfacing a capillary GC with the ICP-MS are:

– to avoid condensation of the components before the ICP.

– to ensure penetration of the analytes into the plasma.

– to position and fasten the analytical column end to avoid instrumental noise from vibrations.

– to prevent formation of an arc between the (metal) injector tube and the plasma RF-coil.

– to achieve the possibility to optimize the system.

EXPERIMENTAL

Instrumentation

The instruments used were a PE-Sciex ELAN 5000 ICP-MS (Perkin-Elmer), a home modified PE-AutoSystem Gas Chromatograph (Perkin-Elmer) and a home built transferline and injector unit. The analytical columns were a 22 m DB-5, 0.25 mm × 0.25 μm, J&W Scientific (column 1), and a 14 m DB-5, 0.25 mm × 0.10 μm, J&W Scientific (column 2). As retention gap, a 1 m deactivated 0.53 mm column was used. As interface column a 1.5 m deactivated 0.25 mm column was used.

Chemicals

For direct analysis. Me_4Sn 99.5% (Johnson Matthey), Et_4Sn (Johnson Matthey), Bu_4Sn 98% (Fluka), Ph_3Sb 99% (Aldrich), Ph_3As > 98% (Merck), Ph_3AsO > 98% (Merck), Ph_3P 99% (Johnson Matthey), CH_2Cl_2 HPLC-GDG (Rathburn). For ethylation: $BuSnCl_3$ (Ventron), Bu_2SnCl_2 97% (Fluka), Bu_3SnCl > 97% (Fluka), $NaEt_4B$ (Merck), Na-acetat Suprapur® (Merck), $NaOH{\cdot}H_2O$ Suprapur® (Merck), 30% HCl Suprapur® (Merck), Na_2SO_4 p.a. (Merck), Methanol LiChrosolv® (Merck), n-hexan HPLC-grade (Rathburn),

Millipore water 18 MΩ/cm, Silica gel 60 for column chromatography 0.063–0.200 mm (Merck).

For optimizing the GC-ICP-MS system. 1 µl/L arsine in argon (Messer Griesheim).

The HRGC-ICP-MS interface

The developed interface system is shown in Figure 1, and the numbers in brackets in the text refers to the numbers on this figure.

The injector unit (injector port [9] and—tube [6]) were made of stainless steel. Is was dimensioned very closely to the original teflon/ceramic unit, to ensure easy handling of the system. The inner diameter of the injector tube was 4 mm. The injector unit was fastened to the end of the transferline with three screws.

From the GC-oven the analytical and optimization columns [3] were led through a stainless steel capillary tube [5] (2 mm out. d., 1 mm i.d.) inside a thermostated transferline (20–350°C) to the injector. The capillary tube ended appr. 2 cm from the tip of the injector tube, and was fastened by two small screws [4]. The columns ended appr. 5 mm outside the steel capillary.

The nebulizer gas stream of the traditional ICP-MS was used as penetration gas, and by a two positioning valve placed at the outlet from the nebulizer gas mass flow controller led into a 7 m 3.3 mm i.d. copper tube [13] forming a 6 m coil in the GC-oven and via the heated transfer line ending in the injector port. The connection between the torch box and the injector body was established through the original injector screw [12] at the inlet to the box, which further served to electrically ground the unit. To facilitate the coupling of the HRGC and the ICP-MS, the GC was placed on a guide way sledge on a separate table.

Optimizating of the system

To allow optimization of the interface and the ICP-MS when coupled to the HRGC an uncoated capillary column was led into the GC-oven and along with the analytical column through the transfer line and into the torch. Through this, a continuous stream of a volatile elemental species in a appropriate concentration could be led through the system, and used to optimize the different gas flows, RF-power etc. With the ICP-MS operating in the Graphic Peak Hop (SIM) mode.

Testing of the HRGC-ICP-MS system

The performance of the HRGC-ICP-MS system was evaluated by analyzing different non-polar species of phosphorus, arsenic, tin and antimony.

The ICP-MS was operated in the Graphic Peak Hop (SIM) mode with settings as shown in Table 1. The injections were 1 µl on-column, interface temperature 270°C and carrier gas flow 1 ml helium per min. Further chromatographic parameters are listed on the chromatograms.

