

# Speciation of Trace Elemental Species using GC-ICP-MS and GC-HR-ICP-MS

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- Key Words**
- ELEMENT 2
  - XSERIES 2
  - Gas Chromatography
  - Mercury
  - Speciation
  - Tin

## Introduction

The significance of speciation for accurately understanding the true nature of trace elements in the environment, industrial processes and biochemical pathways is a well acknowledged fact. Physiochemical information such as toxicity, bioavailability, mobility and reactivity are dependent on the specific form of an element and cannot be assessed from total element concentrations alone. Due to this fact, requirements for speciation information are emerging in legislation, particularly for highly toxic species such as organotins, methylmercury and brominated flame retardants. For example, recent amendments to the EU Water Framework Directive ([www.euwfd.com](http://www.euwfd.com)) stipulate annual average and maximal concentrations at sub-ng/L level for organotins and pentabromodiphenylether (Table 1).

| Species                   | AA  | MAC |
|---------------------------|-----|-----|
| Mercury and its compounds | 50  | 70  |
| Tributyltin compounds     | 0.2 | 1.5 |
| Pentabromodiphenylether   | 0.5 | NA  |

AA - annual average, MAC - maximum allowable concentrations, NA - not applicable

Table 1: Environmental quality standards for inland surface waters, concentrations in ng/L.

GC-ICP-MS is one of the only speciation techniques capable of reaching the ultra trace levels required by this legislation. GC-ICP-MS coupling kits for the Thermo Scientific XSERIES 2 (Quadrupole ICP-MS) and Thermo Scientific ELEMENT 2 (Sector-Field ICP-MS) offer an off-the-shelf and simple solution for this type of application.



Figure 1: Thermo Scientific TRACE GC Ultra coupled to the XSERIES 2.

The dual mode GC interfaces allow simultaneous introduction of both a nebulized aqueous solution and the volatile species from the GC into the plasma. In this way, external standards can be simultaneously analyzed and a more robust plasma for superior stability is produced (Figure 3). A direct comparison of the two techniques, GC-ICP-Q-MS and GC-ICP-SF-MS was performed for mercury and tin species. Chromatographic reproducibility between the two techniques was evaluated and the potential advantage of the higher sensitivity offered by Sector-Field ICP-MS for the extremely demanding reporting limits which will be required to meet such legislation as the EUWFD was investigated by comparing limits of detection (LOD).



Figure 2: TRACE GC Ultra™ coupled to the ELEMENT 2.

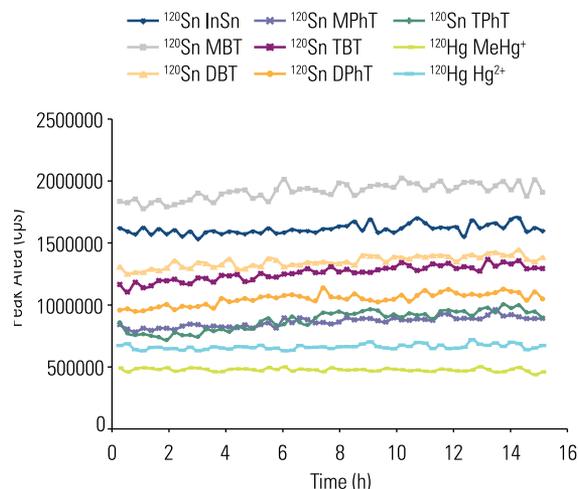


Figure 3: Stability of trace elemental species over a period of 15 h of repeat injections.

## Experimental

The GC parameters for the XSERIES 2 and ELEMENT 2 are shown in Table 2. For comparative purposes, wherever possible, analytical conditions were matched for both ICP-MS instruments. The XSERIES 2 was used in Xs-mode for high sensitivity and the ELEMENT 2 was used with X cones.

|                            |  |
|----------------------------|--|
| Injection mode             | PTV, splitless   |
| Injection port temperature | 250 °C with ramp to 400 °C                                       |
| Injection volume           | 1 µL   |
| Carrier gas flow           | He at 3 mL/min   |
| GC oven parameters         | 50°C (1 min), ramp at 30°C/min to 300°C (1 min)                  |
| Column                     | Thermo Scientific TRACE Tr-5 GC column, 30 m x 0.25 mm ID, 25 µm |

Table 2: GC parameters.

