Speciation of Organic Compounds, Using a Newly Developed, Experimental GC-ICP-MS Interface

Application Note

ICP-MS
Environmental

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Introduction

Tin has been an important metal for thousands of years, having been used in the formulation of alloys such as bronze, in mirrors and in the production of glass. More recently, organotin compounds have been used as industrial materials such as stabilizers in polymers. The trialkylated forms are efficient biocides and fungicides and their properties have been used in many applications. For example, triphenyltin (TPhT) has been used as a pesticide and tributyltin (TBT) was used extensively both as a wood preservative and as the active component in marine anti-fouling paints, applied to the hulls of sailing vessels. While organotin compounds degrade rapidly under photolytic conditions, some trialkyltin compounds are persistent once introduced in the environment (e.g. TBT). Despite of the fact that TBT has been banned from use on small boats for over a decade, it is still commonly used on the hulls of large ships, to prevent the growth of marine organisms. In 1989, TBT was banned in all states of the USA on vessels of 25 meters or less in length. Despite a general reduction in the use of organotin compounds, they can accumulate in sediments over many years and can be ingested and absorbed by marine organisms, leading to accumulation in the marine food chain and ultimately presenting a potential threat both to the environment and later to human consumption.

Recent studies provide strong evidence that many organotin compounds can act as endocrine disruptors, even at very low concentrations. Endocrine disruptors interfere with the action of many hormones, and can be very damaging to the development of animal embryos. As a consequence, there is an increasing demand for a new analytical method for these compounds, which is fast, sensitive and offers high chromatographic resolution.

Capillary Gas Chromatography (GC) offers fast and high-resolution speciation, and is well suited for organotin compounds. Measurement limits using currently available GC detectors (FPD, MS and AED) are good, but the need for determination of organotins at ever-lower levels of concentration has fuelled the investigation of alternative detection systems. Further the presence of sulfur compounds in many of the samples requires a highly selective and sensitive detector.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) offers ultra trace detection limits and high selectivity for most elements. The principles of ICP-MS are summarized in Figure 1. Samples are introduced into a high temperature argon plasma, where they are decomposed, atomized and ionized. The resultant ions are transported, through a sampling interface, into a mass spectrometer for measurement. The high temperature in the ICP source means that all forms of an element are decomposed into individual atoms, so ICP-MS results represent total element levels. However, in combination with an on-line separation technique, such as Liquid Chromatography (LC), Ion Chromatography (IC) or Capillary Electrophoresis (CE), ICP-MS is increasingly being used as a sensitive and highly specific detector in a wide variety of speciation applications.

Combining the separation capabilities of a GC with the selectivity and sensitivity of ICP-MS could offer benefits in the measurement of ultra-trace levels of organically bound metals. In this paper, we describe some initial investigations into the coupling of GC to ICP-MS, for the analysis of organotin compounds.

