

# New Applications of GC-ICP-MS



Agilent Technologies

Setting standards in analytical science



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## Suitability of ICP-MS as a detector for GC

ICP-MS uses a high temperature electrical discharge (plasma) to decompose, atomise and ionise samples introduced via an argon carrier gas flow. The resulting ions are extracted into a vacuum system, separated using a quadrupole mass spectrometer and measured using a sensitive electron multiplier detector. Most elements (including As, P, S) can be determined, and ICP-MS is particularly suitable for the sensitive and specific determination of metals and halogens.

GC-ICP-MS is ideal for the low-level analysis of trace organometallic species, such as organomercury and organotin species, and the ICP-MS detector is also suitable for the measurement of a wide range of other elements, opening up the possibility for this method to be used for the sensitive determination of pesticides and sulphur compounds in fuels, for example.

## Determination of Organometallic Species

ICP-MS has several benefits for the analysis of trace organometallic species. It is very sensitive (<ng/L levels can be measured) and highly selective (mass specific detection). Also, the ICP-MS mass spectrum consists of elemental isotopes, so analysis of isotope ratios is possible (isotope tracer and isotope dilution studies). The development of Agilent's new commercial GC-ICP-MS interface has opened up new research and analysis possibilities.

## Uses of Organotin

Organotin (OT) compounds are used as:

- Fungicides, bactericides, molluscicides (TBT anti-fouling), pesticides
- Preservatives in wood, textile, paper, leather & glass
- Industrial applications: catalyst, PVC stabilisers

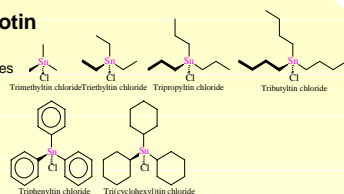
OT production has paralleled PVC production:

- 70 - 90% of OT used as PVC stabilisers, remainder as biocides

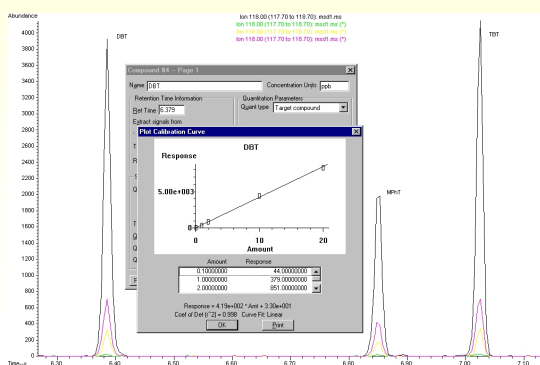
Historically: Environmental concerns (butyl- & phenyltin)

Now: Human health concerns (methyl-, octyl-, butyl- & phenyltin species).

Target analytes for GC-ICP-MS are: TBT, DBT, TPnT, DPnT, Tert-DBT, TPnT, MBT, MPnT, TeBT, DOT, TPnT



## Measurement of Organotin by GC-ICP-MS



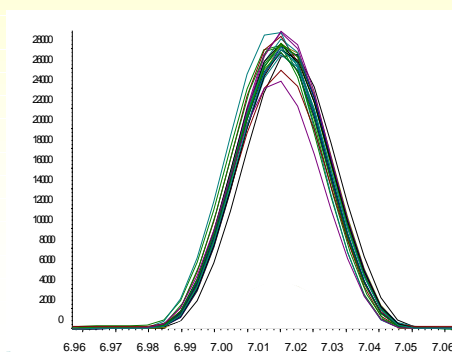
Routine LC methods for separating organotin species exist and these methods have been coupled successfully to ICP-MS, allowing accurate measurement of OT species, using isotope dilution calibration. Routine methods also exist for the extraction and derivatisation of OT species to allow separation using GC.

ICP-MS is an ideal detector for GC separations, due to its speed, sensitivity and selectivity. A calibration for dibutyltin (DBT) in a mixed OT standard solution is shown on the left. The injection volume was 1µL and calibration standards below 1pg/mL of each Sn compound can be measured.

