A Comparison of GC–ICP-MS and HPLC–ICP-MS for the Analysis of Organotin Compounds

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Introduction

The environmental effects of organotin compounds have been well documented[1] and have led to extensive research into analytical methodologies for their determination. As a consequence of their widespread use organotin compounds have been detected in most marine and fresh-water sediments, as well as in open-ocean waters.[2] In recent years, the focus of research in organotin analysis has shifted to include matrices with human health implications, such as seafood,[3] artificial matrices (PVC pipes used for drinking water distribution[4]) and human blood samples.[5]

Organotin analysis has traditionally been performed by chromatographic separation, gas chromatography (GC) or high performance liquid chromatography (HPLC), coupled to a variety of detectors. GC separations enable the analysis of many different groups of organotin compounds (e.g., butyl-, phenyl-, octyl- and propyl) in a single analysis after derivatization.[6] However, derivatization is time consuming and yields may vary between species and in terms of efficiency, depending on matrix components. GC–inductively coupled plasma mass spectrometry (ICP-MS) has the potential to facilitate simultaneous multi-elemental speciation analysis, because species of Se,[7] Pb,[8] Hg[9] and Sn[10] have volatile forms and can be analysed in a single run. For example, organotin species such as tributyltin, and organomercury species such as methylmercury, in sediments can be derivatized using sodium tetraethylborate and, hence, make such an application practically feasible. Organotin separations by HPLC offer the advantage that derivatization is not required, which eliminates a potential source of uncertainty in the final result and can reduce analysis time significantly. However, the range of compounds that can be analysed in a single run is limited compared with GC. The use of ICP-MS as a detector enables calibration by isotope dilution mass spectrometry (IDMS) as well as providing very low limits of detection (pg–ng range). In conjunction with isotopically labelled organotin species this approach offers many advantages from an analytical point of view, including reduced measurement uncertainties and greater precision compared with external calibration methods.

Experimental

Reagents and standards: Acetonitrile (UpS™ ultra-purity solvent grade) was obtained from Romil (Cambridge, UK). Glacial acetic acid (TraceSelect) and anhydrous sodium acetate (Microselect ≥ 99.5% NT) were obtained from Fluka (Gillingham, Dorset, UK). Triethylamine (TEA), methanol and hexane were used as HPLC grade. De-ionized water was obtained from a water purification unit at >18 MΩ (Elga, Marlow, UK). Sodium tetra-ethylborate ($NaBEt_4$) was obtained from Aldrich (Gillingham, Dorset, UK). Tributyltinchloride (TBTCl), dibutyltinchloride ($DBTCl_2$), triphenyltinchloride (TPhTCl) and diphenyltinchloride ($DPhTCl_2$) were obtained from Aldrich and purified according to the procedure described by Sutton *et al.*[11] The ^{117}Sn isotopically enriched TBTCl was synthesized according to the procedure described in the same paper. Monobutyltinchloride ($MBTCl_3$) and tetrabutyltinchloride (TeBTCl) were obtained from Aldrich and dioctyltin (DOT), tripropyltin (TPrT) and tetrapropyltin (TePrT) were obtained from Alfa Aesar (Johnson Matthey, Karlsruhe, Germany).

Instrumentation: Accelerated solvent extraction was performed using an ASE 200 system (Dionex Corp., Sunnyvale, California, USA).

A 7500i ICP-MS (Agilent Technologies, Palo Alto, California, USA) was used for time-resolved analysis of ^{120}Sn, ^{118}Sn and ^{117}Sn. The shield torch system was used and a second roughing pump was added in-line to increase sensitivity. An 1100 HPLC system (Agilent Technologies) was used for HPLC separations. All stainless steel parts of the HPLC system that come into contact with the sample were replaced by

Figure 1: Sensitivity increase on a 20 ng/mL mixed standard. Peaks: 1 = MBT, 2 = DBT, 3 = MPhT, 4 = TBT, 5 = TeBT, 6 = DphT, 7 = TPhT.