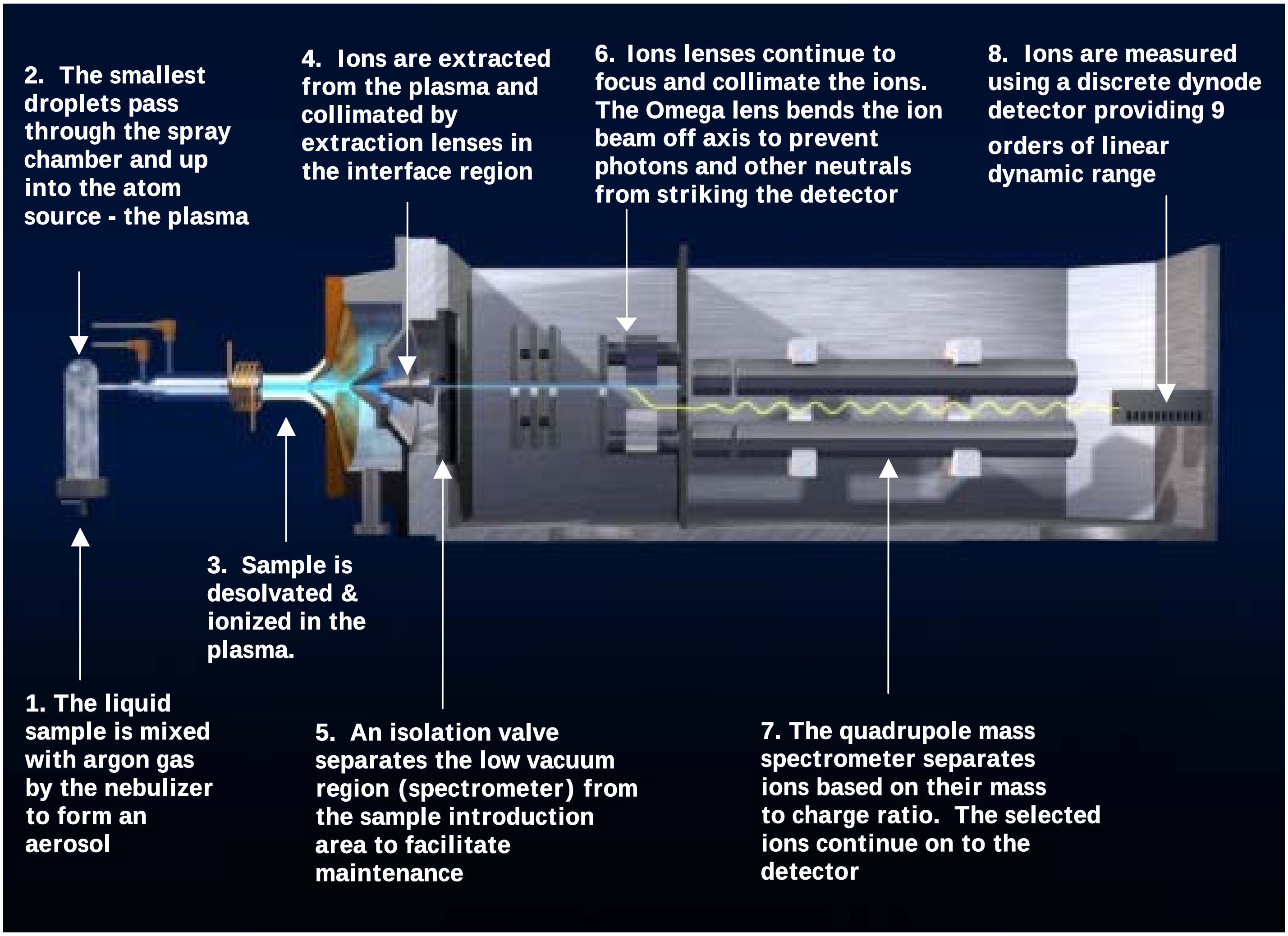

Figure 1. Schematic of an ICP-MS

The interface is not yet commercially available, but it shows some promise. We have used the GC-ICP-MS device to separate and quantify organotin compounds – monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPhT), diphenyltin (DPhT), and triphenyltin (TPhT) - in marine environmental samples of oyster tissue and sediment, collected from the same locality.

Instrumentation

The GC used in these studies was a model 5890, and the ICP-MS was a 4500, both from Agilent Technologies.

The general principal of combining GC with ICP-MS is simple. The end of the capillary GC column is fastened to the base of the ICP torch, so that separated species are carried directly into the plasma by a heated Ar flow.

Using a heated transfer line to connect the GC to the ICP-MS prevents material condensing within the interface and so enables the analysis of high boiling point compounds. Figure 2 is a schematic that describes the interface used during these experiments. Xenon was added to the argon make-up gas as a means of optimizing the ICP-MS operating conditions. The Xe:Ar gas mixture was preheated by passing it through a stainless steel coil mounted within the GC oven.

Initial evaluations of the interface were undertaken at the laboratory of O.F.X. Donard at the University of Pau in France. Figure 3 is a chromatogram of a GC-ICP-MS separation of a 1µL injection of a standard, which contained a mixture of organotin species. Each peak in Figure 3 represents the equivalent of 5 pg tin.