Analysis of standard solutions. All solutions were prepared in dichloromethan. The following standards were analyzed: Tetramethyltin and tetrabutyltin in concentrations of

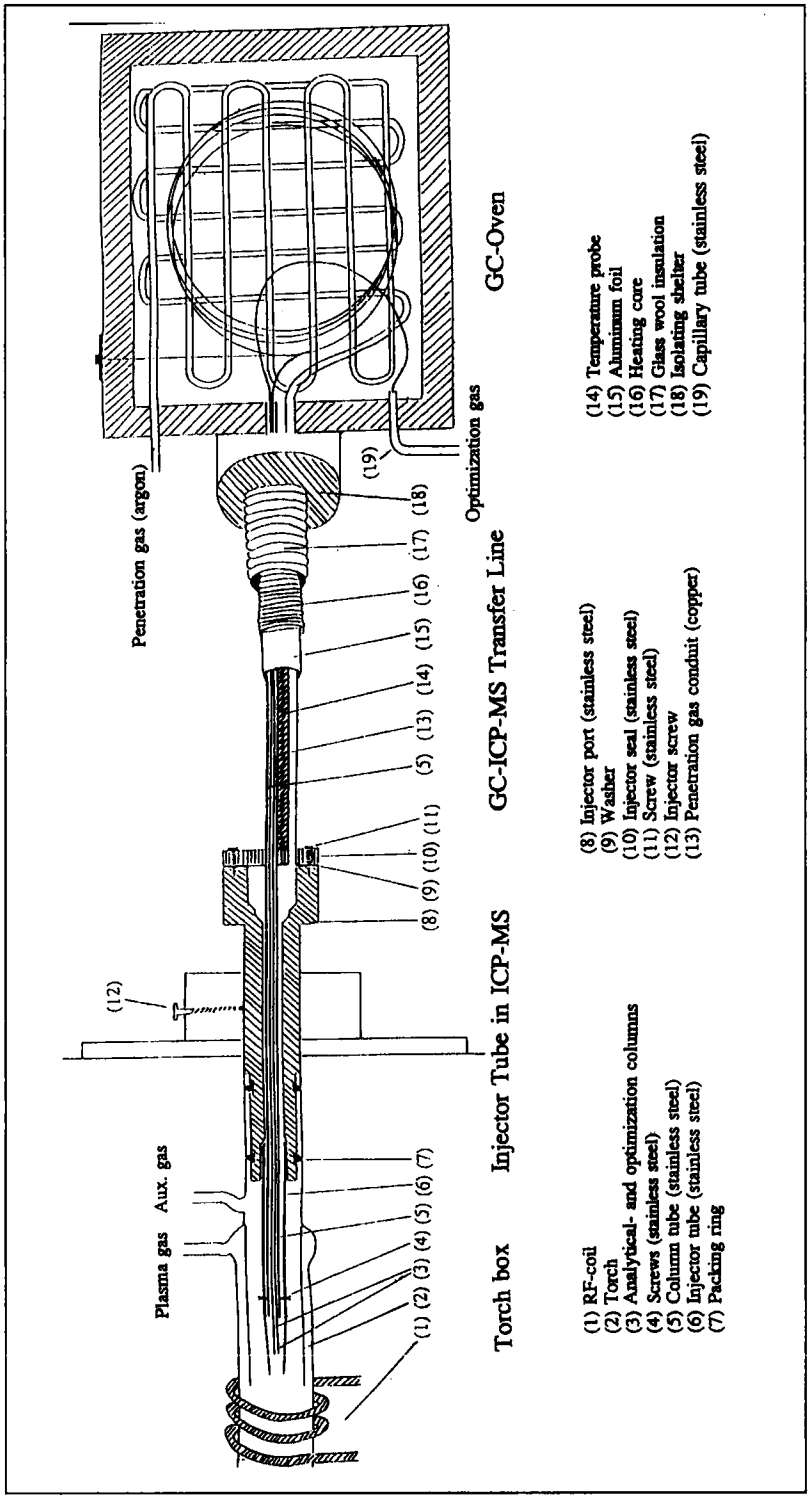

Figure 1 Diagram of the capillary GC-ICP-MS interfacing.

Table 1 Typical HRGC-ICP-MS parameter settings.

