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LECTURE

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Capillary gas chromatography-ICP mass spectrometry: a powerful hyphenated technique for the determination of organometallic compounds

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Abstract The development and improvement of a gas chromatography inductively coupled plasma mass spectrometry system, GC-ICP-MS, is described. The GC and ICP-MS are coupled with a heated stainless steel transfer line. Xe, present in the GC carrier gas, is used to facilitate the nebuliser gas flow rate setting and the positioning of the torch. Alkyltin compounds are separated by GC using a 30 m capillary column within 9 min. The necessity of applying double internal standardisation (use of Bu_3PeSn and Xe gas as internal standards) is shown. The repeatabilities at 50 μg/l concentration for both retention time and peak are better than 0.25% and 5%, respectively. The detection limits for alkyltin compounds are better than those of existing methods and range between 15 and 35 fg Sn. Finally, GC-ICP-MS is applied to the determination of mono-, di- and tributyltin in some harbour waters, after extraction and Grignard derivation with PrMgCl. Concentrations between 1 and 20 ng/l are found.

Introduction

As toxicity of metals in the environment is strongly dependent on the chemical form in which they appear [1], separation has become an important topic of present research. Of all hyphenated techniques developed for the metal speciation, GC-AAS, GC-MIP-AES, HPLC-AAS and HPLC-AES [2–4] are most commonly used today. During the last decade, ICP-MS has been proved to be a highly sensitive technique for the determination of trace and ultra-trace amounts of metals in various samples. Therefore, the coupling of capillary gas chromatography, known for its high resolving power of numerous organic compounds in complex samples, with the ICP mass spectrometer opens new perspectives for the accurate and precise determination of several organometallic compounds [5–12].

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Experimental

GC and ICP-MS instrument. Element specific detection was performed with a Perkin Elmer Sciex Elan 5000 ICP mass spectrometer coupled with a Perkin Elmer Autosystem gas chromatograph. The operating conditions are summarised in Table 1. The raw data were further processed with the additional Chromafile MS software (Perkin Elmer, Lab Control GmbH, Köln, Germany).

GC-ICP-MS transfer line. The gas chromatograph was connected to the Elan 5000 ICP-MS via a home made transfer line (Fig. 1). A detailed description of the coupling and the transfer line was given before [13]. Since then, our home-made transfer line has been further improved. Although condensation of the organotin compounds was nearly completely reduced for 'clean' standard solutions [13], it was found that subsequent analysis of environmental samples gave rise to severe peak tailing after only few injections. This is due to condensation of high boiling species, co-extracted from the sample matrix during sample preparation, in the capillary part in the torch. Therefore, the section of the transfer line, to be inserted in the torch, was redesigned, so that heating in the torch became possible. This is shown in Fig. 2. A 15 cm section of the transfer line was lengthwise cut in two halves. These two halves were electrically isolated over the entire length with polyimide isolation tape (RS Components Ltd., Corby, UK). At the end of the transfer line, the two halves were electrically contacted. Finally, a thin polyimide layer was wrapped around the two transfer line halves to obtain the original tube shape. By applying an alternating voltage over these two halves, the transfer line can be equably heated while positioned in the torch.

Reagents and standards. Butyltripropyltin ($BuPr_3Sn$), dibutyldipropyltin (Bu_2Pr_2Sn), tributylpropyltin (Bu_3PrSn) and tributylpentyltin (Bu_3PeSn) were prepared by a Grignard reaction on the

Table 1 Instrumental parameters for GC-ICP-MS

Gas Chromatograph	Perkin Elmer Autosystem
Column:	RSL-150; 30 m; 0.25 mm i.d.; $d_f = 0.25$ µm
Injection technique:	splitless
Injection volume:	1 µl
Injection temperature:	240 °C
Temperature programme:	80 °C (1 min) – 40 °C/min – 140 °C (1 min) – 20 °C/min – 230 °C (0.5 min)
Carrier gas/inlet pressure:	H_2/30 psi
Transfer line	home-made transfer line; heated stainless steel tube
Transfer line temperature:	250 °C
ICP-MS	Perkin Elmer Sciex Elan 5000
RF power:	1300 W
Sampling depth:	10 mm
Carrier gas flow rate:	1.10–1.30 l/min
Auxiliary gas flow rate:	1.20 l/min
Plasma gas flow rate:	15 l/min
Sampling cone:	Ni; 1 mm aperture diameter
Skimmer cone:	Ni; 0.75 mm aperture diameter
Dwell time:	50 ms; 10 ms (^{126}Xe internal standard)
Sweeps/replicate:	1
Data analysis:	Chromafile MS, Perkin Elmer