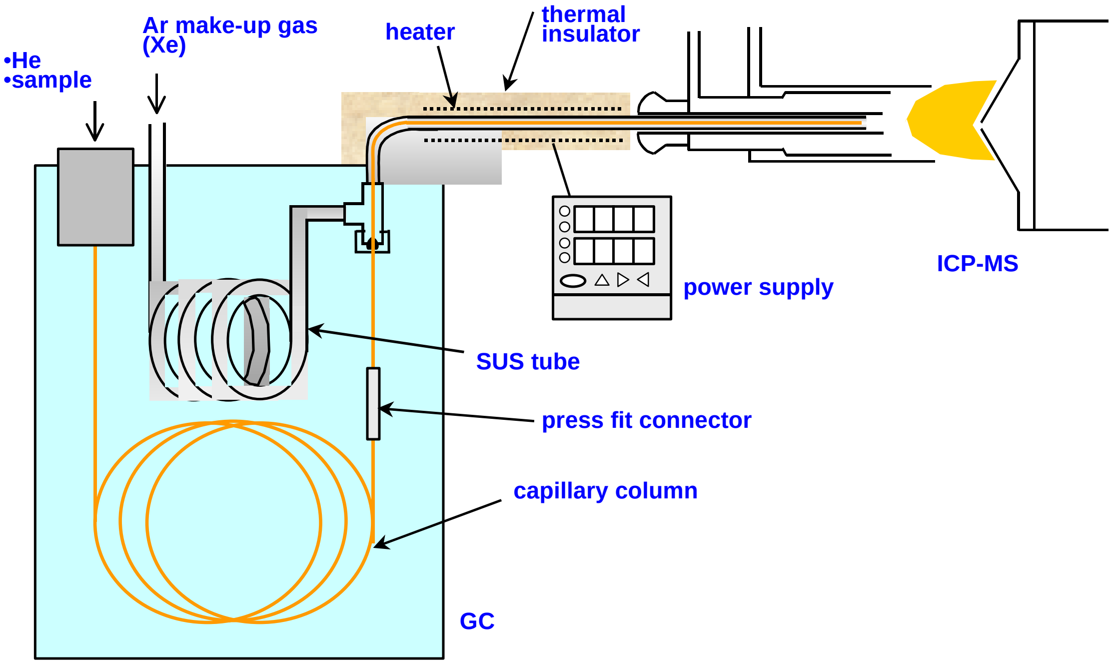

Figure 2. Schematic of the GC-ICP-MS and Interface

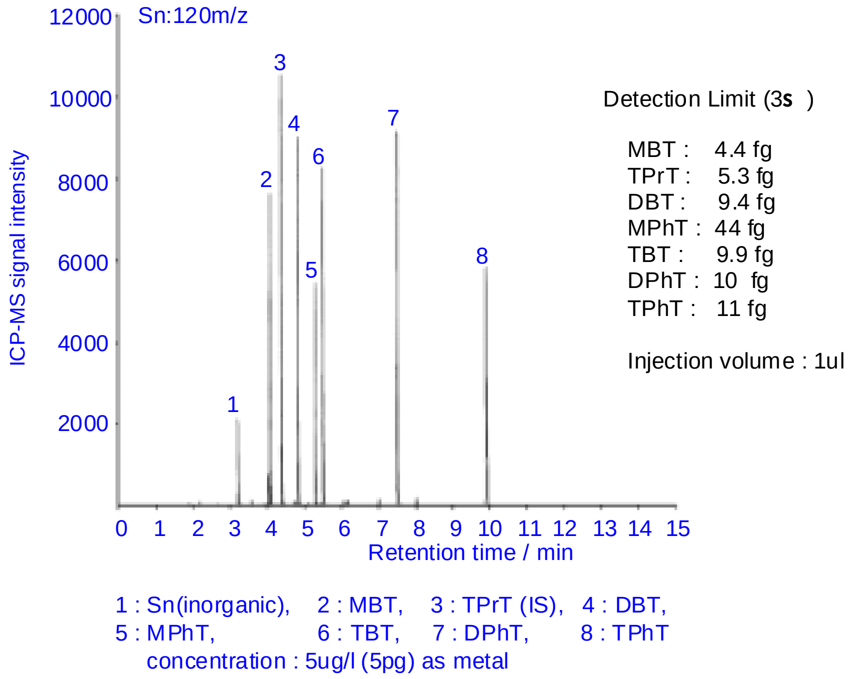

Figure 3. GC-ICP-MS Chromatogram of a 1uL Injection of a 5ppb Organotin Mixed Standard

Table 1 GC-ICP-MS Acquisition Conditions

GC	
Injection mode	Splitless
Injection volume	1uL
Inlet temp	290° C
Column	Non-polar capillary – HP-1 (30m,0.32mm, 0.25um)
Carrier gas	He – 1.0mL/min
Oven program	70°C (1 min):ramp to 190°C (30°C/min): ramp to 270°C (15°C/min)
Interface temperature	250° C
ICP-MS	
RF power	1300W
Sampling depth	8mm
Carrier gas flow	0.8L/min
Oxygen gas flow	0.02L/min (added to auxiliary gas)

Ethylation using sodium tetraethylborate ($NaBEt_4$) was chosen as the derivatization method for this work. The reaction between the organotin compound and the $NaBEt_4$ is in aqueous conditions, which makes it much more suitable for environmental and biological samples than a normal Grignard reagent.

