Application Note: 30153

Simultaneous Mercury and Tin Speciation using GC-HR-ICP-MS

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Key Words

- ELEMENT 2
- Gas Chromatography
- Mercury
- Speciation
- Tin

Introduction

The significance of speciation for accurately understanding the true behavior of trace elements in the environment and biogeochemical cycles is a well acknowledged fact. Physiochemical information such as toxicity, reactivity and mobility are dependent on the specific form of an element and cannot be assessed from total element concentrations alone. Pollutants, such as mercury species and organotins have generated the most interest over recent years due to their high toxicity and persistent nature in the environment. Mercury species, renowned for their toxicity, find their way into the environment from natural and anthropogenic sources. Methylation of inorganic mercury (Hg^{2+}) in aquatic compartments is of particular concern as methylmercury ($MeHg^{+}$) is one of the most toxic compounds known and it bioaccumulates in the marine food chain. Organotin species (principally tributyltin, TBT) are introduced into the aquatic environment due to their use as anti-fouling agents in paints on ship hulls. Flaking of the paint, sedimentation and subsequent migration of the species into other marine compartments leads to their widespread occurrence. The coexistence of these toxic species in water, sediments and marine biota has led to the development of methods for their multi-element, multi-species determination.

Capillary GC coupled with HR-ICP-MS detection offers the ultimate resolution of trace element species and exceptional sensitivity, a combination resulting in limits of detection capable of measuring Hg and Sn species at ultra-trace levels in the environment. This application note describes the use of a GC coupled to a HR-ICP-MS (Figure 1) with a recently developed GC Interface Kit for ultra-trace speciation analysis. In this application note the higher sensitivity of the sector field instrument is investigated to determine its advantages for the determination of ethylated Hg and Sn species by GC-HR-ICP-MS.

Figure 1: Thermo Scientific TRACE GC Ultra coupled to the Thermo Scientific ELEMENT 2 HR-ICP-MS.

Experimental

A Thermo Scientific TRACE GC Ultra with AS3000 autosampler was coupled to the Thermo Scientific ELEMENT 2 using the new GC Interface Kit. The GC-HR-ICP-MS with GC Coupling Kit is described in more detail in PS30154. The Coupling Kit includes all the required components to establish electrical and analytical connections between the GC and the HR-ICP-MS. A unique, dual mode sample introduction system is used to allow the simultaneous introduction of both a nebulised aqueous solution and the volatile species from the GC. This results in a more robust plasma for superior stability and provides the means to simultaneously aspirate external standards during the GC analysis.

The GC parameters and operating conditions for the ELEMENT 2 are shown in Tables 1 and 2 respectively.

Column	TRACE™ TR-5, 30 m, 0.25 mm i.d., d_f 0.25 µm (PN260E142P)
Injection mode	PTV, Splitless
Injection port temperature	250 °C with ramp to 400 °C
Injection volume	1 µL
GC Carrier gas flow	He @ 2 mL min^{-1}
Make up gas flow	Ar @ 600 mL min^{-1}
Transfer line temperature	320°C isothermal
Oven parameters	
Initial temperature	50 °C
Initial time	1 min
Ramp rate	30 °C min^{-1}
Final temperature	300 °C
Final time	1 min

Table 1: TRACE GC Ultra parameters.

Nebulizer	Glass Expansion MicroMist™, 0.2 mL min^{-1}
Spray Chamber	Glass Expansion Twinnabar™ mini-cyclonic
Cones	Nickel Sample and X Skimmer
Nebulizer gas	0.35 L min^{-1}
Additional gas	Ar @ 600 mL min^{-1}
Forward power	1300 W
Data Acquisition Mode	'Speed' mode
Isotopes	^{118}Sn, ^{120}Sn, ^{121}Sb, ^{123}Sb, ^{200}Hg, ^{202}Hg, ^{203}Tl, ^{205}Tl
Resolution	Low (R=300)
Time per Scan	146 ms
Number of Scans	5812
Total analysis time	14 m 09 s
Aspirated external standard	Aqueous Sb and Tl solution (5 ng mL^{-1}) pumped at 200 µL min^{-1}

Table 2: ELEMENT 2 HR-ICP-MS parameters.

