

A New GC Interface for Sector Field ICP-MS

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Introduction

Many governing bodies now recognize that some elemental species rather than the total elemental concentration should be controlled. Toxic species, such as methylmercury and organotins have generated much interest over recent years with efforts to understand their reactivity and mobility in the environment. Subsequently, the recognition of the acute toxicity of these species has led to their inclusion in future amendments to the EU Water Framework Directive (WFD) which will impose ppt limits of mercury species and sub-ppt limits for tributyltin compounds as annual average concentrations in inland waters.

TABLE 1. Environmental quality standards in the field of water policy for inland surface waters, concentrations in ng/L.

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

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

To address the need for determination of ultratrace concentrations representative of real world samples, a sensitive and highly specific technique such as GC-ICP-MS is needed. A commercial GC speciation kit was recently developed for the Thermo Scientific ELEMENT 2/XR (Figure 1).

FIGURE 1. Thermo Scientific TRACE GC Ultra™ coupled to the ELEMENT XR.



FIGURE 2. Modified ELEMENT 2/XR torchbox for GC analysis.



Its concept is based on the already existing GC speciation kit available for the Thermo Scientific XSERIES 2 with a dual mode sample introduction system. The ELEMENT 2/XR torch holder was modified to accommodate the simultaneous introduction of the GC gases and a liquid aerosol (Figure 2.).

Advantages:

- Easy setup, tuning and performance testing with aqueous solutions
- Gas and solution analyses are possible without reconfiguring the interface
- Robust plasma conditions for GC-ICP-MS analysis due to wet plasma
- On-line addition of aqueous internal standards
- Online mass bias correction
- Entrained air from the spray chamber burns up carbon from the solvent GC injection, preventing carbon build up on the cones and improving long term stability (no need to add oxygen to the plasma)

Sensitivity and Limits of Detection

The newly developed interface was evaluated for standard mercury and tin species prepared by both ethylation and propylation. Typical limits of detection (LODs) based on 5 replicate blank injections are shown in Table 2.

TABLE 2. Limits of detection of Hg and Sn species in ng/L.

	MeHg ⁺	Hg ²⁺	InSn	MBT	DBT	TBT	MPhT	DPhT	TPhT
Ethylation	2.46	4.14	2.83	1.62	3.68	6.78	1.60	0.50	0.85
Propylation	6.35	4.54	8.64	31.15	2.53	3.76	5.31	8.39	9.79

The performance characteristics of the XSERIES 2 and ELEMENT 2/XR GC-ICP-MS coupling were compared using similar instrumental parameters. The XSERIES 2 was used in Xs- mode for high sensitivity and the ELEMENT 2 was used with X cones.

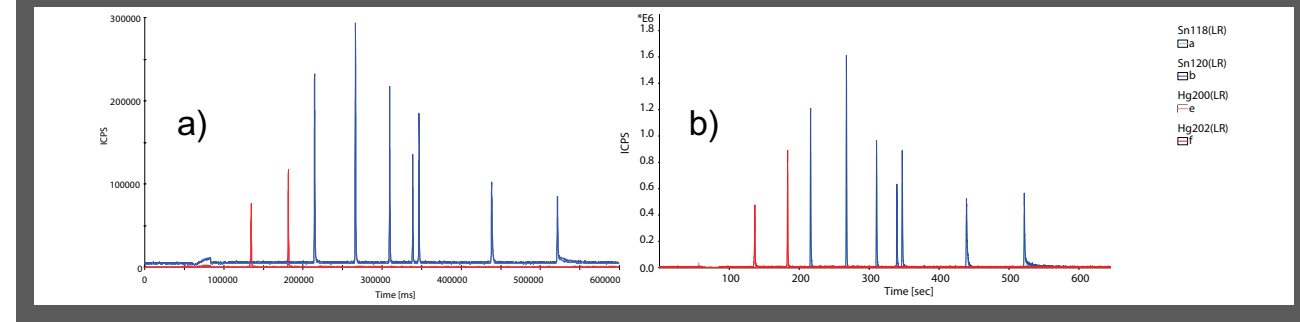
TABLE 3. GC and ICP-MS parameters.