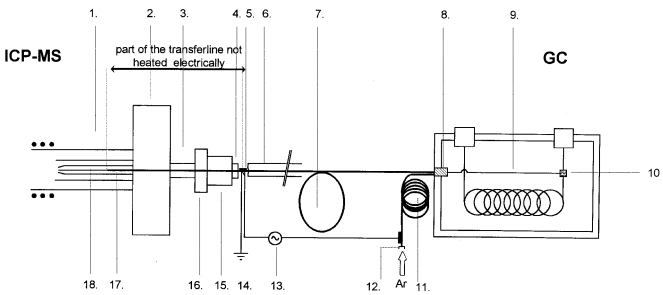

Fig. 1 Scheme of coupling of the GC with the ICP-MS instrument via a home-made transfer line. *1*, torch; *2*, torch box; *3*, injector supply; *4*, teflon adapter; *5*, electrical contact point; *6*, thermal isolation:(glass wool + fiber wrapped into aluminum foil); *7*, curled part of the transfer line:transfer line becomes slightly adjustable in length; *8*, home-made T-joint, integrated in the GC oven wall; *9*, transfer capillary; *10*, effluent splitter; *11*, Ar gas heating coil (stainless steel, approx. 2.5 m); *12*, female Swagelok adapter; *13*, variable AC supply; *14*, earthing; *15*, teflon coupling piece; *16*, attaching screw to torch; *17*, stainless steel transfer tube; *18*, transfer capillary

appropriate organotin salts [14–15], $BuSnCl_3$ (95% purity, Sigma-Aldrich, Bornem, Belgium), Bu_2SnCl_2 (97% purity, Sigma-Aldrich) and Bu_3SnCl (96% purity, Sigma-Aldrich). The salts were dissolved in iso-octane (p.a. UCB, Leuven, Belgium) to react with propyl magnesium chloride (PrMgCl) (2 mol/l in diethylether, Sigma-Aldrich) and pentyl magnesium bromide (PeMgBr) (2 mol/l in diethylether, Sigma-Aldrich). Tetrapopyltin (Pr_4Sn) was prepared by a Grignard reaction of PrMgBr with anhydrous $SnCl_4$ (1 mol/l $SnCl_4$ dissolved in n-heptane, Sigma-Aldrich). The purity of the alkylated organotin salts was checked by GC-ICP-MS. The organotin compounds were further diluted to ppb level with iso-octane.

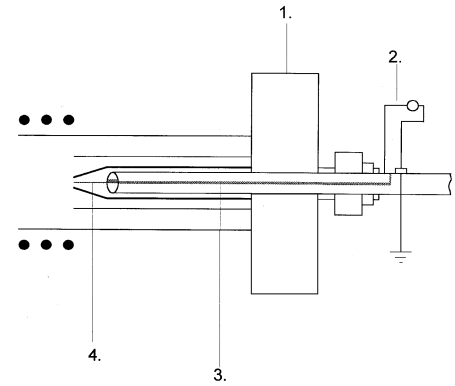

Fig. 2 Detail of part of transfer line heated in torch. *1*, torch box; *2*, variable AC supply; *3*, polyimide tape:electrical insulation between two transfer line halves; *4*, transfer capillary

Internal standards. In order to correct for volume errors due to sample evaporation and variation of the sample amount injected, Bu_3PeSn was added to all standard and sample solutions. Instrumental instabilities of the ICP-MS during analysis were corrected by measuring simultaneously the ^{126}Xe nuclide of Xe, present in the GC carrier gas (1% Xe in H_2, L'air liquide Belgium, Liège, Belgium).

