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Speciation without chromatography

Part I. Determination of tributyltin in aqueous samples by chloride generation, headspace solid-phase microextraction and inductively coupled plasma time of flight mass spectrometry

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An analytical procedure was developed for the determination of tributyltin in aqueous samples. The relatively high volatility of the organometal halide species confers suitability for their headspace sampling from the vapour phase above natural waters or leached solid samples. Tributyltin was collected from the sample headspace above various chloride-containing matrices, including HCl, sodium chloride solution and sea-water, by passive sampling using a polydimethylsiloxane/divinylbenzene (PDMS/DVB)-coated solid-phase microextraction (SPME) fiber. Inductively coupled plasma time-of-flight mass spectrometry (ICP-TOFMS) was used for detection following thermal desorption of analytes from the fiber. A detection limit of 5.8 pg ml^{-1} (as tin) was realized in aqueous samples. Method validation was achieved using NRCC PACS-2 (Sediment) certified reference material, for which reasonable agreement between certified and measured values for tributyltin content was obtained.

Introduction

Speciation analysis of typical compounds of interest such as mono-, di- and tributyltin, monomethylmercury, trimethyl- and triethyllead, *etc.*, has been achieved exclusively by combining chromatographic/electrophoretic separation and element selective detection methods.[1] A significant fraction of such determinations is based on gas chromatographic methods.[2] Because of the relatively low volatility and high polarity of these compounds, direct GC analysis is usually not simple.[3] Most of the methods employ various derivatization techniques, such as hydride generation or alkylation with tetraalkyl borate reagent or by Grignard reagent to transform the ionic species into volatile, GC-compatible compounds.[1] The derivatization process is generally tedious and involves several sample manipulation steps. On the other hand, the process transforms a complex analytical problem of trace element speciation into a relatively simple GC application. As the cost of the analysis of these species is very high, at least from an inorganic analytical viewpoint, it is imperative to develop inexpensive, high-throughput screening methods.

The extremely high selectivity, matrix tolerance and sensitivity of atomic spectrometric detectors typically used in speciation analysis offers the possibility of directly handling complex matrices without major pretreatment. These attributes make such systems formidable chromatographic detectors, but, at the same time, they are somewhat 'over-sized' because most of the matrix separation is performed by chromatography prior to detection. The robustness and selectivity of these systems also permits different approaches for speciation analysis. Following a selective extraction, a targeted analyte can be directly introduced into the detection system. Chromatographic separation of the above mentioned species is relatively simple compared with, for example, analysis of polychlorinated biphenyls (PCB), where 40–50 compounds must be separated during a single GC run using significantly less-selective detectors. By comparison, chromatographic separation of alkyltins from environmental samples encompasses <10 tin-containing compounds, wherein only 3 are routinely analysed! The challenge is whether the role of the chromatographic separation can be incorporated into a well-designed extraction procedure. Results for determination of methylmercury in environmental matrices by combining solid-phase microextraction (SPME) with inductively coupled plasma mass spectrometry (ICP-MS) have recently been presented.[4] The speciation method is based on the selective extraction of the analyte and its direct detection using an atomic spectroscopic system without employing any intervening chromatography. A dedicated thermal-desorption sample introduction port was designed to permit transfer of the collected analyte from the SPME fiber to the ICP-MS instrument. This is fundamentally a small, heated glass- or Teflon-lined desorption chamber (a modified GC injector) mounted on the base of the plasma torch. Desorbed volatile compounds are transferred to the plasma with an argon flow and, because of the proximity of the plasma, no additional heated transfer line is required. The principal advantages of this arrangement are that the sample introduction efficiency is 100% and the plasma operates under dry conditions. The same instrument setup has been used for the determination of metal hydrides[5] and inorganic and organoarsenic chloride species.[6] Because of the transient nature of the sample introduction, ICP-MS with time-of-flight detection is the detector of choice, especially for multielemental studies. This unique sample introduction port also presents a possible approach for the introduction of organic solvents and natural gas condensate samples, which remain an unsolved challenge in the ICP-MS field.

