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

Application

Environmental

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Abstract

An inductively coupled plasma mass spectrometer (ICP-MS) was used as a detector for gas chromatography (GC) and high performance liquid chromatography (HPLC) analysis of organotin compounds. ICP-MS is a highly sensitive detector with detection limits in the pg–ng range, as well as enabling calibration by isotope dilution mass spectrometry (IDMS). Calibrating using isotopically labeled organotin species reduces measurement uncertainties and leads to greater precision compared to external calibration methods. This application note details the relative merits of the two techniques for the analysis of organotin compounds.

Introduction

The toxic effects of organotin compounds in the environment have been well documented [1] and have led to extensive research into analytical methodologies for their determination in a variety of matrices. The widespread use of organotin compounds has resulted in their detection 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 begun to include matrices with human health implications, such as seafood [3], manufactured products (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 (for example, 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-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 could be analyzed in a single analysis. 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 analyzed in a single run are limited compared to GC. The use of ICP-MS as a detector enables calibration by isotope dilution mass spectrometry as well as providing very low limits of detection (pg–ng range). In conjunction with isotopically labeled organotin species, this approach offers many advantages from an analytical point of view including reduced measurement uncertainties and greater precision compared to 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, methanol and hexane were used as HPLC grade. Deionized water was obtained from a water purification unit at >18MΩ (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 carried out using a Dionex ASE 200 system. An Agilent 7500i ICP-MS was used for time-resolved analysis of ^{120}Sn, ^{118}Sn, and ^{117}Sn. The ShieldTorch system was used, and a second roughing pump was added in-line to increase sensitivity.

An Agilent Technologies (Palo Alto, California, USA) 1100 HPLC system was used for HPLC separations. All stainless steel parts of the HPLC system that come into contact with the sample were replaced by polyether ether ketone (PEEK) components. A 100-cm length piece of PEEK tubing was used to connect the analytical column to the 100-µL min^{-1} PFA MicroFlow nebulizer of the ICP-MS. Optimization of the ICP-MS conditions 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^{-1} 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 carried out using ^{103}Rh added to the HPLC mobile phase. To reduce the solvent loading on the plasma, the double-pass spray-chamber was Peltier-cooled to -5 °C. Oxygen (0.1 L min^{-1}) was mixed into the make-up gas and added post-nebulization 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 C-18 ACE column (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 flow rate was 0.2 mL min^{-1}, and 20 µL of sample blends and mass-bias blends were injected. See Table 1.

GC separations were performed on an Agilent 6890 GC. The Agilent G3158A GC interface [12] 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.

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^{-1}	14.5–14.9 L min^{-1}
Carrier gas flow	0.65–0.75 L min^{-1}	0.80–0.85 L min^{-1}
Make-up gas flow	0.15–0.25 L min^{-1}	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 5% O_2 added post-nebulization ShieldTorch fitted	5% N_2 or O_2 added to enhance sensitivity ShieldTorch fitted

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-minute cycles at 100 °C and 1500 psi after a 2-minute preheat and 5-minute heat cycle. 0.5 M sodium acetate/ 1.0 M acetic acid in methanol was used as the extraction solvent [13]. A calibrated solution (mass-bias blend) was prepared 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 seconds with 60% of the volume and purged with N_2. Prior to analysis, the extracts were diluted two- to five-fold in ultrapure water for HPLC-ICP-MS analysis. For GC-ICP-MS analysis, 5 mL of sample-, blank-, and mass-bias blend solutions were derivatized with 1 mL of 5% $NaBEt_4$ and shaken for 10 minutes with 2 mL of hexane. An aliquot of the hexane fraction was then injected for analysis.

