The Determination of Organometallic Compounds in Various Matrices Using GC-ICP-MS

Daniel Kutscher and Shona McSheehy-Ducos
Thermo Fisher Scientific, Bremen, Germany

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Overview

Purpose: To demonstrate the potential of gas chromatography (GC) hyphenated to ICP-MS for the speciation analysis of organometallic compounds.

Methods: A Thermo Scientific™ TraceGC™ was coupled to a Thermo Scientific™ iCAP Q™ and was used for the determination of organotin species and methylated mercury (MeHg+).

Results: The results demonstrate the potential of GC-ICP-MS for the determination of organometallic compounds at trace levels.

Introduction

The determination of toxic organometallic compounds in the environment, foods and clinical samples has become a sought after application due to the implications to human and environmental health. Although methodologies based on liquid chromatography (IC, HPLC) hyphenated to ICP-MS have shown some potential for the separation of organometallic species such as alkylated forms of Hg, Pb or Sn, GC is an appealing alternative as it can provide improved separation relative to LC and lower levels of detection for these compounds.

Furthermore the determination of volatile S and P containing compounds in reformulated fuel products like gasoline is a predetermined application for GC-ICP-MS.

Methods

Sample Preparation

All derivatization reactions were carried our using a 2% NaBEt$_4$ solution. Appropriate amounts of standards and samples (typically 100 μL) were added to 5 mL of 0.1 mol L^{-1} ammonium acetate solution at pH 5. After verification of the pH value, 2 mL of 2,2,4 trimethylpentane (isooctane) and 1 mL of derivatization solution were added and the sample was shaken for 5 minutes. After phase separation had occurred, 1 mL of the organic layer was taken for GC-ICP-MS analysis.

Reformulated fuels were injected with no sample preparation or dilution.

Gas Chromatography (GC)

A Thermo Scientific TraceGC Ultra together with a TriPlus™ autosampler was used for all separations. Both instruments were controlled using Chromeleon™. Typical separation conditions were as shown in Table 1:

TABLE 1. GC operating parameters.

Parameter	Value
Column	Thermo Scientific TG-5HT, 0.25mm x 30m
Temperature profile	50 to 320°C in 12 minutes
Injection mode	PTV splitless
Injection volume	2 μL

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

An iCAP Qc ICP-MS was used to detect the previously separated species. The instrument was fitted with the GC interface kit. The instrument was operated in CCT mode with the QCell pressurized with He in order to improve detection sensitivity due to collisional focusing. For all measurements, a 10 ng g^{-1} solution of Sb (for Sn) or Tl (for Hg) in 2% HNO$_3$ was added as an internal standard . All data handling was performed using the Qtegra™ ISDS controlling the instrument. Typical operating parameters are listed in Table 2:

TABLE 2. ICP-MS operating parameters.

Parameter	Value
Forward power	1550 W
Additional gas 1 (GC transfer line)	0.93 L min^{-1}
Nebulizer gas	0.25 l min^{-1}
CCT gas flow	6.4 mL min^{-1} (100% He)

Hyphenation of GC to ICP-MS

Overview

Hyphenation of GC to ICP-MS enables the transfer of the separated species eluting from the GC column to the ICP-MS for subsequent elemental analysis.

The GC column is directly inserted into the heated transfer line by means of a T-piece. The entire line is flushed with preheated argon gas (supplied by the additional gas module on the iCAP Q) to sweep compounds eluting from the column into the ICP ion source. In order to maintain separation between compounds, the transfer line is heated electrically to approx. 300°C and fed into to the iCAP Q injector.

The laboratory set up of the combined system in is shown in Figure 1.

FIGURE 1. Picture of the TraceGC and TriPlus Autosampler hyphenated to the iCAP Q (left) and detail of the Dual Mode Interface (right).

Dual Mode Interface

The unique design of the GC interface developed for the iCAP Q allows the simultaneous introduction of a liquid solution to the plasma in combination with the eluted species from the GC. This design has several important advantages:

▪ The plasma is humidified, improving detection sensitivity and robustness

▪ Daily instrument optimization can be accomplished using the standard autotuning protocols or modified for mass specific optimization.

▪ Online addition of internal standards is accomplished easily and can be tailored for each application

▪ Online determination of mass bias for each chromatographic run

Optimization

All measurements were carried out in CCT mode using pure He as cell gas. CCT mode on the iCAP Q enhances detection sensitivity for isotopes with m/z ≥ 100 up to a factor of three due to improved transmission resulting from collisional focusing. Table 3 shows the typical performance of the iCAP Qc ICP-MS in the operation modes.