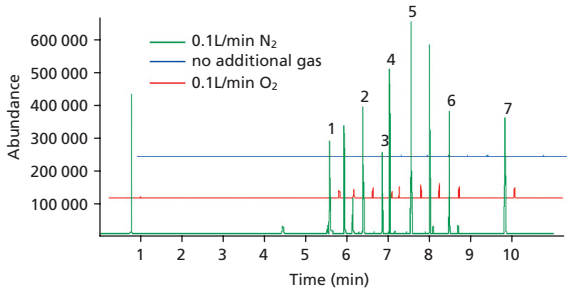


Table 1: ICP-MS parameters used.

	HPLC–ICP-MS	GC–ICP-MS
Interface cones	Platinum	Platinum
Plasma gas flow	14.5–14.9 L/min	14.5–14.9 L/min
Carrier gas flow	0.65–0.75 L/min	0.80–0.85 L/min
Make-up gas flow	0.15–0.25 L/min	Not used
RF power	1350–1550 W	1100–1200 W
Sampling depth	4–7 mm	6.5–7.5 mm
Integration time per mass	300 ms	100 ms
Isotopes monitored	^{120}Sn ^{117}Sn ^{103}Rh	^{120}Sn ^{118}Sn ^{117}Sn
Other parameters	ICP torch injector diameter: 1.5 mm Peltier cooled spray chamber at −5 °C 0.1 L/min O_2 added post nebulization ShieldTorch fitted	0.1 L/min N_2 or O_2 added to enhance sensitivity ShieldTorch fitted

polyetheretherketone (PEEK) components. A 100 cm length of PEEK tubing was used to connect the analytical column to the 100 µL/min PFA MicoFlow nebulizer of the ICP-MS. Optimization of the ICP-MS was achieved prior to HPLC analysis by adjusting the torch position and tuning for reduced oxide and doubly charged ion formation with a standard tuning solution containing 10 ng/g of ^{7}Li, ^{89}Y, ^{140}Ce and ^{205}Tl in 2% HNO_3. After this preliminary optimization, the HPLC system was coupled to the nebulizer and a final optimization was performed using ^{103}Rh added to the HPLC mobile phase. System optimization can also be achieved by making up a 10 ng/g Sn standard in the mobile phase, but it should be noted that Sn is not stable in this solution and the tune solution should therefore be prepared fresh on a daily basis. To reduce the solvent loading on the plasma, the double-pass spray chamber was peltier-cooled to –5 °C. Oxygen (0.1 L/min) was mixed into the make-up gas and added post-nebulization in order to convert organic carbon to CO_2 in the plasma and avoid a carbon build-up on the cones. The final optimization was important because the nebulizer gas and make-up gas flows had to be adjusted to ensure plasma stability with the organic mobile phase conditions. HPLC separations were performed using a C18 ACE column (Advanced Chromatography Technologies, Aberdeen, UK) (3 µm particle size, 2.1 mm × 15 cm) with a mobile phase of 65:23:12:0.05 %v/v/v/v acetonitrile/water/acetic acid/TEA. The use of acetonitrile in the mobile phase was preferred to methanol although the plasma stability with methanol was better, because the peak shape and resolution were substantially improved with acetonitrile. The flow-rate was 0.2 mL/min, and 20 µL of sample blends and mass-bias blends were injected.

GC separations were performed on a 6890 gas chromatograph (Agilent Technologies). The G3158A GC interface[12] (Agilent Technologies) was used to couple the GC to the ICP-MS. The GC method was used as described by Rajendran *et al.*[6] The analytical column was connected to a length of deactivated fused silica, which was inserted along the ICP transfer line and injector. After installation of the interface, the torch position and the ion lenses were tuned using a 100 ppm xenon in oxygen mixture, which was added to the ICP-MS carrier gas at 5% volume via a T-piece. The isotope monitored for this adjustment was ^{131}Xe. The ICP-MS parameters used for HPLC and GC couplings are shown in Table 1.