Column	Thermo Scientific TRACE™ TR-5 GC Column, 30 m x 0.25 mm ID, 25 µm
Injection mode	PTV, splitless
Injection port temperature	250 °C with ramp up to 400 °C
Injection volume	1 µL
Carrier gas flow	He @ 3 mL min ⁻¹
GC oven parameters	50°C (1 min), ramp at 30°C/min to 300°C (1 min)
Nebulizer and spray chamber	Concentric with impact bead (free aspiration)
Nebulizer gas	0.35 L min ⁻¹
Additional gas	Ar @ 600 mL min ⁻¹
Forward power	1400 W

A direct comparison of the GC-ICP-MS data generated by the XSERIES 2 and the ELEMENT 2 for ethylated species is presented in Figure 3. The chromatograms show that identical peak shapes and retention times are generated with both instruments.

The superior sensitivity of the ELEMENT 2 is highlighted by the 5 fold increase in peak intensity compared to the XSERIES 2. LODs typically show a 2 to 5 fold improvement for the GC-ELEMENT 2 system when compared with the GC-XSERIES 2.

FIGURE 3. Multielement chromatographic data of a 0.5 ng/mL standard acquired with a.) GC-XSERIES 2 and b.) GC-ELEMENT 2.



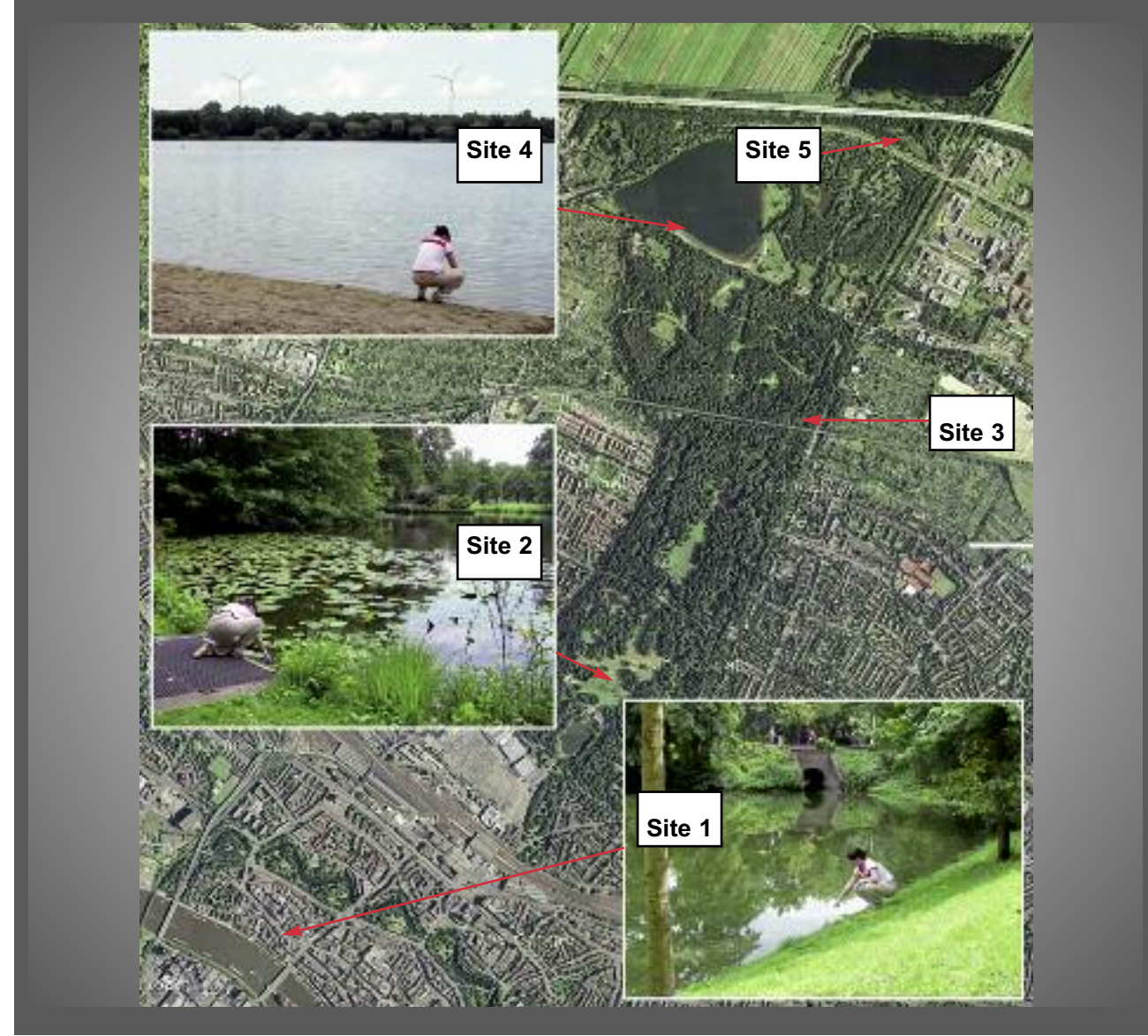
Speciation of Mercury and Tin in Inland Waters