The MicroMist nebulizer and Twinnabar spray chamber were employed with a specially designed glass elbow and torch to allow the introduction of solutions into the dual mode sample introduction system (Figure 2). A 5 ng mL^{-1} solution of antimony and thallium was continuously aspirated throughout all GC analyses to monitor sensitivity and stability. Tin, antimony, mercury and thallium isotopes were measured using the ELEMENT Method software; each scan took 146 ms and the total run time was 14 minutes.

Data acquisition by the ELEMENT 2 is initialised by the TRACE GC Ultra™ using a 5V TTL signal (contact closure triggering is also possible).

Figure 2: Dual Sample Introduction System.

Sample Preparation

Individual stock solutions of tin and mercury species were prepared by dissolving appropriate quantities of commercially available salts in an ultra-pure methanol/ 2% HCl mixture. A mixed working standard was prepared on the day of analysis by diluting appropriate aliquots of the individual stock solutions in 2% HCl. Working calibration standards were then prepared in the 0.1-2.0 ng mL^{-1} range and derivatized by agitating for approximately 5 minutes with 1% $NaBEt_4$ and 1 mL hexane in 5 mL acetate/acetic acid buffer (0.1 M) at pH 4.9. The top, organic layer was then transferred to a 2 mL GC vial for injection.

Results and Discussion

The chromatographic data is displayed in the Show program of the ELEMENT 2 software (Figure 3). Peak integration and quantification was performed off-line in Thermo Scientific Xcalibur software.

Chromatographic data from all analyses in a single Sequence is automatically batch exported from the ELEMENT 2 sequence editor. The chromatographic peak integration and data processing properties are defined in the Processing Set-up section of Xcalibur™ (Figure 4). Calibrations and quantification is then automatically performed for a Sequence in Xcalibur Quan Browser (Figure 5).