**TABLE 3. Performance of a typical iCAP Qc instrument in STD, KED and CCT modes**

Isotope	STD mode [cps ppb^{-1}]	KED mode [cps ppb^{-1}]	CCT mode [cps ppb^{-1}]	Factor CCT/STD
^{7}Li	93,533	373	9,186	0.1
^{59}Co	118,329	41,265	132,526	1.1
^{115}In	255,203	72,485	414,063	1.6
^{140}Ce	258,760	177,487	483,867	1.87
^{238}U	392,218	488,379	1,277,818	3.25

For other applications, reactive gases such as mixtures of He with H_2, O_2 and NH_3 as well as pure O_2 can be used. Together with the automatically configured low mass cut-off, the QCell is a powerful and versatile tool for both interference suppression and performance optimization in quadrupole based ICP-MS.

Analysis of Methymercury

Organomercury species are known to be highly toxic. MeHg$^+$ is of particular concern due to its ability to cross the blood-brain barrier and its elevated residence time in human beings. MeHg$^+$ is routinely monitored in soils and sediments, as well as in food samples like predator fish such as tuna or sword fish. An example GC-ICP-MS chromatogram for Hg species is shown in Figure 2.

**FIGURE 2. GC-ICP-MS chromatogram of MeHg$^+$ and inorganic Hg.**
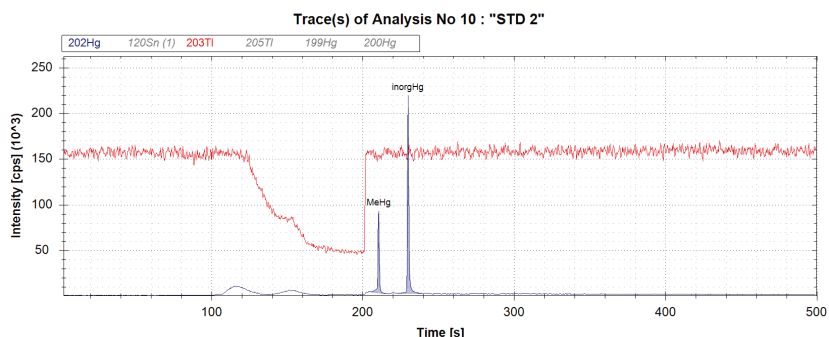
Using the integrated compound specific data evaluation features of Qtegra ISDS, calibration graphs for each compound can be generated. Figure 3 shows the combination of compound specific retention times and peak integration features for the evaluation of transient signals.

FIGURE 3. Automated peak detection and integration features in Qtegra ISDS
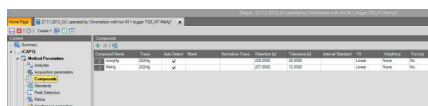
1. Define compounds to be quantified

2. Specify retention time and tolerance

3. Select Smoothing and Peak Integration Parameters
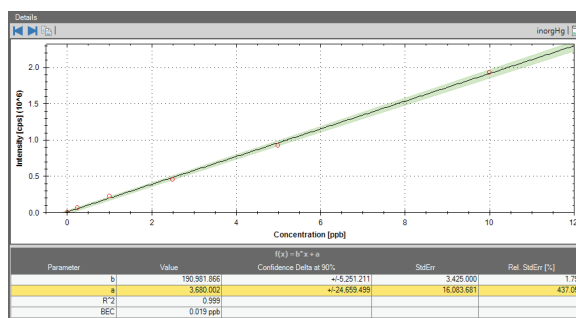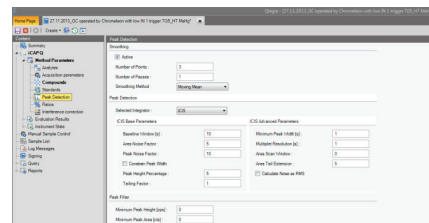
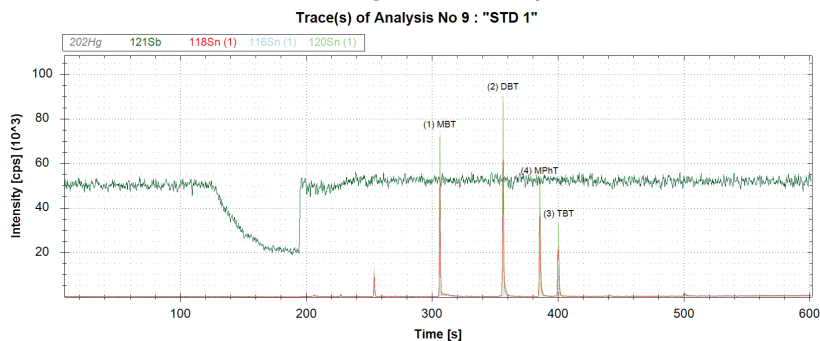Analytical figures of merit are as shown in Table 4.

TABLE 4. Sensitivity and detection limts (LoD) for MeHg$^+$ and inorganic Hg by GC-ICP-MS.