## Reproducibility and Long-term Stability of OT Analysis by GC-ICP-MS

The overlaid chromatograms (below) show the repeatability of the GC-ICP-MS for 15 injections of a TBT mass bias solution. No correction for sensitivity or retention time drift was required. Good reproducibility and long-term stability are essential for a system that is to be used for routine analysis of large sample batches, where aspects such as species decomposition and inter-conversion may be of interest. Excellent long-term reproducibility was demonstrated (<4%SD), illustrating the system and method stability for routine analysis. GC sample introduction delivers almost no sample matrix to the ICP-MS, so tuning is maintained for weeks or months and routine maintenance is almost eliminated.

### Long-term stability of repeated injections of a mixed OT sample (TBT peak shown)



	<sup>120</sup> Sn	<sup>117</sup> Sn	Ratio <sup>120</sup> Sn / <sup>117</sup> Sn
Mean	54363	55989	0.971
Std Dev	2119	2077	0.016
RSD	3.90	3.71	1.68

## Conclusions - Organotin

This first commercially available GC-ICP-MS interface has been shown to provide high sensitivity and access to more OT species than HPLC-ICP-MS. Detection limits are superior, although the GC-ICP-MS method is slower than HPLC-ICP-MS, due to the GC oven cycle time. The system is stable and suitable for routine analysis and ICP-MS offers lower limits of detection than alternative detectors for GC.

Data courtesy of LGC (Teddington) Ltd

## Introduction to GC-ICP-MS

There is growing interest in the determination of the chemical form or species of elements in natural and man-made materials. This interest is prompted both by the potential toxicity of such materials to humans and the limited understanding of how such compounds behave in natural systems.

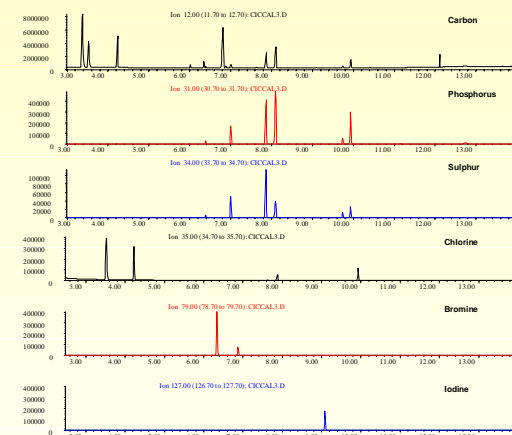
The recent introduction of a commercial interface to link Gas Chromatography (GC) to Inductively Coupled Plasma Mass Spectrometry (ICP-MS) provides an ideal combination for these speciation measurements. The new interface has been applied to the analysis of organometallic species and GC-ICP-MS is also being evaluated as a sensitive multi-element technique for many other species of interest.



## Determination of Pesticides by GC-ICP-MS

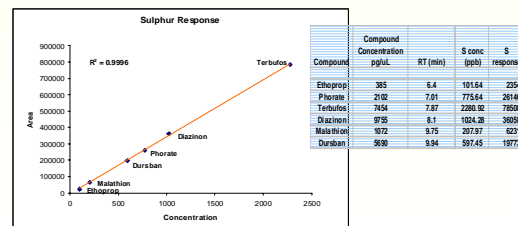
In addition to the well-established application of GC-ICP-MS to the determination of trace organometallic species of toxic heavy metals, GC-ICP-MS also offers many advantages for the measurement of other species, including pesticides containing elements such as phosphorus, sulphur and the halogens.

The measurement of these elements by ICP-MS is simplified when GC is used as the sample introduction method, as the sample is delivered to the ICP in a clean gas stream, so the formation of interfering polyatomic species is minimised, allowing these "difficult" elements to be measured at analytically useful levels. The determination of a range of pesticides and herbicides is shown below, illustrating the simultaneous acquisition of the identifier ion for each compound.



## Compound Independent Calibration (CIC)

The ICP-MS signal produced for a particular element is virtually unaffected by the retention time of the compound on the GC. As a result, it is possible to use the responses from different compounds as calibration standards for an element, from a single injection of a mixed standard. This compound independent calibration is illustrated below, where 6 sulphur-containing pesticides at different concentrations have been used to construct a single S calibration curve.



The application of ICP-MS as a detector for GC opens up many possibilities for the sensitive and selective determination of trace compounds in environmental, petrochemical, agricultural, food and clinical fields, as almost all elements may be determined directly in a single acquisition, in contrast with some alternative element-specific GC detectors.