Isotope Dilution Mass Spectrometry (IDMS) Methodology

The method used for IDMS consisted of analyzing 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], [15]. The estimation of the standard uncertainties for the measured isotope amount ratios was different to the one described in [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 Agilent ICP-MS chromatographic software. The mass fraction obtained from the measurement of each sample blend injection was then calculated according to:

$$w'_X = w_Z \bullet \frac{m_Y}{m_X} \bullet \frac{m_{Zc}}{m_{Yc}} \bullet \frac{R_Y - R'_B \bullet \frac{R_{Bc}}{R'_{Bc}}}{R'_B \bullet \frac{R_{Bc}}{R'_{Bc}} - R_Z} \bullet \frac{R_{Bc} - R_Z}{R_Y - R_{Bc}}$$

R'_B	Measured isotope amount ratio of sample blend (X+Y)
R'_{Bc}	Measured isotope amount ratio of calibration blend (Bc=Z+Y)
R_{Bc}	Gravimetric value of the isotope amount ratio of calibration blend (Bc=Z+Y)
R_Z	Isotope amount ratio of Primary standard Z (IUPAC value)
R_Y	Isotope amount ratio of spike Y (value from certificate)
w'_X	Mass fraction of Sn in sample X obtained from the measurement of one aliquot
w_Z	Mass fraction of Sn in primary standard Z
m_Y	Mass of spike Y added to the sample X to prepare the blend B (=X+Y)
m_X	Mass of sample X added to the spike Y to prepare the blend B (=X+Y)
m_{Zc}	Mass of primary standard solution Z added to the spike Y to make calibration blend Bc (=Y+ Z)
m_{Yc}	Mass of spike Y added to the spike Y primary standard solution Z to make 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 analyzed. The final mass fraction was recalculated back to the original sample and corrected for moisture content.

Results and Discussion

General Comparison

Analysis of mixed organotin standard solutions showed that the GC method could separate a greater number (10–12) of compounds in a single run compared to HPLC-ICP-MS (5–6). The injection-to-injection time was ~40% shorter for HPLC-ICP-MS, due to 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 5% 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 to 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 (3s) for TBT from 0.4 ng mL^{-1} (no gas) to 0.03 ng mL^{-1} (with 5% O_2 added) to 0.006 ng mL^{-1} (with 5% N_2 added). The table below summarizes detection limits based on analysis of a calibration standard for MBT, DBT, and TBT.