As the chromatogram illustrates, the peak shapes obtained are excellent, suggesting little or no broadening caused by the interface.

Initial results

Preliminary studies on organotin content of oysters and sediments were done in collaboration with the University of Pau . We have taken here samples from the Bay of Arcachon since it is one of the most productive areas for oyster farming. Despite of the fact that organotin concentrations have declined in the water and the sediment of the bay, organotin compounds can be founds in oysters, due to bioaccumulation. In general there is an increasing concern about the occurrence of organotin in shellfish worldwide, particularly as many species are used for human consumption. Samples of oysters and sediment were collected and analysed using the GC with ICP-MS detection.

Some care had to be exercised in the preparation of the oyster tissue, to prevent any potential decomposition of the analyte. The sample preparation method is summarized in Figure 4. Tripropyl tin (TPrT) was added to each sample as an internal standard.

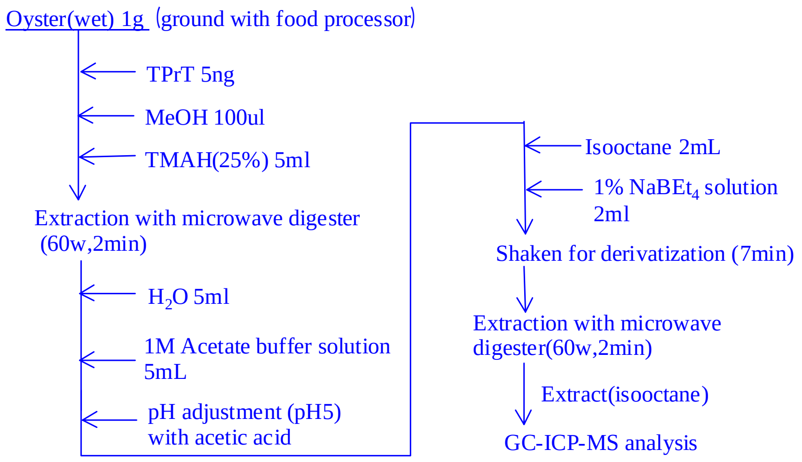

Figure 4. Sample Preparation Steps for the Oyster Tissue

A similar procedure was used for the preparation of sediment samples (Figure 5), except that acetic acid was used instead of Tetramethyl ammonium hydroxide (TMAH).

Figure 6 is a typical GC-ICP-MS chromatogram from one of the oyster extracts, illustrating excellent separation and peak shape. As the data show, there are substantial and measurable amounts of a variety of organotin compounds in the sample.