## Sample Preparation

Individual stock solutions of tin species were prepared by dissolving appropriate quantities of commercially available salts in ultra-pure grade methanol. Dilutions of the stock were performed in 1% HCl. Working calibration standards were then prepared in the 0.1 - 2 ng/mL range and derivatized by agitating for approximately 5 minutes with 1 mL 1% NaBEt<sub>4</sub> 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

### XSERIES 2

The chromatographic data is displayed automatically in the XSERIES 2 PlasmaLab software (Figures 4a and 4b). A low degree of data smoothing was applied and an automated peak search feature ensured identical integration parameters for each sample in the experiment list. Fully quantitative calibration curves were then generated and show excellent linearity for each species (Figure 5 presents calibration data for monobutyltin (MBT)).

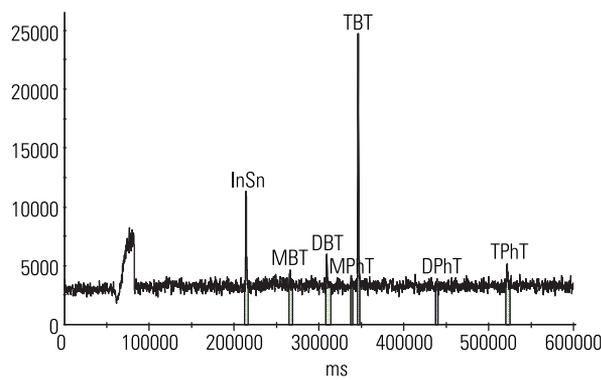


Figure 4a: Chromatographic data for a blank injection displayed in the XSERIES 2 PlasmaLab software.

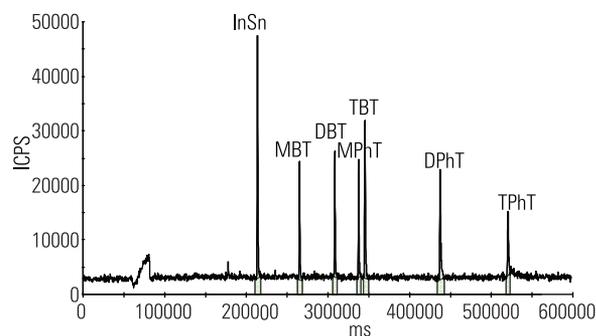


Figure 4b: Chromatographic data for a 0.1 ng/ml standard of various Sn species displayed in the XSERIES 2 PlasmaLab software.

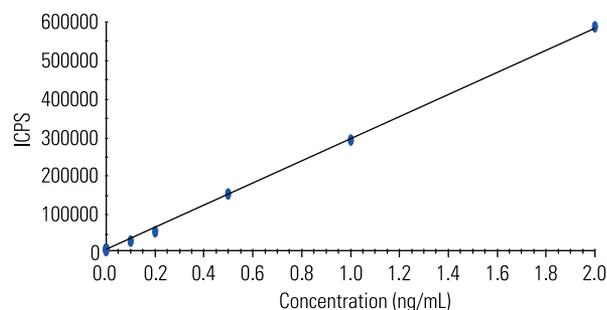


Figure 5: Calibration curve generated in PlasmaLab for MBT.

### ELEMENT 2

The chromatographic data is displayed off-line in Qual Browser of the Thermo Scientific Xcalibur software (Figures 6a and 6b).

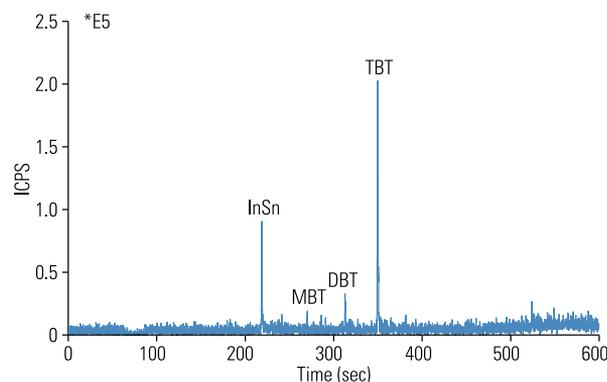


Figure 6a: Chromatographic data for a blank injection on the ELEMENT 2 displayed in Xcalibur Qual Browser.