This sample introduction technique also permits analysis of thermally unstable organometallic compounds, compounds having low volatility and compounds with high polarity that

are typically not suitable for GC measurement. In this study, we present some initial data concerning the determination of butyltin by ICP-TOF-MS following headspace SPME sampling and thermal desorption.

Experimental

Reagents

Stock solutions (1000 mg l^{-1}) of tributyltin chloride (TBT), dibutyltin chloride (DBT), monobutyltin chloride (MBT) and inorganic tin were prepared by dissolution of the salts of the pure compounds obtained from Alfa Aesar (Ward Hill, MA, USA). The organotin chlorides were dissolved in methanol, and the inorganic tin solution was prepared in 4 M hydrochloric acid (prepared in-house by sub-boiling distillation of feedstock). Distilled, de-ionized water (DDW, 18 MΩ cm) obtained from a NanoPure system (Barnstead/Thermolyne, Boston, MA, USA) was used for all solution preparation. Working standards were prepared by serial dilution of the stocks in DDW. All solutions were stored in Pyrex bottles under refrigeration until used. A saturated solution of NaCl was stored in a pre-cleaned polypropylene bottle. National Research Council of Canada CRM PACS-2 (Sediment), certified for butyltin content,[7] was selected for analysis to assess the accuracy of the technique.

Instrumentation

An Optimass 8000 ICP-TOF-MS instrument (GBC Scientific Equipment Pty. Ltd., Australia) was used for detection. Fig. 1 schematically illustrates the thermal desorption sample introduction device interfaced with the ICP. The interface was fully described in an earlier report.[4] The SPME fiber, coated with a 65 μm thick partially cross-linked polydimethylsiloxane/divinylbenzene co-polymer, was conditioned and operated at temperatures specified by the manufacturer (Supelco, Bellefonte, PA, USA). The operating conditions for the ICP-TOF-MS system were optimized with solution nebulization. After use with aqueous sample introduction the instrument was switched to gaseous sample introduction and dry plasma conditions using the thermal desorption interface. Using the thermal desorption interface set at a temperature well below the boiling point of the compounds to be vaporized from the SPME fiber (*i.e.*, TBT and trimethyllead using an 80 °C desorption temperature), a very slow desorption was obtained. Using this quasi-steady-state signal, the sample introduction, plasma and mass spectrometer systems were then fine-tuned. The signals arising from xenon impurities found in the argon supply were continuously monitored during all experiments for diagnostic purposes. The day-to-day start up optimization was performed using the ^{129}Xe signal. The optimized experimental conditions used for ICP-TOF-MS detection and SPME extraction are summarized in Tables 1 and 2, respectively.

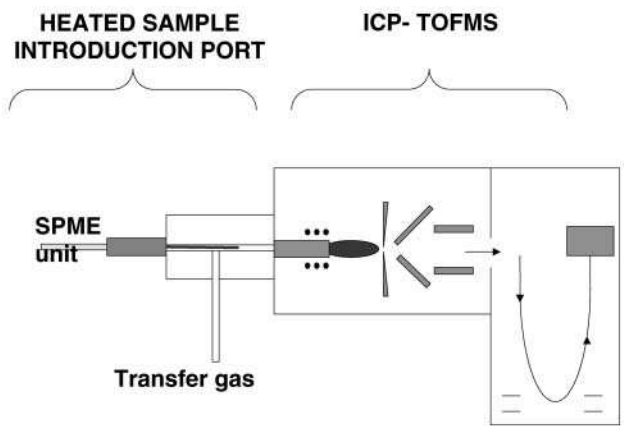

Fig. 1 Schematic of the SPME-TD-ICP-TOF-MS system.