RF-power	1200 W
Plasma argon flow rate	15 dm^3 min^{-1}
Auxilary argon flow rate	1.1 dm^3 min^{-1}
Penetration argon flow rate	1.6 dm^3 min^{-1}
Sweeps per replicate	1
Dwell time per mass	200 ms

0.1, 0.25, 0.5, 1.0, 10 and 100 ng/L; a mixture of tetramethyltin, tetraethyltin and tetrabutyltin at 1.0 ppb each. Signals were aquired at m/z 75 (to get a well defined solvent front from argon chloride, m/z 118 and m/z 120 both tin and m/z 197 gold (to give the instrument a noise level).

Further a mixture of triphenylarsine and triphenylstibine at 50 ppb each and a mixture of triphenylarsinoxide and triphenylphosphine at 500 ng/L each was analyzed, with signal aquisition at m/z 31 (Phosphor), m/z 75 (Arsenic), m/z 120 (tin) and m/z 121 (Antimony).

Analysis of Bu_xSn in sediment. The marine sediment was fractioned in a solid and pore water phase[23], which was alkylated directly with sodium tetraethylborate[24,25].

From a toplayer (0–5 cm) sediment sample from a marina in Jutland, Denmark (Aarhus) porewater was isolated by centrifuging 15 min at 5000 rpm at 4°C. 10 ml of the porewater was buffered to pH 5 with 15% sodium acetate and extracted 3 times with 10 ml n-hexane and 0.25 ml 10% sodium tetraethylborate. The hexane phase was dried with sodium sulphate prior to injection.

To 2.0 g sediment was added 5 g of crushed ice and 1.0 ml HCl. The mixture was mixed every 10 minutes for 1 hour, pH adjusted to 5 with NaOH and 15% sodium acetate, and extracted as the porewater fraction. The extract was purified with 2 g of activated silica gel.

For identification of the ethylated tin species, a standard solution of inorganic tin, monobutyltin, dibutyltin and tributyltin was ethylated as described for the porewater fraction.

RESULTS AND DISCUSSION

The HRGC-ICP-MS interface

Because of chemical resistance, mechanical robustness paired with good workability and poor heat transfer capacity, stainless steel was used to the injector unit and the column capillary tube. The poor heat capacity was a necessity because the overall concept of the system did not allow any external heating of the injector part enclosed in the torch box. The mechanical properties allowed an easy development of a precise geometry and made the system robust for coupling/un-coupling and positioning in connection with optimization. The two small screws in the injector tube allowed the positioning of the columns towards the centre of the plasma and futher prevented inherent natural oscillation in the capillary columns caused by the vibrations from e.g. the roughing pumps. A possible arcing caused by the metallic injector tube was prevented by grounding the injector unit to the torch box by the injector screw.

Penetration of the analytes into the plasma is a problem because of the low flow (1–2 ml/min) coming from the capillary column, and the slight overpressure in the plasma. This was overcome by using a penetration gas forming a gas shield around the column effluent, and adding sufficient flow to secure a proper penetration. The penetration gas was heated by passing through the copper coil in the GC-oven and through the transfer line to prevent cooling of the columns, the injector and the analytes.

Although no oxygen was added to plasma gases, no formation of carbon deposits at the skimmer cone during 200 analysis was observed, as reported by some LRGC-ICP-MS studies.[19]

Coupling the GC to the ICP-MS was performed by loosening the injector screw at the torch box, drawing out the normal injector, sliding the GC in position, leading the GC injector unit into the torch, fasting the injector screw and switching the valve at the nebulizer gas outlet. Coupling the instruments takes under 1 minute.

Optimizating of the system

The optimization column system made it possible to optimize the flows of penetration gas and the auxiliary gas, the RF-effect, alignment of the instrument, the lens settings and the positioning of the analytical column on-line with the GC interface in working position.

Figure 2 shows the variation in signal intensity with respect to the flow of the penetration gas, auxiliary gas and RF-effect using commercially avaiable 1 µL/L arsine in argon as optimization gas. As for normal nebulization ICP-MS, the flow of penetration gas (nebulization gas) is a very important factor. The main difference being that the optimum for GC-ICP-MS is on a higher level, between 1.3–1.6 L/min. The same behavior was seen with respect to the flow of the auxilliary gas, the flow/intensity dependence being more marked than by normal ICP-MS. The dependency between intensity and RF power is more complex, showing an optimum at appr. 1050–1250 W, and, very unusual for conventional ICP-MS, the existence of a local minimum. A set of typical aquisition parameters are shown in Table 1.