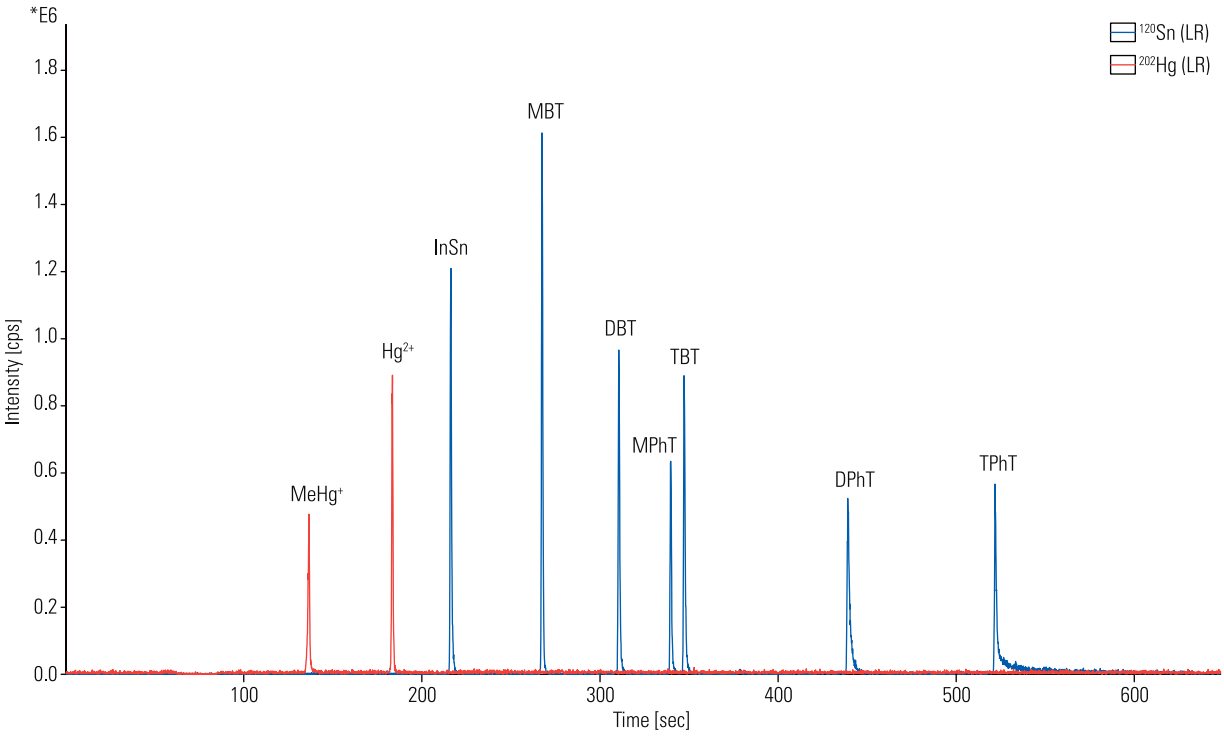

Figure 3: Multi-element chromatographic data of ethylated standard Hg and Sn species (0.5 ng mL^{-1}) acquired with GC-ELEMENT 2 and displayed in the Show program of the ELEMENT software ($MeHg^+$ - methylmercury; Hg^{2+} - inorganic mercury; InSn – inorganic tin, MBT – monobutyl tin; DBT – dibutyl tin; TBT – tribuyl tin; MPhT – monophenyl tin; DPhT – diphenyl tin; TPhT – triphenyl tin).

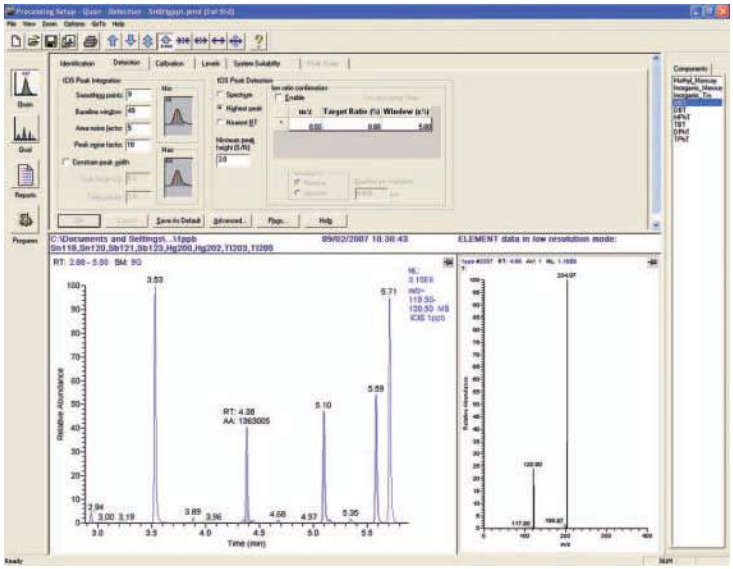

Figure 4: Peak processing parameters are defined for a mixture of elemental species in Xcalibur Processing Set-up, in this case for MBT.

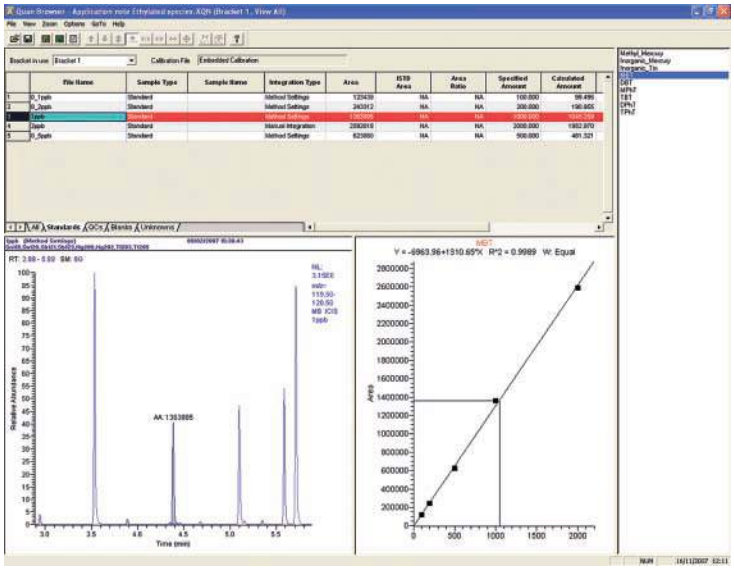

Figure 5: Xcalibur Quan Browser is used to apply the processing properties to all standards and samples in a sequence and generate calibration curves and fully quantitative data.