Table 1 ICP-TOF-MS operating conditions

ICP source	
Rf power (27.12 MHz)	1200 W
Plasma gas flow rate	10 l min^{-1}
Auxiliary gas flow rate	1.0 l min^{-1}
Nebulizer gas flow rate	603 ml min^{-1}
Mass spectrometer	
Ion optics	
Skimmer	2900 V
Skimmer base	0 V
Extraction	−900 V
Z1	−900 V
Y mean	−325 V
Y deflection	10 V
Z lens mean	−1350 V
Z lens deflection	−10 V
Lens body	−230 V
Pulse shaping	
Fill	−36 V
Fill bias	1.35 V
Fill grid	38 V
Pushout plate	380 V
Pushout grid	−518 V
Spectral frequency	33 kHz
Reflectron	650 V
Detection	
Multiplier gain	2500 V
Ion threshold	2.0 mV
ADC offset	22.0 mV
Integration window	0.8 u
Measurement mode	Pulse counting

Sample preparation and extraction

Sediment samples (1 g) were leached for 1 h in 40 ml glass vials using 20 ml of 25% acetic acid and subsequently diluted to 60 ml with 2 M HCl. All operations were performed using vials sealed with a Teflon-lined septum cap. The headspace was subsequently sampled by SPME at room temperature using a 4 min exposure time.

Results and discussion

Over the past decade, several methods have been described for active and passive headspace sampling of butyltin species from aqueous samples using purge and trap, cryotrap and SPME methods. However, most of them relied on prior chemical derivatization to produce a more volatile form of the butyltin species. One of the few exceptions noted is a study by Swami and Narang,[8] who attempted to directly sample TBT from seawater by purging it from solution and collecting it in an XAD-2 resin-filled trap. In natural environmental settings, TBT is considered to be non-volatile because of its ionic structure, but it is present in dissociated ionic forms in aqueous systems. However, the dissociation and association constitute an equilibrium process and, depending on the concentration of counter ions and on further conversion of the products, the equilibrium can be shifted in one direction or another. If a fraction of these species remains in an intact molecular form,

Table 2 Conditions of SPME and thermal desorption

Fiber coating	65 μm PDMS/DVB
Extraction time	4 min
Extraction temperature	22 °C
Thermal desorption temperature	270 °C
Transfer gas	Argon
Transfer gas flow rate	25 ml min^{-1}

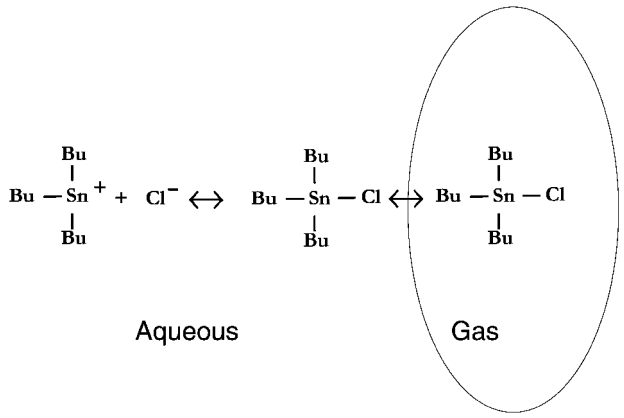

Fig. 2 Simplified transformation process for tributyltin in a chloride-containing aqueous environment.

the question is whether it can escape from the aqueous phase into the vapor phase. By increasing the counter ion concentration (in our case a halide ion, Cl^-) the reaction may be forced in the direction of association as opposed to that of dissociation (Fig. 2).

It is very likely that the reaction involving TBT stops at the formation of Bu_3Sn^+. When the steric effect of the ligands is small, *i.e.*, in the case of trimethyltin chloride, hydrolysis may lead to formation of an R_3SnOH type compound. The latter species is capable of forming a stannoxane dimer (*e.g.*, Bu_3Sn-O-$SnBu_3$). However, the concentration of the tin compound is very low in our samples, and the large steric effect of the 6 butyl ligands probably prevents dimer formation. In contrast, DBT and MBT exhibit a considerably smaller steric hindrance than TBT, and hence the hydrolysis of these species takes place to a greater extent. The resulting compounds having an Sn–OH functional group cannot be detected in the vapour phase for at least two reasons: (1) the presence of the -OH group allows the species to form hydrogen bond(s) with water molecules, making solvation energetically much more favourable than in the case of the original tin compound; and (2) the resulting stannoxane is a much larger molecule than either DBT or MBT, and hence it exerts a negligible vapour pressure as compared to its precursor molecule. Although stannoxane formation is usually much more reversible than siloxane formation, it can be assumed that the cleavage rate of the Sn-O-Sn bond is too low in the time scale of our experiments to allow the accumulation of a detectable amount of tin on the extraction probe.