Detection limits (ng mL^{-1} as Sn) by GC-ICP-MS

	No gas added	5% N_2 added
MBT	0.7	0.01
DBT	0.5	0.008
TBT	0.4	0.006

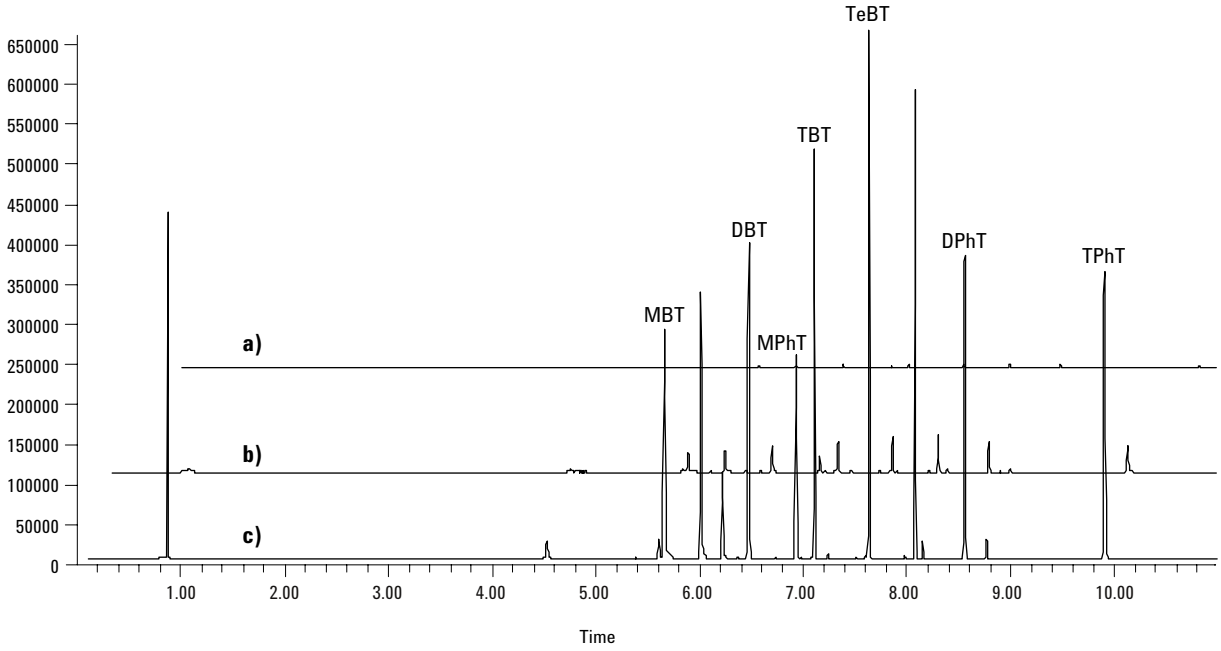

Figure 1. Sensitivity increase on a 20 ng mL^{-1} mixed standard by using a) no additional gas, b) 5% O_2, and c) 5% N_2.

Table 2. Effect of Different Additional Gases on Sensitivity of Organotin Compounds by GC-ICP-MS

Compound	Retention time (min)	a) No gas added (peak area)	b) 5% O_2 added (peak area)	Response factor compared to a)	c) 5% N_2 added (peak area)	Response factor compared to a)	Response factor compared to 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

Comparison of HPLC-ICP-MS and GC-ICP-MS for Analysis of TBT in Sediment

Table 3 shows the comparative data obtained by analysis of the same sediment extracts by both methodologies. There is no statistically significant difference between the two data sets. This confirms that the chromatographic separation and the different sample pretreatment (dilution/derivatization) used has no influence on the analytical result obtained. The chromatography for both methods appears in Figure 2 and Figure 3. The isotope amount ratio measurement precision, measured for 15 injections over a 6–8 hour 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 a result of broader peaks (50–60s by HPLC, compared to 4–6s by GC) and greater baseline noise.

Detection limits for sediment analysis are estimated by peak height measurements (3s) as 3 pg TBT as Sn for HPLC-ICP-MS and 0.03 pg TBT as Sn for GC-ICP-MS with 5% O_2 addition. This demonstrates the superior sensitivity of GC-ICP-MS even without sample preconcentration.

The accuracy of the analytical procedure was evaluated by measuring extractions of the certified reference sediment PACS-2 (NRC, Canada). The mean mass fraction obtained by the HPLC-ICP-MS analysis of four extracts was 864 ±35 ng g^{-1} TBT as Sn compared to a certified value of 980 ±130 ng g^{-1} TBT as Sn.