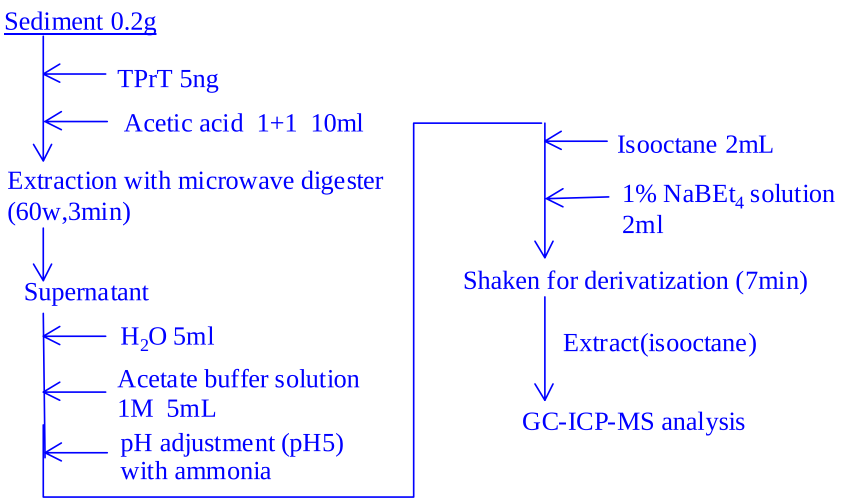

Figure 5. Sample Preparation Steps for the Sediment

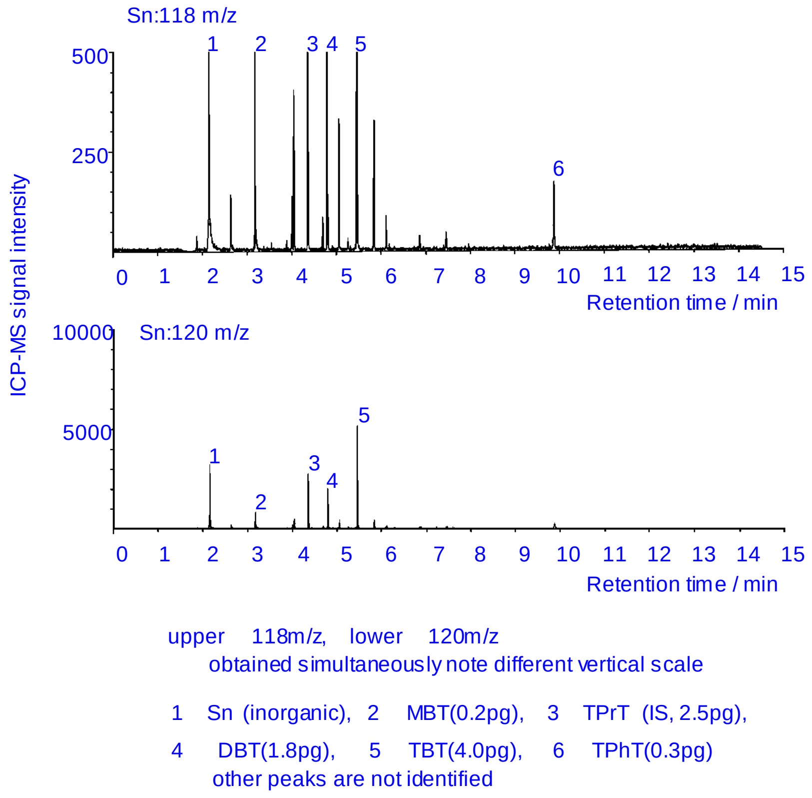

Figure 6. GC-ICP-MS Chromatogram from the Analysis of One of the Oyster Tissue Samples

Table 2. Results Summary from the Analysis of Oyster Samples across Arachon Bay, Plus Analysis of a Sediment Sample

Area	water(%)	concentration / ng/g (Dry)					
		MBT	DBT	TBT	MPhT	DPhT	TPhT
Area1	85	8.3	13	28	0.3	*N.D.*	*N.D.*
Area2	81	0.8	9.5	21	*N.D.*	*N.D.*	1.6
Area3	85	3.7	15	46	1.3	*N.D.*	*N.D.*
Area4	81	1.1	12	42	*N.D.*	*N.D.*	*N.D.*
Area5	86	0.7	11	51	*N.D.*	*N.D.*	2.1
Area6	83	1.8	13	39	*N.D.*	*N.D.*	*N.D.*
Area7	81	0.5	5.3	16	*N.D.*	*N.D.*	1.6
Area8	82	1.7	18	54	*N.D.*	*N.D.*	*N.D.*
Area9	83	2.4	20	141	*N.D.*	*N.D.*	*N.D.*
sediment	36	6.0	5	7	3.0	*N.D.*	2.0

Table 2 summarizes data from oysters sampled in and around Arachon Bay, as well as a sediment sample. Tributyltin (TBT) is the single largest component in each case, although there are several other species present at significant levels. Monobutyltin (MBT) and Dibutyltin (DBT) are breakdown products of TBT. Although the use of TBT in marine antifouling paints has been discontinued in France, the organotin compound still exists in the sediment where the oysters develop. Of particular interest is Area 9, which is a part of the Bay where oyster production has been poor. This also coincides with the largest level of TBT.

The exceptional resolution of the chromatographic separation allows an anticipation of the formation of metabolite products from organotin compounds (e.g. methylation of butyltin compounds) opening the way to new understanding of environmental and biometabolic pathways for these contaminants after further identification.

Summary

These preliminary results suggest that GC-ICP-MS offers a highly sensitive and selective method for the determination of organometallic compounds in environmental matrices The exceptional chromatographic separation capability of the CGC, coupled to the sensitivity, selectivity and multielemental capability of the ICP-MS detector, certainly makes this combination a very promising tool for environmental studies. The interface used in these studies is not yet commercially available and will require some further refinement and characterization. The robustness of the heating system will require some refinement to ensure long-term reliability. Future applications work is under way evaluating the potential of this interface for the simultaneous determination of other organometals such as tin, lead and mercury compounds.

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