Hydrolysis of the Bu_3Sn^+ ion takes place according to the following equation:

$$Bu_3Sn^+ + H_2O = Bu_3SnOH + H^+$$

As this reaction produces an acid, it is expected that the hydrolysis is suppressed in hydrochloric acid solution compared to a neutral chloride-rich medium.

To address this issue, a series of experiments were designed. In a closed system, the release rate of TBT was monitored from different aqueous matrices. These matrices included distilled water, 20% m/v sodium chloride solution, sea-water and 2 M HCl. A 20 ml aliquot of a 5 ppb solution of TBT in each of these matrices was placed in a 40 ml septum sealed vial. The solution was vigorously stirred to facilitate the mass transfer. The vapour phase within the vial was sampled with an SPME fiber for 4 min. The results of these experiments are shown in Fig. 3. The high chloride concentration matrices provided very similar responses. However, the possible contact of the polymeric extraction phase with the corrosive HCl solution or with the condensed HCl vapour could lead to early deterioration of the extraction medium. As a consequence, a simple sodium chloride solution was typically used, although

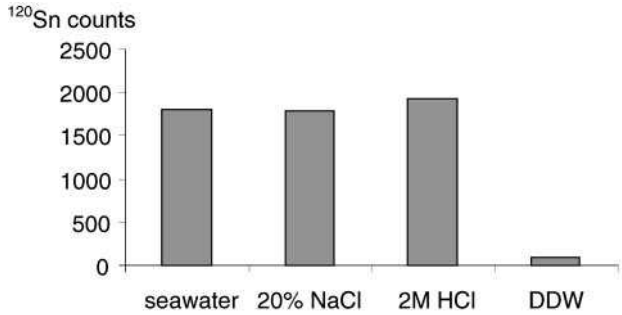

Fig. 3 Signal obtained by headspace sampling above a 5 ppb TBT solution in various matrices.

the fairly concentrated HCl solution led to about an 8% higher response than the NaCl solution, as expected. The effect of sodium chloride concentration in the aqueous phase was studied over the range 1–20% m/v. Although no significant effect on the extraction efficiency of TBT was observed, an optimum condition was found at 5% m/v. Fig. 4 shows the effect of extraction time on the signal intensity under such conditions. Because of the relatively low volatility of TBT-Cl, sampling equilibrium was not attained during an exposure as long as 20 min. For practical reasons, longer extraction times were not considered; actual sampling time can always be tailored to the individual needs for lower detection limits. Most experiments were accomplished by using 3–5 min sampling times.

In the case of headspace sampling, two equilibria are of significance. One establishes the distribution of the analyte between the liquid and gas phase (headspace), and the second one governs the relative concentrations of analyte in the gas phase and the SPME coating. In the present case, the target analyte is a semi-volatile compound. Equilibrium between the gas and the stirred liquid phase is likely to be achieved relatively slowly compared to the equilibrium between the gas phase and the SPME extraction phase. Nevertheless, both processes leading to the extraction are of the first order with respect to the analytical concentration of TBT; hence, the linear relationship between the original TBT concentration and the detector signal is ensured.

Analytical figures of merit

Analytical figures of merit, based on peak area quantification of the transient signal using the ^{120}Sn isotope, are summarized in Table 3 and include the detection limit, limit of quantification (LOQ), sensitivity and precision. All results were generated using synthetic standard solutions, a 4 min SPME fiber exposure time and 5% (m/v) sodium chloride solution at room temperature. A significant advantage of the speciation approach is that the determination is virtually blank free, because the glass vials and containers used contain no volatile tin species. The use of plastic and rubber-coated labware

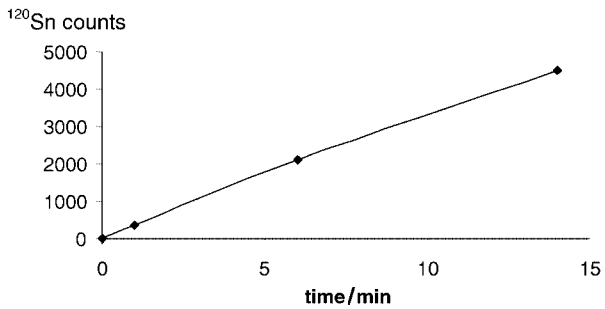

Fig. 4 Response *versus* extraction for TBT (1 ppb) from a 5% NaCl solution at room temperature.