Figure 3 show the signal of arsine as a function of the temperature in the GC-oven. It can be seen that arsine is thermally labile and thus it is important to optimize the system at a constant temperature well below 200°C.

Testing of the HRGC-ICP-MS system

Figure 4 shows a chromatogram of tetramethyltin, tetraethyltin, and tetrabutyltin at 1 ng/g each, elucidating the capability of the system. The tin species produced sharp, well separated symmetrical peaks. From a series of six different concentrations (0.1, 0.25, 0.5, 1.0, 10 and 100 ng/g), the linearity of the system was demonstrated over 4 orders of magnitude (Figure 5). The limits of detection for the different species were estimated from the chromatograms as twice the noise level. The limits of detection for tetramethyltin are 0.1 pg, for tetraethyltin 0.5 pg and for tetrabutyltin 1 pg, injected into the column.

One focus of the study was to develop an analytical method for aromatic organoarsenic compounds. Arsenic being mono-isotopic challenges the multielement capability of the ICP-MS in order to find a suitable compound for use as an internal standard.

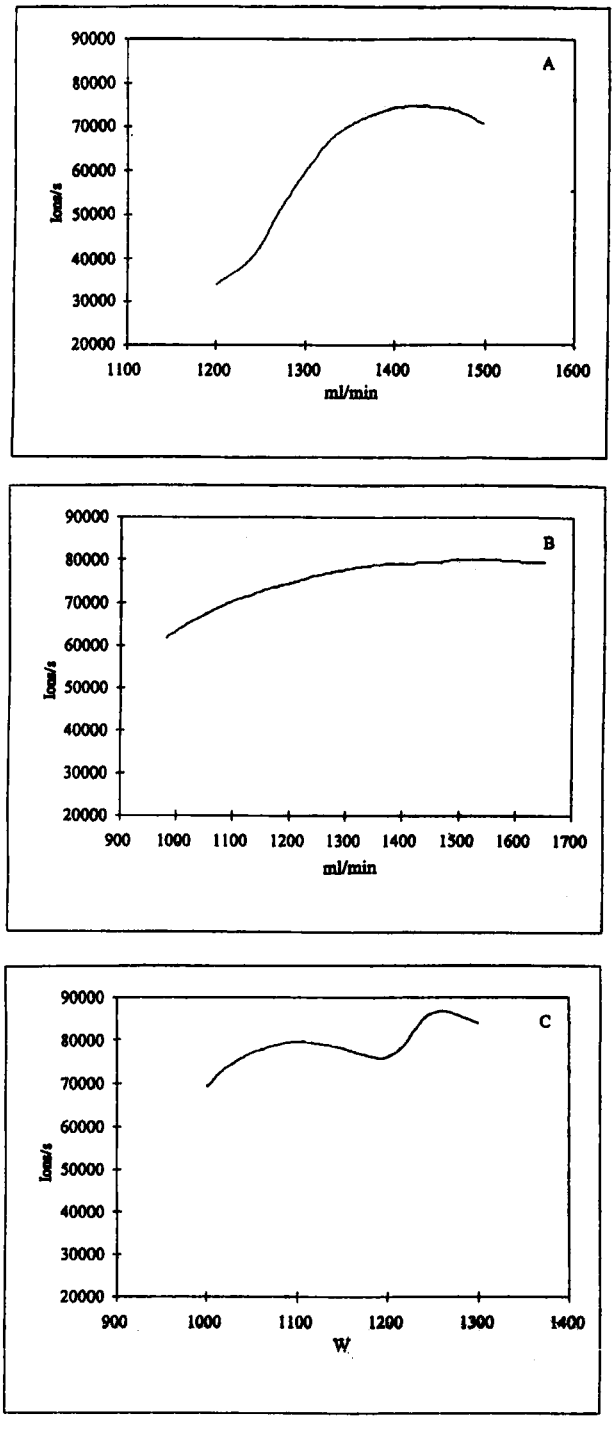

Figure 2 Optimizing with arsine gas at 1 ml/min. m/z 75 (As). Intensities as a function of A) Penetration gas; B) Auxilliary gas; C) RF–power.