Recovery experiments. The efficiency of the extraction of alkyltin compounds and the subsequent Grignard derivation was investigated by recovery experiments [14, 16]. 500 ml Millipore Milli Q water was spiked with $BuSnCl_3$, Bu_2SnCl_2 and Bu_3SnCl in a separating funnel. The concentration of the alkyltin salts in the water was around 50 ng/l level. 2 ml of an aqueous 1 mol/l sodium diethyl dithiocarbamate solution (p.a. Merck, Darmstadt, Germany) was added after pH adjustment with 200 ml Na_2HPO_4/citric acid buffer (p.a. UCB, Leuven, Belgium) to pH 5. Thereupon, 10 ml of n-pentane (p.a., UCB, Leuven, Belgium) was added and the mixture was manually extracted during 5 min. The liquid phases were allowed to separate. The pentane phase was collected in a 50 ml Erlenmeyer flask, and the aqueous phase was extracted again with a fresh portion of 10 ml pentane. The combined pentane phases were evaporated to dryness with a rotary evaporator at 25 °C. The residue was redissolved in 500 µl iso-octane, which contains Bu_3PeSn as internal standard, and next transferred into a test tube. Thereafter, 1 ml PrMgCl was added. The mixture was shaken carefully and allowed to stand. After a reaction time of 10 min, the excess of Grignard reagent was destroyed with 5 ml of 10% w/v NH_4Cl (p.a., UCB, Leuven, Belgium). The iso-octane layer was washed successively with another 5 ml of 10% w/v NH_4Cl and 5 ml 0.5 mol/l H_2SO_4 (subboiled). The rinsed organic layer, about 500 µl was finally transferred into a conical vial and stored at 4 °C until analysis.

Sample preparation. As an application, GC-ICP-MS was used for the determination of alkyltin compounds in harbour waters. Water samples were taken from different Belgian harbours. The samples were collected in polyethylene bottles. Concentrated HCl was added to adjust the pH to 2. The samples were stored in the dark at 4 °C. 500 ml water was sampled and transferred into a separating funnel. Sodium diethyl dithiocarbamate was added, the sample extracted and further handled as described under section 'recovery experiments'.

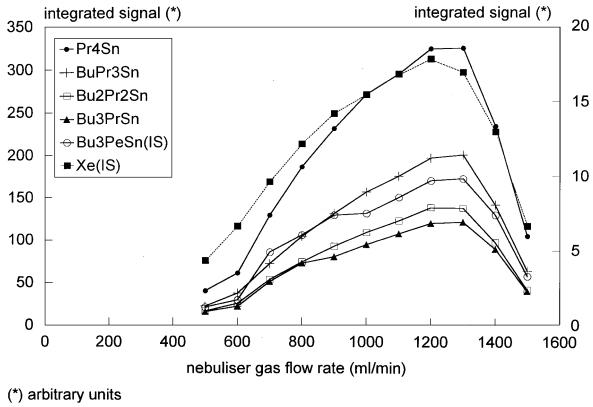

Fig. 3 Nebuliser gas flow curve for an organotin mixture and Xe measured at different nebuliser gas flow rates

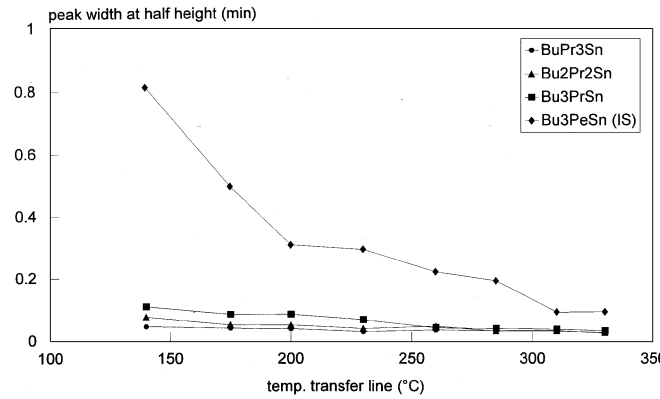

Fig. 4 Influence of the tranfer line temperature on the peak shape

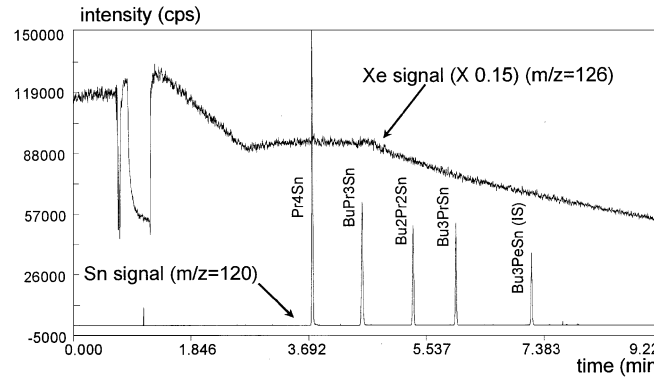

Fig. 5 Chromatogram of an alkyltin mixture recorded with the ICP-MS coupled to the GC with the custom made transfer line. Chromatographic conditions:see table 1; Pr_4Sn 110.1, $BuPr_3Sn$ 43.6, Bu_2Pr_2Sn 43.6, Bu_3PrSn 41.1 and Bu_3PeSn 37.5 µg/l Sn. Sn measured at m/z = 120; continuous Xe signal measured at m/z = 126