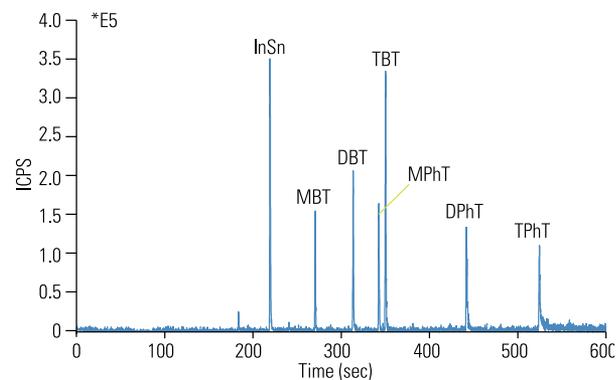


Figure 6b: Chromatographic data for a 0.1 ng/mL injection on the ELEMENT 2 displayed in Xcalibur Qual Browser.

Peak integration and quantification was performed in Xcalibur Quan Browser and a fully quantitative calibration curve is presented for dibutyltin (DBT) in Figure 7.

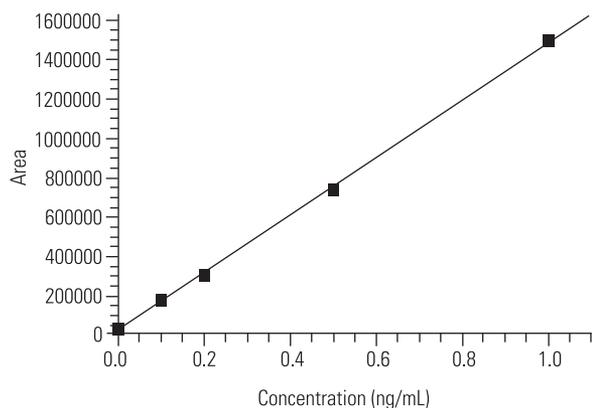


Figure 7: Calibration curve generated in Xcalibur Quan Browser for DBT.

### Sensitivity and Limits of Detection

GC-ICP-MS data acquired with the XSERIES 2 and the ELEMENT 2 were directly compared to assess the reproducibility and robustness of the techniques. Comparison of the chromatographic separation of the Hg and Sn species by both instruments is presented in Figures 8a and 8b respectively. The chromatograms show identical peak shapes and retention times. The superior sensitivity of the ELEMENT 2 is highlighted by the 8-fold increase in peak intensity compared to the XSERIES 2.

Furthermore, the sensitivities, assessed as peak area per ng/mL, of the XSERIES 2 and ELEMENT 2 (Figure 9a) clearly demonstrates the higher sensitivity of the ELEMENT 2. Limits of detection were calculated as 3 times the standard deviation of species concentrations determined in 5 blanks and are shown in Figure 9b.

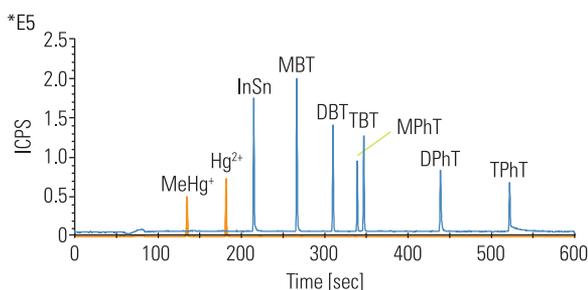


Figure 8a: Multi-element chromatographic data of a 0.5 ng/mL standard acquired with GC-XSERIES 2.

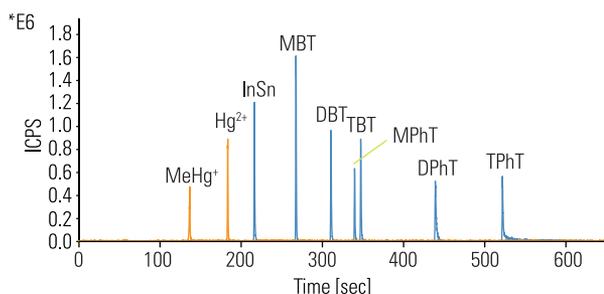


Figure 8b: Multi-element chromatographic data of a 0.5 ng/mL standard acquired with GC-ELEMENT 2.

