APPLICATION NOTE

AN43371

Ultratrace Tin Speciation with GC-ICP-MS using the Thermo Scientific GCI 100 Interface

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Keywords
Gas Chromatography, GCI 100, iCAP RQ ICP-MS, Speciation, Tin

Goal

To develop a robust and accurate method for tin speciation using the Thermo Scientific iCAP RQ ICP-MS coupled with the Thermo Scientific TRACE 1310 GC.

Introduction

Often the total elemental concentration of an analyte is not sufficient to accurately assess the impact of that analyte on the environment or human health. That is because the toxicity and mobility (as well as other physicochemical properties) are dependent on the chemical form or the species of the analyte. Tin, for example, can be found in a variety of molecules, each with different degrees of toxicity and persistence in the environment. It is, therefore, necessary to use a chromatographic technique in order to separate and identify the different species of Tin that are present.

Tributyltin (TBT) has been used for several decades as an antifouling paint on ships until its use was prohibited in 2001 by the International Convention on the Control of Harmful Anti-fouling Systems in Ships. Despite prohibited use, TBT is widespread in the environment due to leaching and its mobile and persistent nature. As TBT is toxic at very low concentrations, strict legislative limits have been set (e.g. 0.0015 $\mu g \cdot L^{-1}$ for inland surface waters[1]). To accurately quantify TBT (and other tin compounds) at these low levels, highly sensitive analytical techniques are required.

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Due to its superior resolution, along with its specificity and sensitivity, GC-ICP-MS has evolved as an ideal tool to meet these measurement criteria and is the analytical technique recommended by the European Water Framework Directive (EWFD) for Tributyltin (TBT) analysis.

The Thermo Scientific™ GCI 100 Interface was evaluated as part of a seamlessly integrated solution for compound specific quantification of tin species in water samples.

Method

A Thermo Scientific™ TRACE™ 1310 GC (equipped with a Thermo Scientific™ TriPlus RSH™ AS) was coupled with a Thermo Scientific™ iCAP™ RQ ICP-MS via the GCI 100 Interface. The fully integrated system was driven by the Thermo Scientific Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software with ChromControl plug-in.

The GCI 100 Interface is a simple and flexible transfer line (Figure 1) that enables easy installation, handling and tuning of the GC-ICP-MS set up and operation. The instrument configuration and operation parameters are shown in Table 1.

Figure 1. New GC-ICP-MS hyphenation with GCI 100 Interface.

Table 1. Instrument configuration and operation parameters.

GC Parameters	Value
Oven Program	Initial temp of 60 °C for 1 min Ramp at 50 °C·min^{-1} to 300 °C Keep final temp of 300 °C for 9.2 mins
Column	TG 5MS 5% PMS 30m x 0.25mm x 0.25 µm (P/N 26098-1420)
Injection Volume	1 µL
Carrier Gas	He
Injection Mode	Splitless
Injection Port Temperature	300 °C
Flow Rate	2.2 mL·min^{-1}
Septum Purge Flow	5 mL·min^{-1}
Purge Flow	10 mL·min^{-1} from 1 min
Transfer Line Temperature	300 °C
ICP-MS Parameters	**Value**
Injector	Sapphire, non-tapered, 1.8 mm ID injector
Torch	Quartz, demountable
Interface	Pt-tipped sampler and Pt-tipped skimmer with High Sensitivity insert
RF Power	1550 W
Transfer Line Gas Flow	Ar at 0.9 L·min^{-1}
Dwell Time	10 ms (^{118}Sn, ^{120}Sn)
Duration	15 min

Calibration standards at concentrations of 0.02, 0.05, 0.1, 1, 2 and 10 ng·mL^{-1} were prepared by adding the appropriate quantities of an organotin standard mixture of TBT, tri-n-propyl Tin (TPT) and Triphenyltin (TPhT) to 1% HCl. The standards were ethylated in the presence of hexane (Fisher Scientific™) and the hexane phase was transferred to a GC vial for injection.

Each standard was run in triplicate with a blank after each standard batch. Ten replicates of the blank were analyzed at the beginning and at the end of the Qtegra ISDS Software LabBook for the limit of detection (LOD) calculation. After setting up the sample list, the system performed 41 analyses over 10 hours of automated and unattended operation.

