# Ultrasensitive High Throughput Elemental Speciation Analysis using GC-ICP-MS

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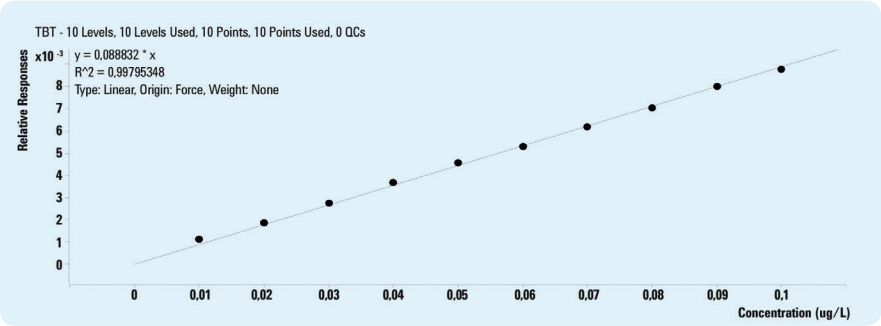


**Figure 1.** Calibration curve for tributyltin from 0 to 100 ng/L (ppt)

GALAB is an independent service laboratory that analyzes and evaluates contaminant elements and compounds in food, food packaging, sanitary products, industrial products, biopharmaceutical products, and environmental samples. We are well-equipped with the latest analytical equipment, and use a broad range of standard and tailored analytical methods to provide our clients with high-quality data. Our analytical database comprises more than 5000 single substances and more than 1000 different analytical methods. Despite this range, we are constantly developing new methods on behalf of our clients to ensure the quality and safety of their products.

## Speciation of organotin compounds

Organometallic species may occur naturally in the environment or be present as a result of human activity [1]. Organometallic compounds are often more bioavailable and toxic than inorganic compounds of the same element. This is especially true for organotin compounds (OTCs), such as tributyltin (TBT) and triphenyltin (TPhT). Trisubstituted OTCs are extensively used as biocides in agrochemicals, antifouling paints, wood preservatives and for material protection. Mono-alkyl and dialkyl tin compounds are widely used as PVC stabilizers in packaging and coating materials, foils, and various types of piping [2]. Both TBT and TPhT are well-known endocrine disruptors that have contaminated the environment for more than 50 years [3]. The biological effects of OTCs on organisms depend on both the nature and number of organic groups bound to the Sn(IV) cation, with the highest level of toxicity being exhibited by the trisubstituted compounds like TBT [4].

There is a trend towards more stringent environmental regulations, with tighter control of potential contaminants. Actual or expected changes to the regulatory framework create a demand for more sensitive and robust analytical procedures. In this article, a sensitive, high-throughput technique is presented for the detection of organometallic species in different matrices.

Currently, most laboratories use GC/MSD, GC-FPD, or GC-AED for the detection of organometallic compounds. None of these techniques offers the required sensitivity, stability, or robustness to meet evolving environmental requirements. However, ultrasensitive high throughput elemental speciation analysis (UHTESA) is now possible using GC-ICP-MS with a suitable sample preparation technique [5].

## Experimental

### Reagents and samples

Analytical grade reagents were bought from Merck, Germany, and were used without further purification. Single compound and mixed organotin standards were obtained from Campro Scientific, Germany. Sodium tetraethylborate was from Synthese Nord, Germany.

### Instrumentation

An Agilent 7890 GC was coupled to an Agilent 7900 ICP-MS using the Agilent GC-ICP-MS interface (G3158D). The GC was fitted with an Agilent J&W DB-5ms Ultra Inert column. The ICP-MS was fitted with platinum-tipped interface cones.

**Table 1.** GC-ICP-MS operating parameters

| Parameter | Value |
|---|---|
| RF power (W) | 1100 |
| Injection port temperature (°C) | 280 |
| Helium carrier gas flow rate (mL/min) | 19.6 |
| Injection volume (µL) | 1 |

**Table 2.** GC temperature program

| | |
|---|---|
| Start temp (°C) | 50 |
| Heating rate (°C/min) | 40 |
| Max temp (°C) | 320 |
| Hold time (min) | 3 |

Appropriate sample preparation (extraction and derivatization) techniques are an important prerequisite to the accurate determination of organometallic species by GC. The species must be transformed into their peralkylated nonpolar derivatives. A detailed description of the sample preparation steps is given in reference [1].

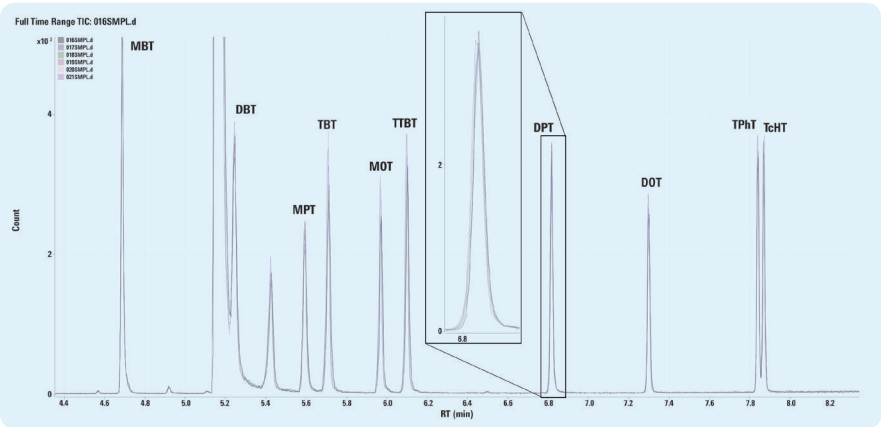


**Figure 2.** Six injections of a standard containing 10 organotin species at 1.0 µg/L (ppb)

## Results and discussion

### Calibration

A calibration curve was generated by measuring Sn in the TBT calibration standard solutions as shown in Figure 1. The limit of detection (LOD) and limit of quantification (LOQ) obtained for TBT, calculated according to the method defined in DIN 32645, were 2 ng/L (ppt) and 7 ng/L respectively.