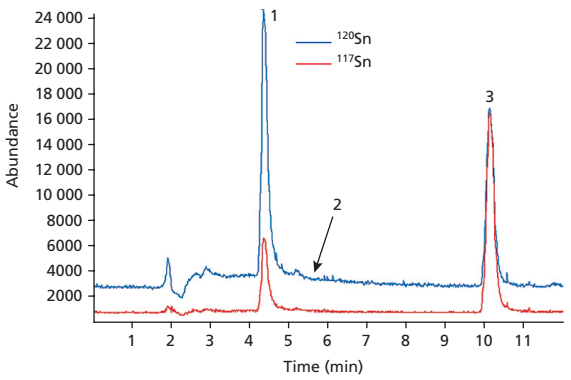
Table 2: Effect of different additional gases on sensitivity of organotin compounds by GC–ICP-MS.

Compound	Retention Time (min)	(a) No gas added	(b) 0.1 L/min O_2 added	Response factor compared with (a)	(c) 0.1 L/min N_2 added	Response factor compared with (a)	Response factor compared with (b)
MBT	5.57	2274	27029	12	309702	136	12
DBT	6.38	3247	29238	9	340436	105	12
MPhT	6.84	2026	18173	9	215182	106	12
TBT	7.02	3490	33132	10	399868	115	12
TeBT	7.54	3717	34225	9	558916	150	16
DPhT	8.46	3181	29665	9	338057	106	11
TPhT	9.81	4287	41119	10	450803	105	11

Table 3: Detection limits based on analysis of a calibration standard for MBT, DBT and TBT.

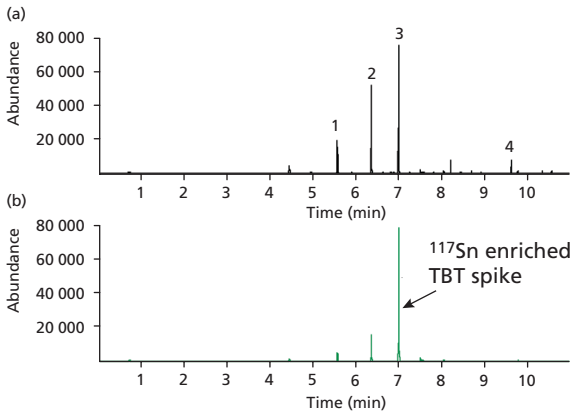
	Detection limits (ng/mL as Sn) by GC–ICP-MS	
	No gas added	**0.1 L/min N_2 added**
MBT	0.7	0.01
DBT	0.5	0.008
TBT	0.4	0.006

Figure 2: HPLC–ICP-MS chromatogram of a sediment extract. Peaks: 1 = DBT, 2 = TPhT, 3 = TBT.



Extraction of organotin compounds: The ASE extraction cells were fitted with PTFE liners and filter papers, and filled with dispersing agent. The sediment and the isotopically enriched spike were added and left to equilibrate overnight. Each cell was extracted using five 5 min cycles at 100 °C and 1500 psi after a 2 min preheat and 5 min heat cycle. 0.5 M sodium acetate/1.0 M acetic acid in methanol was used as the extraction solvent.[13] Mass-bias blend solutions were obtained by adding the appropriate amounts of both ^{120}Sn TBTCl and ^{117}Sn TBTCl into an ASE cell filled and extracting under the same conditions as the samples. Digestion blanks were prepared by extracting ASE cells filled with hydromatrix and PTFE liners. After the extraction, each cell was flushed for 100 s with 60% of the volume and purged with N_2. Prior to analysis, the extracts were diluted 2–5-fold in ultra-pure water for

Figure 3: GC–ICP-MS chromatogram of a sediment extract. (a) = ^{120}Sn, (b) = ^{117}Sn. Peaks: 1 = Et_3BuSn, 2 = Et_2Bu_2Sn (DBT), 3 = $EtBu_3Sn$, 4 = $EtPh_3Sn$ (TPhT).