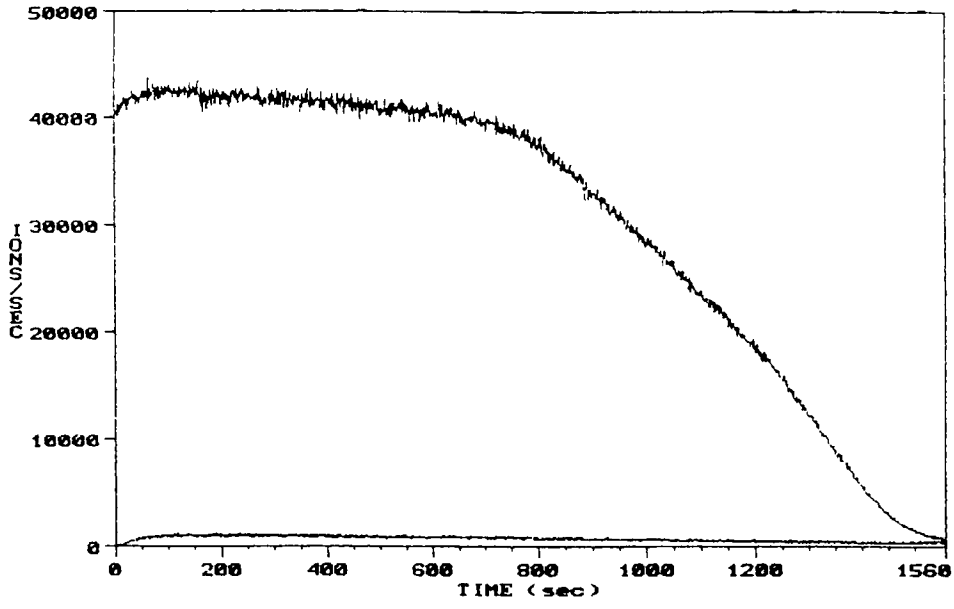

Figure 3 Intensity of arsin gas (m/z 75) as function of GC temperature. Start temperature = 150°C, gradient 5°C/min, temperature at 10 minutes is 200°C.

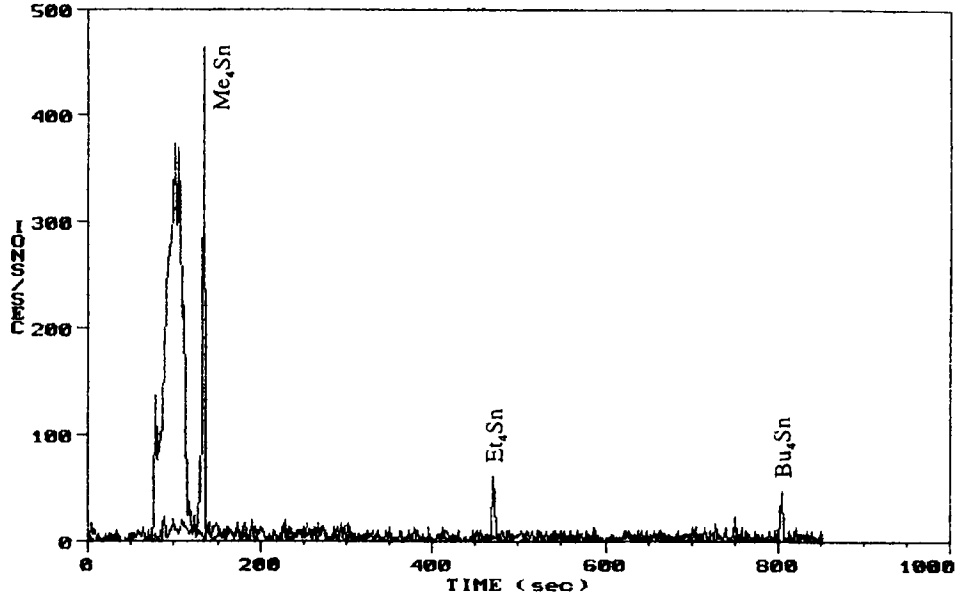

Figure 4 Chromatogram of tetramethyltin, tetraethyltin and tetrabutyltin. Flow: 1 ml/min. Temperature program: 32°C (1 min), 5°C/min 45°C, 15°C/min 270°C (15 min). Column 1.