Excellent precision was achieved from six injections of a standard containing 10 organotin species at 1.0 µg/L, as shown in Figure 2.

### Analytical results for real samples

A slightly modified version of the method, using a 1 minute hold of the start temperature, has been implemented for routine analysis of OTCs in several sample types. The chromatogram in Figure 3 shows tin species present in a sediment. The results in Table 4 show the different distributions of tin species in samples of drinking water, surface water, sediment, fish, and a PVC children's toy.

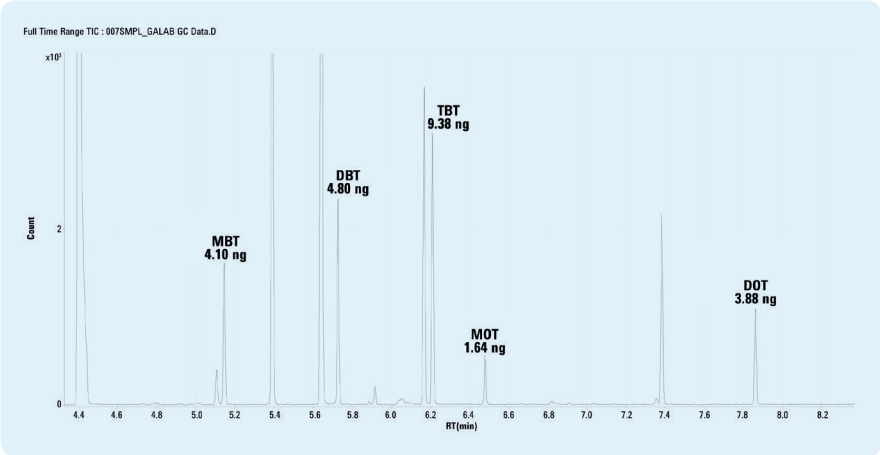


**Figure 2.** GC-ICP-MS chromatogram of a sediment sample showing OTCs from leachate contamination

**Table 3.** Concentration of OTCs in various sample types

| OTC | RT, min | Sample and concentration | | | | |
|---|---|---|---|---|---|---|
| | | Drinking water, ng/L | Surface water, ng/L | Sediment, µg/kg | Fish, µg/kg | PVC toy, µg/kg |
| Monobutyltin (MBT) | 5.13 | 0.07 | 1.66 | 4.1 | 0.35 | 14.01 |
| Dibutyltin (DBT) | 5.71 | 0.06 | 0.75 | 4.8 | 0.71 | 55.04 |
| Monophenyltin (MPT) | 6.03 | <0.01 | 0.16 | <0.1 | <0.01 | <1 |
| Tributyltin (TBT) | 6.22 | <0.01 | 1.05 | 9.38 | 0.05 | 3.16 |
| Monooctyltin (MOT) | 6.49 | 0.01 | 0.15 | 1.64 | 0.04 | <1 |
| Tetrabutyltin (TTBT) | 6.53 | <0.01 | <0.01 | <0.1 | <0.01 | <1 |
| Dioctyltin (DOT) | 7.74 | <0.01 | 0.015 | 3.88 | 0.01 | <1 |
| Triphenyltin (TPhT) | 8.31 | <0.01 | 0.07 | <0.1 | 0.07 | <1 |
| Tricyclohexyltin (TcHT) | 8.35 | <0.01 | <0.01 | <0.1 | <0.01 | <1 |

Internal standards: tripropyltin (TPT), tetrapropyltin (TTPT), monoheptyltin (MHT), and diheptyltin (DHT)

### Surface water surveillance directives

In 2000, Directive 2000/60/EC of the European Parliament and of the Council was adopted. This EU Water Framework Directive sets out the objectives for Community action in the field of water policy and defines a strategy to reduce water pollution. The strategy involves the identification of priority substances among those substances that pose a significant risk to, or via, the aquatic environment at European Union level. Decision No 2455/2001/EC established a list of 33 substances or groups of substances that were prioritized at EU level for inclusion in Annex X to Directive 2000/60/EC [6]. Directive 2013/39/EU specifies an annual average content for tributyltin of 0.2 ng/L in surface water.

## Conclusions

The GC-ICP-MS method is robust, reproducible, and highly sensitive. It meets the requirements of current legislation, including the low specifications for tributyltin specified in Germany's WRRL (2013/39/EW) framework for surface water surveillance monitoring of 0.2 ng/L.

The method is suitable for a wide variety of sample matrices, but sample preparation remains the most challenging step.

Currently, in our labs at GALAB, we routinely use GC-ICP-MS to measure OTCs in 300–400 samples every month. Typical sample types include food and infant food, animal feed, beverages, consumer products, plus many types of environmental samples.

## References


1. E H E Jantzen et al. Fresenius J Anal Chem (1995) 353, 28–33
2. R Airaksinnen et al. Environ Research (2010) 110, 544–547
3. A. Prange, E. Jantzen, J Anal At Spectrom (1995) 10, 105–109
4. J B Graceli et al. Reproductive Toxicology (2013) 36, 40–52
5. E H E Jantzen et. al. J. of Chrom. A (2017), in press.
6. Directive 2013/39/EU of the European Parliament and of the Council, **http://eur-lex.europa.eu/homepage.html**