HPLC–ICP-MS analysis. For GC–ICP-MS analysis 5 mL of samples, blank and mass-bias blend extracts were derivatized by shaking with 1 mL of 5% $NaBEt_4$ and 2 mL of hexane for 10 min. An aliquot of the hexane fraction was then injected for analysis.

IDMS methodology: The method used for IDMS consisted of analysing a blend of the sample together with a mass-bias calibration blend. Each sample blend was injected four times and bracketed by injections of the mass-bias calibration blend. The mass-bias calibration blend was prepared to match the concentration and isotope amount ratio in the sample by mixing the same amount of spike added to the sample with a primary standard of the analyte of interest.[14] The estimation of the standard uncertainties for the measured isotope amount ratios was different to the one described in reference 14 as they were calculated as peak area ratios and not spectral measurement intensities. The chromatographic peaks were integrated manually using the RTE integrator of the ICP-MS chromatographic software. The mass fraction obtained from the measurement of each sample blend injection was then calculated according to:

Table 4: TBT data for sediment extracts.

Sample	**HPLC–ICP-MS (ng/g as Sn) n = 4**	**Standard uncertainty k = 1 (ng/g as Sn)**	**GC–ICP-MS (ng/g as Sn) n = 4**	**Standard uncertainty k = 1 (ng/g as Sn)**
1	827	19	853	12
2	805	38	846	13
3	845	9	838	8
Mean	826	22	846	11
Expanded uncertainty (k = 2)	87		39	

$$w'_X = w_Z \cdot \frac{m_Y}{m_X} \cdot \frac{m_{Zc}}{m_{Yc}} \cdot \frac{R_Y - R'_B \cdot \overline{R'_{Bc}}}{R'_B \cdot \frac{R_{Bc}}{R'_{Bc}} - R_Z} \cdot \frac{R_{Bc} - R_Z}{R_Y - R_{Bc}} \qquad [1]$$

where R'_B is the measured isotope amount ratio of sample blend ($X + Y$), R'_{Bc} is the measured isotope amount ratio of the calibration blend ($Bc = Z + Y$), R_{Bc} is the gravimetric value of the isotope amount ratio of the calibration blend ($Bc = Z + Y$), R_Z is the isotope amount ratio of primary standard Z (IUPAC value), R_Y is the isotope amount ration of the spike Y (value from certificate), w'_X is the mass fraction of Sn in sample X obtained from the measurement of one aliquot, w_Z is the mass fraction of Sn in primary standard Z, m_Y is the mass of spike Y added to the sample X to prepare the blend B ($= X + Y$), m_X is the mass of sample X added to the spike Y to prepare the blend B ($= X + Y$), m_{Zc} is the mass of primary solution Z added to the spike Y to make the calibration blend Bc ($= Y + Z$) and m_{Yc} is the mass of spike Y added to the primary standard solution Z to make the calibration blend Bc ($= Y + Z$).

The representative isotopic composition of Sn taken from IUPAC was used to calculate the isotope amount ratios of the primary standard. For the spike TBTCl, the isotopic composition was obtained from the certificate supplied with the ^{117}Sn-enriched material from AEA Technology plc (UK). For the measured isotope amount ratio of the calibration blend (R'_{Bc}), the average of the two ratios measured before and after each sample blend isotope amount ratio (R'_B) were taken. A mass fraction was calculated for each sample blend injection and the average of the bracketing mass-bias calibration blend injections. The average of the four mass fractions was then reported as the mass fraction obtained for the blend analysed. The final mass fraction was recalculated back to the original sample and corrected for moisture content.