Table 3. 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**	

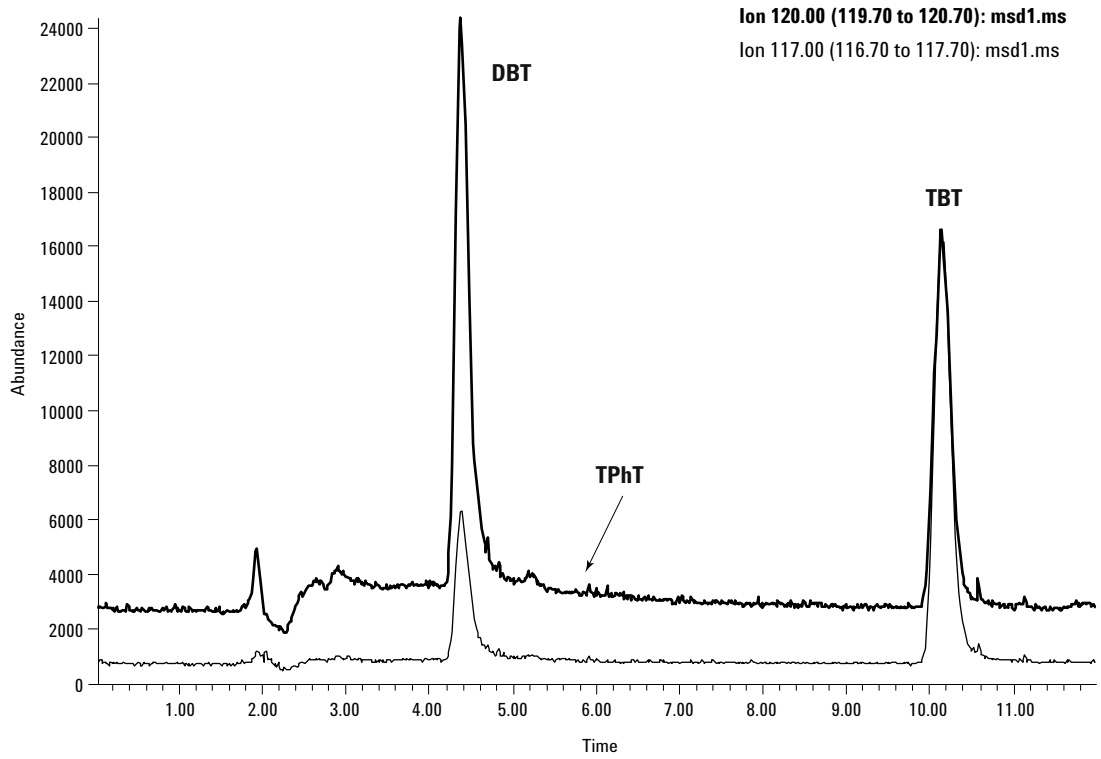

Figure 2. HPLC-ICP-MS chromatogram.

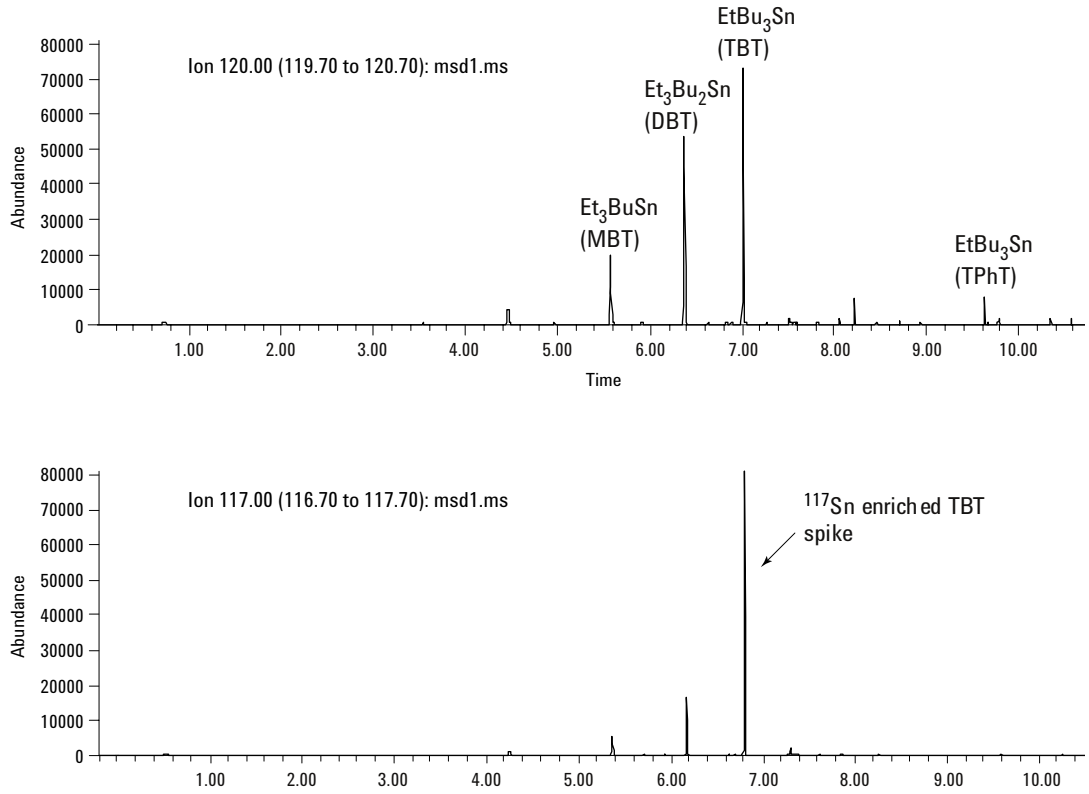

Figure 3. GC-ICP-MS chromatogram.

Conclusions

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

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