Compound	Sensitivity [kcps/ppb]	LoD [ppt]
Methylmercury	110	1.7
Inorganic mercury	190	1.0

Analysis of Organotin compounds

Butylated and phenylated tin compounds have been widely used e.g. in antifouling paint for ships. However, due to toxicity their use has been restricted and are routinely monitored. An example GC-ICP-MS chromatogram for Sn species is shown in Figure 4.

FIGURE 4. GC-ICP-MS chromatogram of Sn compounds

Using the integrated compound specific data evaluation features of Qtegra ISDS, calibration graphs for each compound can be generated. Analytical figures of merit are as shown in Table 5.

TABLE 5. Sensitivity, detection limits (LoD) and background equivalent concentrations (BEC) for organotins by GC-ICP-MS.

Compound	Sensitivity [kcps/ppb]	LOD [ppt]	BEC [ppb]
Monobutyltin	213	10.2	0.12
Dibutyltin	309	2.7	0.095
Tetrabutyltin	150	30.9	0.15
Monophenyltin	134	4.9	0.005

Analysis of sulfur containing compounds in reformulated fuels

Another challenging application for GC-ICP-MS is the analysis of reformulated fuels (gasoline etc.) for sulfur containing compounds. Although the analysis of S in liquid solutions by ICP-MS is complicated by the presence of water based spectral interferences, dry plasma conditions such as GC enable direct analysis of ^{34}S. Example chromatograms are shown in Figure 6 where it is clear to see the difference between a gasoline sample that contains principally thiophene and a diesel sample that contains heavier fractions and sulfur compounds with higher boiling points.

FIGURE 6. Direct analysis of sulfur containing compounds in gasoline (upper chromatogram) and diesel (lower chromatogram) by GC-ICP-MS.
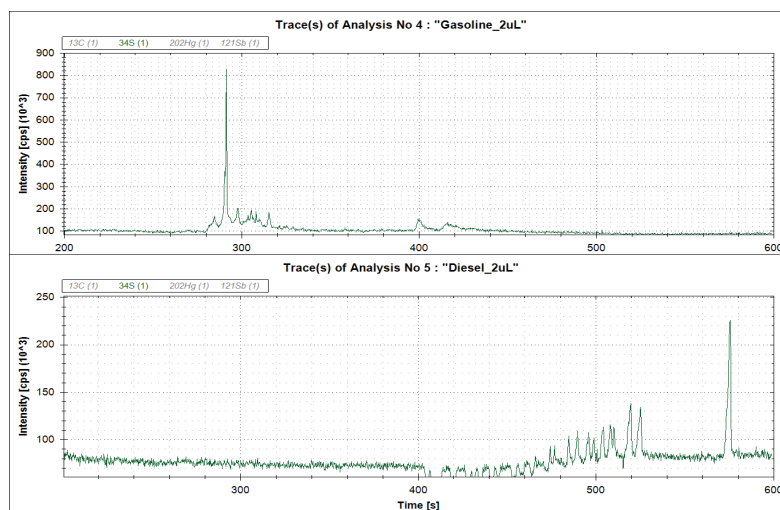
Driven by Qtegra ISDS

Dedicated peak integration and data evaluation

Qtegra ISDS offers automated peak integration based on definition of compound retention times and tolerance values. Other features implemented in the chromatographic data evaluation routines include:

• Four different peak integration algorithms

• Manual modification of peak areas, where any change is recognized by the software as a change to the original data set for improved traceability in accredited analytical environments.

• A normalize trace routine that compensates for changes in detection sensitivity during gradient elution.

• Isotopic ratios of species. As the different organotin compounds tend to interconvert triple spike isotope dilution analysis is often applied to correct for interconversion effects. With Qtegra ISDS ratios between different compounds can be defined for each sample (Figure 5), which can then be directly exported into any external calculation package for further data evaluation.

FIGURE 5. Automated peak area ratio calculation in Qtegra ISDS

Qtegra ISDS offers sophisticated autotune routines, adaptable to special requirements for different applications. The optimization procedure can be followed up in real time.

SourceAutotune: Optimizes torch position, nebulizer gas flow and basic ion lenses, daily tuning of all kinds of sample introduction system

Optimization of QCell parameters: Optimizes gas flows and cell voltages independent of the gas used (pure He or mixtures of He with O_2, H_2, NH_3 etc.)

Conclusion

- The combination of GC and ICP-MS is able to detect organometallic compounds at the ultra trace levels found in natural samples due to the extremely high analytical performance.

- Sulfur containing species are easily identified by GC-ICP-MS.

- Straightforward coupling between the GC and the ICP-MS is achieved using a dual mode interface that allow the use of standard tuning procedures and internal standards for online mass bias correction in isotope dilution studies.

- Sophisticated data evaluation routines in Qtegra ISDS allow for complete data manipulation inside a single streamlined user interface.