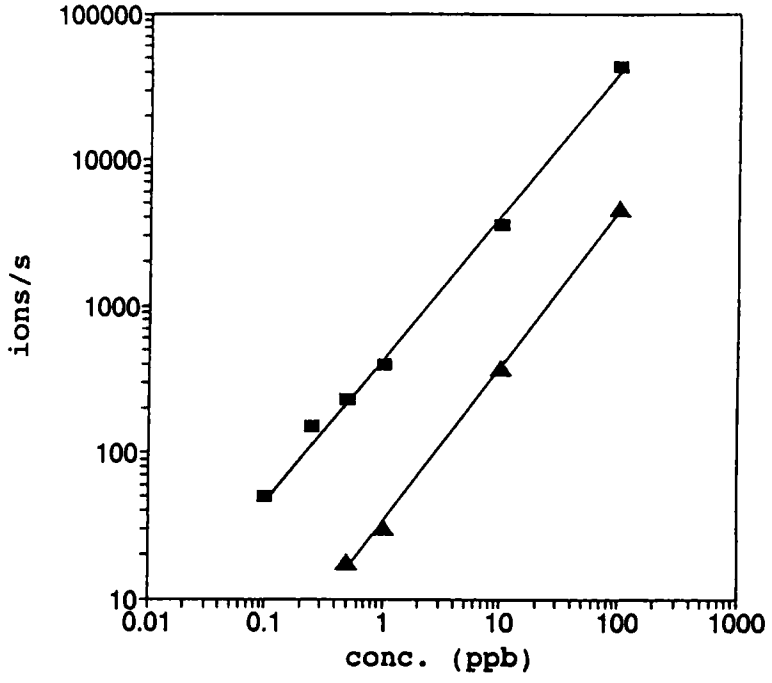

Figure 5 Intensity of m/z 120 (Sn) for different concentrations of tetramethyltin (–■–) and tetrabutyltin (–▲–).

Figure 6 shows a chromatogram of triphenylphosphine and triphenylarsineoxide. As can be seen from the peak shape, triphenylphosphine is not a candidate as As internal standard, although, with the difficulties connected with analyzing organophosphorous compounds, it looks promising. The amounts were 500 pg injected.

Figure 7 shows triphenylarsine and triphenylstibine in amounts of 50 pg injected. It seems that antimony, as in the case with HPLC-ICP-MS analysis of polar arsenicals[13], might be a useful internal standard for the analysis of non-polar arsenicals.

Figure 8 shows partitioning of monobutyltin (MBT), dimethyltin (DMT) and tributyltin (TBT) between pore water and the solid fraction of a relatively unpolluted marina sediment from the east-coast of Jutland, Denmark. A ban on the use of TBT for vessels smaller than 25 m has been in effect for several years in Denmark, but still TBT and the degradation products, DBT and MBT, can be found in sediments and pore waters. The capability of analyzing pore waters will help to elucidate the different behavior of the butyltin species with respect to bioavaibility for different sediment organisms[26]. Of special interest is the occurence of tetraethyltin in the ethylated pore water fraction. This originate from inorganic Sn^{4+}. As pointed out[6] it is only a part of the sediment Sn^{4+}—pool, which seems to be available for direct ethylation. Our study shows that the available part actually is restricted to the water soluble fraction and that the Sn^{4+} fraction bound to the solid phase is essentially not avaiable for ethylation.