Results and Discussion

General comparison: The practical aspects of interfacing both chromatographic systems to ICP-MS detection are very different. The HPLC coupling can be achieved with relative ease by means of a length of PEEK tubing, connecting the HPLC column to the nebulizer of the ICP-MS. This is both simple and inexpensive, whereas for the GC coupling a specialized interface is needed, and although this is now commercially available it is more costly and involved to install. Analysis of mixed organotin standard solutions showed that the GC method could separate a greater number (n = 10–12) of compounds in a single run compared with the HPLC method (n = 5–6). The injection-to-injection time was ~40% shorter for HPLC–ICP-MS because of the temperature profile used for GC separations. Because of the cost of the derivatizing agent, the reagent cost per sample is approximately double for GC sample preparation.

Sensitivity enhancement of GC–ICP-MS by using additional gases: Figure 1 and Table 2 illustrate the effect of adding different additional gases on the signal response for a range of organotin compounds. Adding 0.1 L/min O_2 results in an increase in the measured peak area ranging from 9-fold (DBT and MPhT) to 12-fold (MBT). The addition of N_2 results in a further increase compared with analysis without addition of an optional gas. Response factors range from 105 (DBT and TPhT) to 136 for MBT and 150 for TeBT. This translates to a reduction of the method detection limit (3 s) for TBT from 0.4 ng/mL (no gas) to 0.03 ng/mL (with 0.1 L/min O_2 added) to 0.006 ng/mL (with 0.1 L/min N_2 added). Table 3 summarizes detection limits based on analysis of a calibration standard for MBT, DBT and TBT.

Comparison of HPLC–ICP-MS and GC–ICP-MS for analysis of TBT in sediment: Table 4 shows the comparative data obtained for the analysis of the same sediment extracts by both methodologies. There is no significant difference between the two data sets. This confirms that the chromatographic separation and the different sample pretreatments (dilution/derivatization) used have no influence on the analytical result obtained. The chromatography for both methods is shown in Figure 2 and Figure 3.

The isotope amount ratio measurement precision, measured for 15 injections over a 6–8 hr period is good for both methods (1.6% for HPLC–ICP-MS and 1.7% for GC–ICP-MS). The uncertainty estimates provided by HPLC–ICP-MS tend to be larger than for GC separations. This is because of broader peaks (50–60 s by HPLC compared with 4–6 s by GC) and greater baseline noise.

Detection limits for sediment analysis are estimated by peak height measurements (3 s) as 3 pg TBT (as Sn) for HPLC–ICP-MS and 0.03 pg TBT (as Sn) for GC–ICP-MS with 0.1 L/min O_2 addition. This demonstrates the superior sensitivity of GC–ICP-MS even without sample preconcentration.

The quantification of other organotin species detected in the sediment by species-specific IDMS was outside the scope of this study and therefore no data is presented here for MBT, DBT or TPhT. However, the study of TPhT, in particular, is of interest, because to date there are no publications describing the determination of this compound by IDMS .

The accuracy of the analytical procedure was evaluated by measuring extractions of the certified reference sediment PACS-2 (National Research Council Canada, Ottawa, Canada). The mean mass fraction obtained by the HPLC–ICP-MS analysis of four extracts was 864 ± 35 ng/g TBT as Sn compared with a certified value of 980 ± 130 ng/g TBT as Sn.

Conclusions

Both HPLC–ICP-MS and GC–ICP-MS offer advantages for organotin speciation analysis. Whilst there is no statistical difference in the results obtained, HPLC–ICP-MS can be used for cheaper and faster determinations of large sample batches, whilst the superior sensitivity and the greater number of analytes separated make GC–ICP-MS an ideal tool for monitoring studies at the ultra-trace level.

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After obtaining a BSc in Marine Sciences with French from the University of Southampton, UK, a Maîtrise from the Université Bordeaux I, France and an MSc in Environmental Diagnosis from Imperial College, UK, **Raimund Wahlen** joined the Specialized Techniques section at LGC Limited, UK (formerly, Laboratory of the Government Chemist) in 1999. The majority of his work to date has focused on the development of primary analytical methods for speciation analysis by isotope dilution mass spectrometry (IDMS). In particular, the use of isotopically labelled compounds has been designed to elucidate the processes that influence speciation during sample preparation and extraction.