The new GC interface for Sector Field ICP-MS was also evaluated for the determination of sub-ppt levels of mercury and organotin compounds in natural inland waters. Based on the LODs previously obtained it should theoretically be possible to measure the levels of species outlined in the WFD from a sample volume as low as 40 mL.

Sample Collection

Samples were collected from recreational ponds, a recreational lake and a nature reserve from the Bremen area as indicated below.

FIGURE 4. Map of sample collection points in Bremen, Germany.



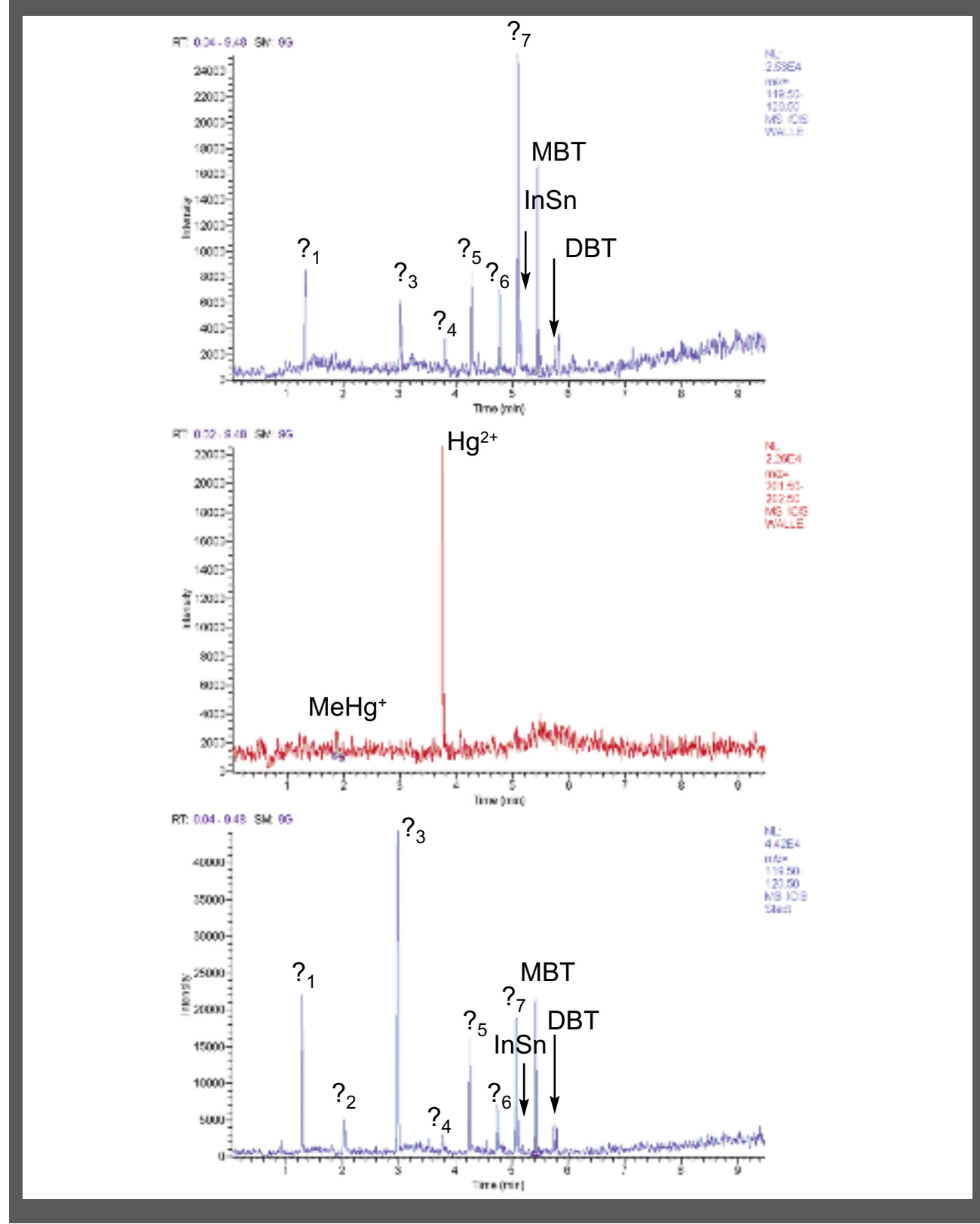
Sample Preparation

40 mL of water from each site was transferred to a clean dry 50 mL headspace vial. Spikes for recovery measurements were made at this point. 5 mL ammonium acetate buffer at pH 4.9, 1 mL hexane and 1 mL 1% NaBPr₄ were added to the headspace vials. The vials were sealed and agitated for 5 mins. The hexane was then pipetted off into a GC vial. A centrifugation step was necessary for samples from sites 1-3 to help in separating the phases. Three blanks and a set of calibration standards at concentrations of 0.2, 1, 5, 10 and 25 ng/L in water, were prepared in an identical manner. Spikes for recovery measurements were made at 2.5 ng/L.

Results

The chromatographic data is acquired in the ELEMENT 2/XR software and reprocessed using Thermo Scientific Xcalibur™ software.

FIGURE 5. Sample chromatography from Site 1 (a) and (b) and Site 3 (c).



Chromatography for some of the samples show the presence of tin species eluting earlier than the butyl tins; these are possibly ethyl or propyl tins. Quantitative results presented in Table 4 show that the MeHg⁺ concentrations were below the LOD in all samples and that only a couple of samples contained any butyltins, (namely MBT). Spike recoveries were between 110 and 180%. Higher recoveries may indicate an improved propylation in the samples compared to the standards.