Results and discussion

Optimisation of the nebuliser gas flow rate and the transfer line temperature

Besides an equably heated connection between the GC and the ICP-MS, a correct positioning of the transfer line in the injector tube is essential and the nebuliser gas flow rate must be adjusted for optimal sensitivity. Therefore, Xe, present in the GC carrier gas, was used to optimise the nebuliser gas flow rate and the torch position. In Fig. 3, the integrated signal intensities of the analysed organotin compounds, measured at m/z = 120, as well as the ^{126}Xe signal intensity, are plotted vs different nebuliser gas flow rates. The shown flow curves were recorded at a power setting of 1300 W. It is clear that all compounds have a maximum around 1200 ml/min. Also the signal intensity of ^{126}Xe shows a maximal signal intensity at the same nebuliser gas flow rate. However, this optimal flow rate can shift towards higher or lower values, depending on the position of the capillary in the torch. From Fig. 3, it can be concluded that Xe can be used to optimise the nebuliser gas flow rate very quickly without doing successive, time consuming GC analyses at different flow rate settings.

Figure 4 shows the effect of the transfer line temperature on the peak shape of the analysed alkyltin compounds. The peak width at half height is plotted vs. the transfer line temperature. Although the peak shape of $BuPr_3Sn$, Bu_2Pr_2Sn and Bu_3PrSn are only slightly affected by the transfer line temperature, it is obvious that Bu_3PeSn shows considerable peak broadening at temperatures below 200 °C. 250 °C was chosen as optimal temperature, since at higher temperatures, the transfer capillary deteriorates more rapidly due to decomposition of the deactivating agent on the capillary surface.

Internal standardisation and reproducibility

As already mentioned above, Bu_3PeSn was added to all standards and samples to correct for solvent evaporation and irreproducibility of manual injections. Nevertheless, Bu_3PeSn can neither correct for signal suppressions in the ICP mass spectrometer, nor for instrument instabilities, such as signal drift during analyses. Hence, ^{126}Xe was measured simultaneously with the ^{120}Sn isotope. In Fig. 5 a chromatogram of different alkyltin compounds is shown as well as the continuous Xe signal. The ^{126}Xe signal decreases during one analysis. This is due to the expansion of the carrier gas when the GC oven is heated up. The signal decrease of ^{126}Xe in the first minutes of the chromatogram coincide with the elution of the solvent. In all calculations the following intensity ratio is used:

$$I_{compound} = \frac{\left[\frac{^{120}Sn}{^{126}Xe}\right]_{compound}}{\left[\frac{^{120}Sn}{^{126}Xe}\right]_{Bu_3PeSn}}$$

Table 2a Repeatability of the retention time of 10 successive 1 µl injections of an alkyltin standard (50 µg/l Sn of each component)

Compound	RSD% retention time
Pr_4Sn	0.23
$BuPr_3Sn$	0.20
Bu_2Pr_2Sn	0.19
Bu_3PrSn	0.16
Bu_4Sn	0.19
Bu_3PeSn	0.16

Table 2b Repeatability of the peak area of 10 successive 1 µl injections of an alkyltin standard (50 µg/l Sn of each component), and the effect of the use of Bu_3PeSn and Xe as internal standards

RSD% of the peak area			
Compound	No internal standard	Bu_3PeSn as internal standard	Bu_3PeSn and Xe as internal standard
Pr_4Sn	23.6	5.2	4.1
$BuPr_3Sn$	24.0	4.8	2.3
Bu_2Pr_2Sn	23.9	3.6	1.7
Bu_3PrSn	23.5	2.8	1.5
Bu_4Sn	24.3	–	1.8
Bu_3PeSn	24.3	–	–

The repeatabilities of the retention times and the peak areas obtained in 10 successive injections of an organotin standard containing 50 µg/l Sn (or 50 pg Sn injected) of each compound are listed in Table 2a and 2b. The RSD% on the retention times amounts to about 0.2% on the average. The effect on the RDS% on the peak area of the use of Bu_3PeSn and Xe as internal standards is illustrated in Table 2b. Without using any of the internal standards, an RSD% of around 24% is caused by the irreproducibility of manual injection. When using Bu_3PeSn as an internal standard, the RSD%'s decrease to values between 2.8 and 5.2%, with Xe as an additional internal standard all RSD% decreases further to values between 1.5 and 4.1%.