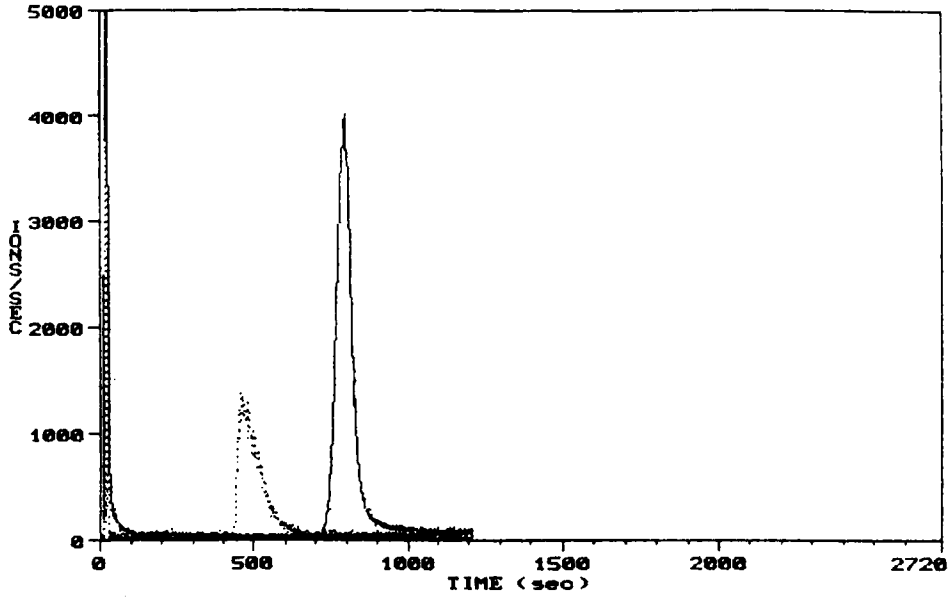

Figure 6 Chromatogram of triphenylphosphine (.....) and triphenylarsineoxide (___). Flow: 2 ml/min. Temperature program: 35°C (1 min), 2 °C/min 45°C, 40°C/min 300°C (10 min). Column 2.

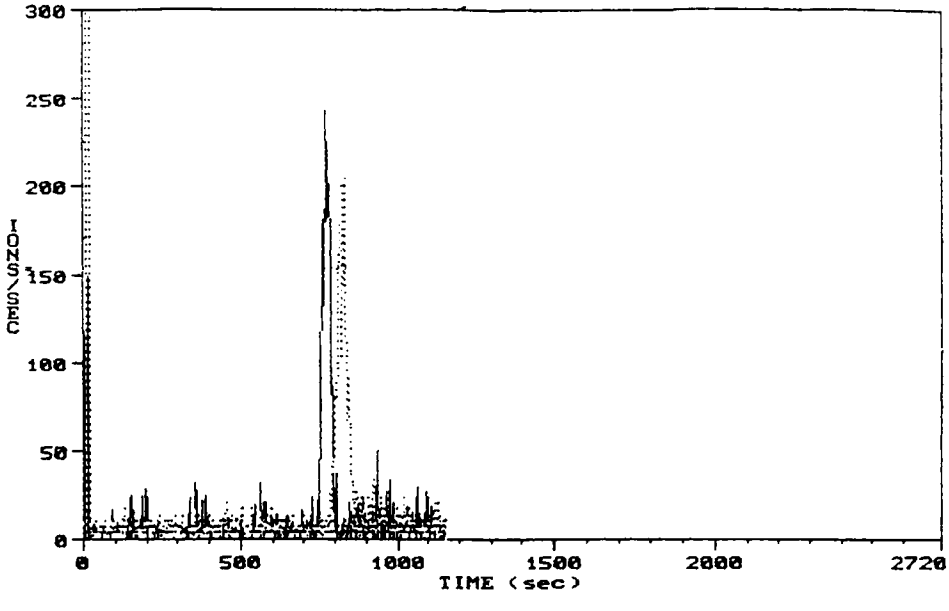

Figure 7 Chromatogram of triphenylarsine (___) and triphenylstibine (.....). Flow: 2 ml/min. Temperature program: 35°C (1 min), 2°C/min 45°C, 30°C/min 300°C (10 min). Column 2.