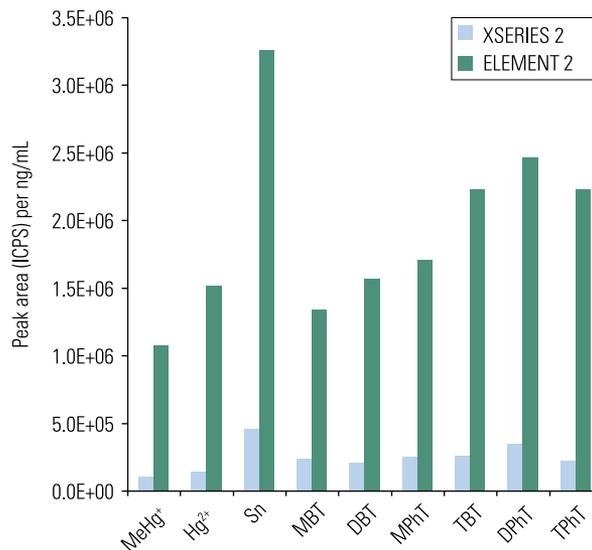


Figure 9a: Sensitivity per ng/mL for the XSERIES 2 and ELEMENT 2.

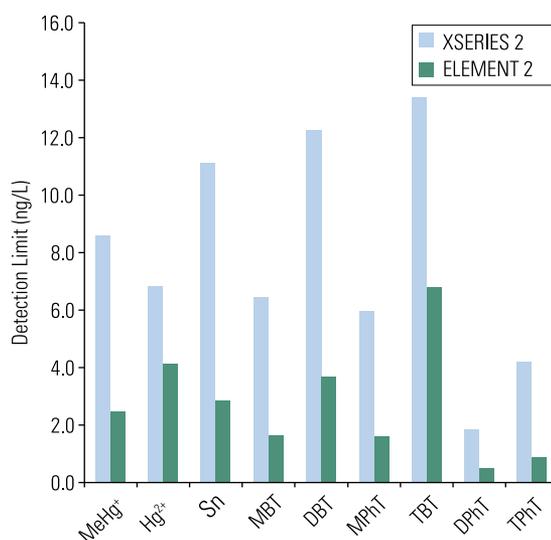


Figure 9b: Limits of Detection in ng/L for XSERIES 2 and ELEMENT 2.

### Conclusions

- GC-ICP-MS is a valuable tool for speciation of ultra-trace elemental species. GC coupling kits with either quadrupole or sector field instruments provide a solution for the multi-elemental speciation of elements such as Hg and Sn. After suitable sample preparation, the speciation methodology shown here can be applied to a number of matrices for direct quantification and monitoring of elemental species. (See AN30132: A Novel GC-ICP-MS Approach for Speciation of Sulfur in Reformulated Fuels as a further example).
- The highest sensitivity and lowest limits of detection were obtained with GC coupled to the ELEMENT 2. Sector Field ICP-MS with GC is therefore more suited for the more demanding applications where extremely low reporting limits would be required.
- For example, with the ELEMENT 2 as detector to the GC, ultra-trace levels of species found in surface waters can be accurately quantified without the need for awkward sample preparation approaches such as large sample volumes or organic phase reduction.

## Thermo Scientific Application Components

|   |             |
|---|-------------|
| XSERIES 2 GC coupling kit (PS40674)               | PN 4600503  |
| ELEMENT 2 GC coupling kit (PS30154)               | PN 1225260  |
| TRACE™ GC column, Tr-5 30 m x 0.25 mm ID, 0.25 µm | PN 260E142P |

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[www.thermo.com/columns](http://www.thermo.com/columns)

## Chemicals used in this Experiment

| Chemical                                      | Fisher Scientific Catalogue Number    |
|---|---------------------------------------|
| Acetic Acid                                   | A38S-500 (US)<br>A/0400/PB15 (Europe) |
| Hexane  | H303-1                                |
| Optima Hydrochloric Acid (500 mL)             | A466-500 (US)<br>H/1205/08 (Europe)   |
| Methanol                                      | A456-1                                |
| Optima Nitric Acid (1L)                       | A467-1 (US)<br>N/2275/15 (Europe)     |
| Sodium Tetraethylborate (NaEt <sub>4</sub> B) | 36388-0010                            |
| Sodium Acetate                                | S210-500 (US)<br>S/2120/53 (Europe)   |

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## Related Products for the Determination of Trace Elemental Species

### Thermo Scientific DFS High Resolution GC/MS

New amendments to the Water Framework Directive will require reporting limits of less than 0.5 ppt of pentabromodiphenylether in inland waters. Using the DFS high resolution GC/MS, polybrominated diphenyl ethers (PBDE) can be analyzed with highest selectivity providing on-column LOQs in the low femtogram range.

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