TABLE 4. Quantitative results in ng/L for Hg and Sn species in collected samples and spiked samples (spike at 2.5 ng/L).

Site	MeHg ⁺	Hg ²⁺	InSn	MBT	DBT	TBT	MPhT	DPhT	TPhT
1	-	2.64	0.3	0.34	-	-	-	-	-
1s	2.68	6.5	1.75	3.83	2.6	3.18	2.89	2.6	2.14
2	-	-	0.17	0.06	-	-	-	0.05	-
2s	3.19	3.67	2.92	3.24	2.84	3.27	3.71	3.54	3.44
3	-	-	-	-	-	-	-	0.26	-
3s	3.63	4.49	2.04	2.3	2.26	3.24	2.93	3.22	3.58
4	-	-	0.38	0.93	-	-	-	-	-
4s	2.21	2.7	1.69	4.72	3.3	3.73	3.51	2.7	2.25
5	-	-	0.24	0.42	-	-	-	-	-
5s	2.19	3.14	3.54	4.45	3.86	4.62	3.32	2.26	3.25
- below LOD									

Conclusions

The objective is the ability to use a sample preparation protocol that does not require large sample volumes in order to attain the LODs required to conform to WFD legislation. The LODs and LOQs obtained for the 40 mL sample volume are shown in Table 5 and indicate that although this analytical method is more than appropriate for the mercury species, the LOD for TBT is difficult to achieve. Cleaner reagents will minimize the tin species found in blanks and improve LODs but other modifications to the approach, such as larger sample volume, are worth investigating .

TABLE 5. Figures of merit for the analytical approach with 40 mL sample volume.

	MeHg ⁺	Hg ²⁺	InSn	MBT	DBT	TBT	MPhT	DPhT	TPhT
LOD (ng/L)	0.17	0.95	0.81	0.88	0.28	0.45	0.16	0.40	1.41
LOQ (ng/L)	0.56	3.17	2.72	2.95	0.94	1.49	0.52	1.32	4.70

This first application for the GC-ELEMENT 2/XR speciation package has shown the advantage of higher sensitivity for the analysis of ultratrace elemental species in real samples.

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