Limits of detection, corresponding to the concentration of the species in the hexane solvent phase, were calculated as 3 times the standard deviation of species concentrations determined in 5 blanks and are shown in Table 3. The blanks determined were derivatized using the same protocol as for the standards. The Detection Limits (LOD) obtained all fall in the low or sub ppt range. The Blank Equivalent Concentrations (BEC) are also shown for each species in Table 3. BECs are essentially equivalent to the concentration of each individual species in the analytical reagents used during the derivatization procedure. It is recommended for ultra-trace determinations to perform a thorough investigation into each of the analytical reagents used to determine potential sources of contamination. Although contamination from analytical reagents will not be completely eliminated, lower BECs will, in general, provide better LODs. An example of this trend can be seen in Table 3 where TBT contamination in the analytical reagents has compromised the LOD.

	$MeHg^+$	Hg^{2+}	InSn	MBT	DBT	TBT	MPhT	DPhT	TPhT
LOD (ng L^{-1})	2.3	4.7	2.7	3.0	3.4	7.3	0.7	2.4	2.1
BEC (ng L^{-1})	5.1	15.4	43.0	24.4	15.2	74.0	9.2	2.5	38.3

Table 3: Figures of Merit.

Conclusions

This application note shows that GC-HR-ICP-MS is a valuable tool for the study of ultra-trace elemental species. The analytical method developed shows the successful separation of 2 mercury species and 7 tin species, including phenyl tins, with a sample throughput time of just over 14 minutes. Due to the high sensitivity of the ELEMENT 2, detection limits in the low ppt range for derivatized Hg and Sn species are achievable. Through this new instrumental development not only can the technique be used for the determination of Hg and Sn species in matrices such as sediments and fish, but also in matrices such as seawater where these species exist at ultra-trace concentrations.

Thermo Scientific Application Components

ELEMENT 2 GC Coupling Kit (PS30154)	PN 1225260
GC column, TR-5 30 m x 0.25 mm ID, 0.25 µm	PN 260E142P

To find out more about our GC columns offering please visit: www.thermo.com/columns

Chemicals used in this Note

Chemical	Fisher Scientific Catalogue Number
Acetic Acid	A38S-500 (US) - A/0400/PB15 (Europe)
Hexane	H303-1
Optima Hydrochloric Acid (500 mL)	A466-500 (US) - H/1205/08 (Europe)
Methanol	A456-1
Optima Nitric Acid (1L)	A467-1 (US) - N/2275/15 (Europe)
Sodium Tetraethylborate	36388-0010
Sodium Acetate	S210-500 (US)- S/2120/53 (Europe)

For more information please contact your local Fisher Scientific organization and/or visit : www.fishersci.com & www.acros.com

Related Products for the Determination of Trace Elemental Species

XSERIES 2 ICP-MS

- The Thermo Scientific XSERIES 2 Quadrupole ICP-MS provides fast multi-elemental detection capabilities.
- Commercially available HPLC and GC Coupling Kits provide solutions for speciation applications.
- Thermo Scientific PlasmaLab software has fully integrated Transient TRA processing features.

Focus GC and Trace GC Ultra

- The Thermo Scientific Focus GC is a single channel gas chromatograph, compact in size and specifically targeted for routine quality control and high productivity laboratories (Figure 6).
- The Thermo Scientific Trace Ultra GC is a multiple channel gas chromatograph, offering a complete range of proprietary inlets and smart accessories suited for providing answers to the evolving requirements of the GC market (Figure 7).

TriPlus Autosampler

- Advanced system automation with the ability to inject into multiple injectors is provided by the triple axis concept of the Thermo Scientific TriPlus AS (Figure 7).
- Liquid sampling or headspace sample handling versions of the TriPlus™ AS are available.
- The TriPlus DUO offers the ultimate in flexibility with both liquid sampling and headspace capabilities.

Thermo Scientific GC Solutions

Figure 6: Focus GC with AS3000.

Figure 7: Trace GC Ultra with TriPlus AS.

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