Linearity

Calibration curves were obtained by injecting 1 µl of standard solutions of alkyltin species in the splitless mode at different concentrations ranging from 0.40 to 65 µg/l Sn. The relative responses (regression coefficient $r(Pr_4Sn) = 0.999924$, $r(BuPr_3Sn) = 0.999981$, $r(Bu_2\ Pr_2Sn) = 0.999555$, $r(Bu_3PrSn) = 0.99966$) show an excellent linearity.

Instrumental detection limits

The instrumental detection limit was determined as three times the standard deviation of the background measured after 10 successive injections of 1 µl iso-octane containing Bu_3PeSn. The results are shown in Table 3. The detection limits obtained range between 15 and 35 fg and are comparable but somewhat better than those obtained by Prange et al. [12] with a similar ICP-MS instrument. Anyhow, it is obvious that detection limits of GC-ICP-MS are far below those of more commonly used hyphenated techniques such as GC-AAS (10–100 pg) [17] or GC-MIP-AES (0.1–18 pg) [18–19] for the analysis of organotin compounds.

Table 3 Instrumental detection limits. Detection limit defined as 3s of the background signal (10 measurements)

Component	Detection limit (ng/l Sn) (fg Sn absolute)
Pr_4Sn	34
$BuPr_3Sn$	15
Bu_2Pr_2Sn	18
Bu_3PrSn	21

Table 4 Extraction yields of alkyltin compounds in waters (50 ng/l Sn)

Component	Recovery (%) and st. dev.[a]
Monobutyltin	69.2 (8.2)
Dibutyltin	58.4 (3.8)
Tributyltin	99.1 (1.1)

[a] RSD% of 5 extractions

Recovery experiments

The extraction recoveries measured in this work are listed in Table 4. Although many papers report extraction yields of nearly 100% for mono-, di- an tributyltin [14, 15, 20], extracted with the same procedure as used in this work, we obtained quantitative extractions for tributyltin only. Stäb et al. [21] found similar extraction recoveries, and explained the high recoveries reported by other authors by relatively high analyte levels they used. Indeed, 100% recovery for all compounds was found at an analyte concentration level of 10 µg/l Sn or higher. This is far above the concentrations used in this work (50 ng/l Sn) and the work of Stäb et al. and also far above the concentration in environmental samples. The reproducibility of the extraction/derivatization procedure was good. The RSD% values for 5 successive extractions are lower than 4% for di- and tributyltin, and about 8% for monobutyltin. Blank values were found in the order of 1 ng/l. This is due to impurities in the Grignard reagent. Studies have been undertaken to eliminate these blank values.

Table 5 Determination of mono-, di- and tributyltin in harbour waters

Concentration (ng/l Sn)			
Place	Monobutyltin	Dibutyltin	Tributyltin
Ghent harbour	16.48 (0.44)[a]	6.08 (0.21)	5.35 (0.65)
Nieuwpoort harbour	8.22 (0.33)	5.20 (0.19)	6.23 (0.62)
Ostend harbour	8.33 (0.32)	3.89 (0.18)	1.65 (0.60)

[a] Standard deviation

Determination of alkyltin compounds in harbour water

The alkyltin contents in the analysed harbour waters are summarised in Table 5. The results are corrected for the individual extraction yields of every component and blank values. As can be seen, the average organotin contents in the Ghent harbour water, sampled in the 'Zuiddok' of the industrial harbour are higher than those from other harbours. The Nieuwpoort harbour is a yacht harbour. The water from Ostend was taken at the ferry terminal. Its lower organotin content can be explained by dilution of the harbour water with fresh sea water.

Conclusions

GC-ICP-MS is a highly sensitive hyphenated technique for the determination of organotin compounds. The use of Xe, present in the H_2 carrier gas of the GC, proved to be very helpful when optimising the nebuliser gas flow rate and the torch position, and correcting for instrument instabilities. Detection limits of CGC-ICP-MS were found to be better than those for GC-AAS and GC-MIP-AES.

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