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Results

The chromatographic data was acquired and evaluated with the tQuant evaluation mode within Qtegra ISDS Software. The peak shapes obtained were intense and Gaussian such that no data smoothing was required. To ensure identical peak integration the automated peak search (with ICIS algorithm) was applied (Figure 2). The high thermal stability of the transfer line produced baseline separated compounds with a signal-to-noise ratio of 55000 for a 0.1 ng·mL^{-1} injection of TBT.

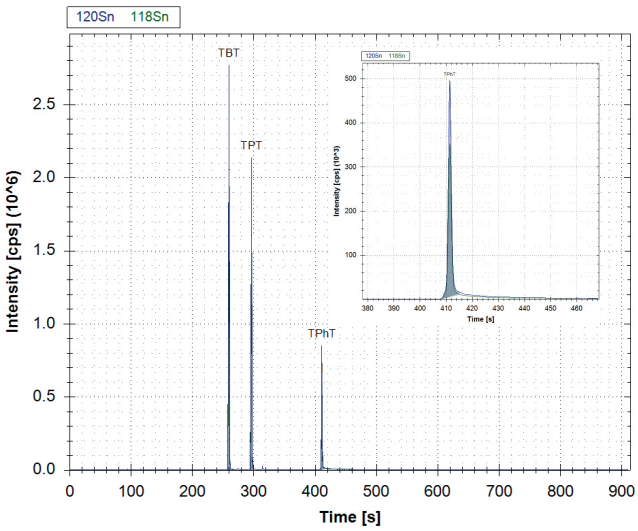

Figure 2. Chromatogram of a 10 µg·L^{-1} Organotin species standard with (inset) zoomed chromatogram of TPhT.

Fully quantitative species specific, calibration curves were generated within the Qtegra ISDS Software LabBook and show linearity of > 0.999 for each species (Figure 3 presents calibration data for TBT). The averaged residuals for all the calibration standards was below 2%.

Detection limits defined in ICH1 Guidance[2] as three times the standard deviation (SD) of the lowest calibration standard were 0.33, 0.28 and 0.38 ng·L^{-1} for TBT, TPT and TPhT (Figure 2), respectively (for a 1 µL injection). This is approximately 4 to 5 times lower than the Maximum Allowable Concentration (MAC) for inland surface waters (1.5 ng·L^{-1}) in the EWFD. Via pre-concentration in the derivatization step of the sample preparation, this LOD can be further improved.

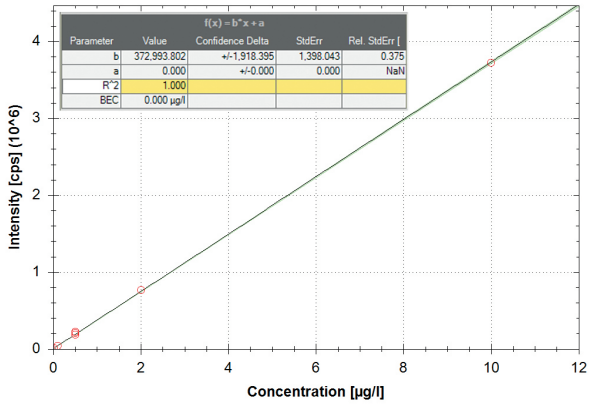

Figure 3. Calibration curve (0.02 - 10 µg·L^{-1}) for TriButyl Tin.

Conclusion

The Thermo Scientific GCI 100 Interface enables seamless coupling of the Trace 1310 GC with the iCAP RQ ICP-MS for ultratrace determination of organotin species.

The proprietary design of the GCI 100 Interface guarantees baseline separated and reproducible chromatographic results, which is ideal for high throughput analysis required in typical environmental labs. The use of ICP-MS enables ultra low limits of detection (pg-ng range) and delivers a reliable solution for the demanding MAC levels required by the EWFD.

Routine, automated analysis with full control over the 1310 GC, GCI 100 Interface and iCAP RQ ICP-MS in one user interface and with just one sample sequence for the whole system is made possible with the ChromControl plug-in.

Automated peak integration and quantification with tQuant evaluation combines the whole workflow in Qtegra ISDS Software. The fully integrated hardware and software simplifies the laboratory workflow, gives reliable speciation analysis and provides full confidence in unattended operation and superior productivity for every laboratory.

References

1. European Water Framework Directive homepage; http://www.cuwcd.com/
2. Q2,R1: Validation of Analytical Procedures

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AN43371-EN 0916