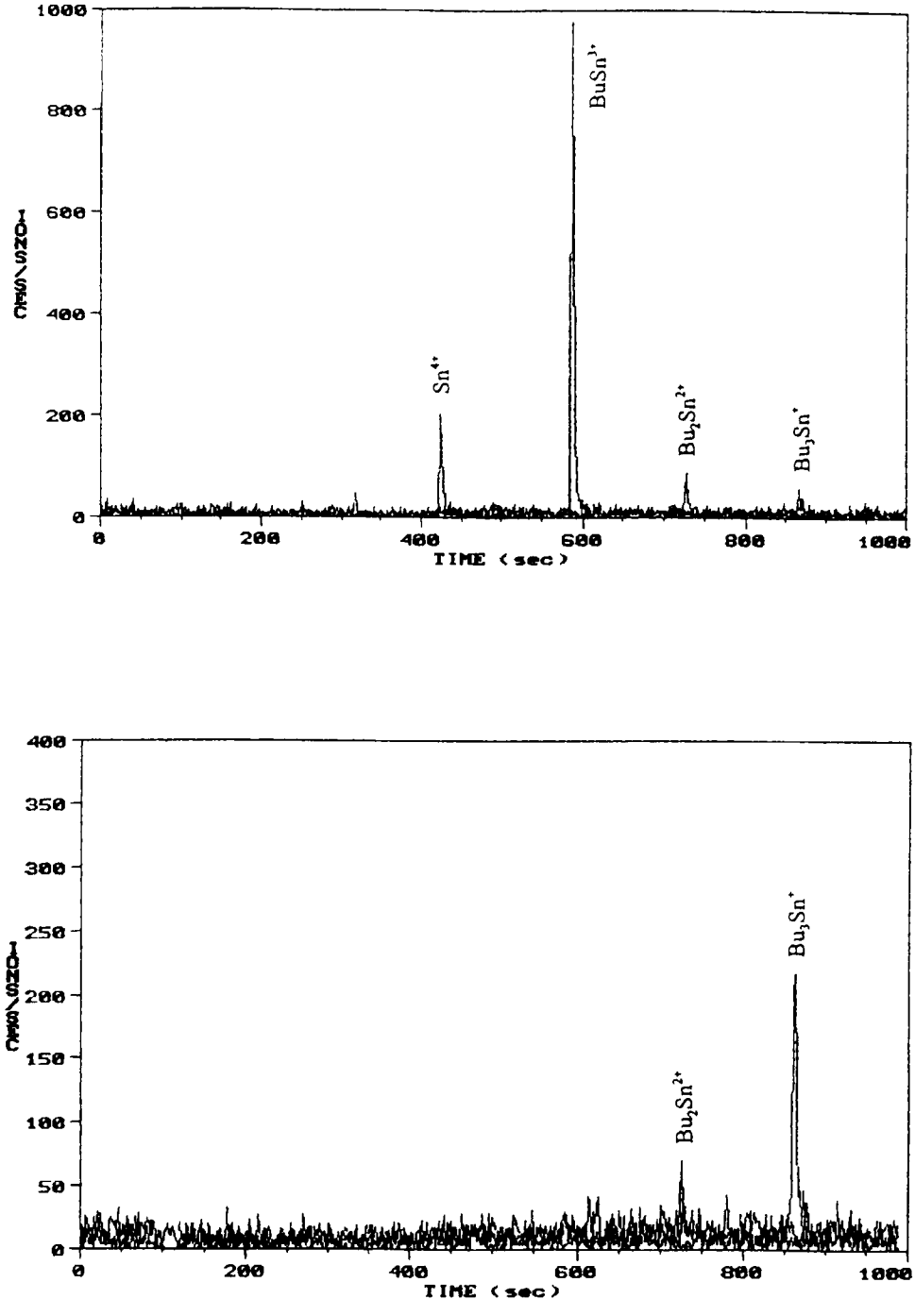

Figure 8 Speciation of butyltins in sediment. Top) Pore water, Below) Solid fraction. Flow: 1 ml/min. Temperature program: 55°C (1 min), 5°C/min 70°C, 10°C/min 270°C (10 min). Column 1.

CONCLUSION

The HRGC-ICP-MS interface has proven to be versatile, low-cost, robust and easily made. It could be coupled to the ICP-MS in less than a minute without demanding any changes to the ICP-MS. The optimizing of the hyphenation can be performed on-line. The system is capable of analyzing complex environmental samples.

Within a few minutes the ICP-MS can be changed from a most versatile multielement detector for normal total analysis of a variety of elements to a very sensitive and robust speciation analytical instrument, covering a broad range of both polar and non-polar element species of environmental concern.

The previous results shown here point out achievable limits of detection for the elements investigated in the low to mid pg/L range, following normal extraction and concentration procedures. The improvements compared with HPLC-ICP-MS are a result of nearly 100% (against 2–4%) of the analyte reaching the plasma, and that no plasma power is used for desolvation.

Compared to LRGC-ICP-MS the chromatographic power of resolution is more adequate for environmental purposes. It might be possible that the low solvent load does not require oxygen addition.

As several of the organometallic compounds show effects in the low ng/L area, the mentioned limits of detection are not simply questions of interest for analytical champions, but indeed, especially in combination with the development of methods for direct ethylation of polar species, points out a interesting future for on-line coupling of HRGC with ICP-MS.

Acknowledgements

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