Table 3 Figures of merit

	LOD (3*s*)/pg ml^{-1}	LOQ (10*s*)/pg ml^{-1}	RSD^{a} (%)	Sensitivity^{b}/counts per ng ml^{-1}
Headspace	5.8	19.6	5.6	4500

$^{a}n=5$, using 1 ng ml^{-1} solution. ^{b}14 min sampling time, room temperature, ^{120}Sn isotope.

Table 4 Analytical results

	HPLC-ICP-MS (ref. 9)	SPME-HPLC-ESI- MS (ref. 10)	GC-MS (ref. 11)	SPME-GC-ICP-MS (ref. 12)	SPME-TD-ICP-MS (this study)
DL/pg ml^{-1}	37	50	20	1.1	5.8

should be avoided because organotin compounds are widely used as plasticizers. New SPME fibers contained a significant amount of volatile tin. However, after the conditioning period recommended by the manufacturer, the tin emission from the fiber was not detectable.

The selectivity of the method was studied by comparing the uptake rate of monobutyl- and dibutyltin and inorganic tin (IoSn) from a 5% (m/v) sodium chloride solution using a 4 min SPME headspace extraction. The concentrations of MBT, DBT and IoSn in solution were 2 ppm, 2 ppm and 10 ppm, respectively. As a comparison, a 1 ppb TBT solution was also sampled for the same length of time. The typical instrumental response for the 1 ppb TBT solution was 1800 ± 150 counts. No tin signal was detected from the headspace sampling of 2 ppm MBT and DBT, and 10 ppm IoSn solutions. At NaCl concentrations in excess of 20% (m/v), the signal for DBT reached about 0.3% of that from TBT. No response was obtained from MBT and inorganic tin. The difference in vapor pressure of the butyltin species studied is relatively small compared to the relative concentration of these species present in the headspace above their aqueous solutions. This suggests that the selectivity of the method originates from the efficiency of formation of the butyl- and inorganic tin chloride species. It is evident that TBT-Cl can be more easily formed in aqueous solution than the di- or monosubstituted species and inorganic species. This occurs because dissociation of the original molecule (schematic shown in Fig. 2) is followed by hydrolysis of the tin-containing ion if the steric hindrance is insufficient to prevent this reaction (DBT or MBT). In contrast, the presence of three butyl ligands in TBT stabilizes the ionic form, and the association with a chloride ion can be enforced by applying a high Cl^{-} concentration.

Because the concentrations of the various butyltin species are interdependent through a decomposition chain, it is unlikely that the concentrations of MBT, DBT and TBT in a sample originally containing TBT only could differ by more than three orders of magnitude. Therefore, one may safely assume that the method is sufficiently selective for TBT to be used for quantification of this species in a mixture.

SPME thermal desorption sample introduction of metal species also serves to eliminate most of the interferences normally accompanying continuous vapour generation. SPME sample introduction accomplishes a complete gas–liquid separation. Any possible transport of small droplets (aerosol) from the bulk solution to the plasma, which may arise from the relatively violent reaction between acid and the sample, can be eliminated. The performance of the method was evaluated by analysis of PACS-2 Sediment certified reference material. The average of three TBT determinations was 0.89 ± 0.08 μg g^{-1}. The results are well within the uncertainty range of the certified value (0.98 ± 0.13 μg g^{-1}) despite the presence of 1.09 ± 0.15 μg g^{-1} DBT and 19.8 ± 2.5 μg g^{-1} IoSn.[7]

Table 4 presents a comparison of detection limits for several popular butyltin speciation methods found in the current literature. Detection limits obtained in this study are generally better than those obtained by HLPC-ICP-MS approaches and comparable to those obtained using derivatization-GC-ICP-MS techniques. It should also be noted that the TOF-MS instrument used here is some 100–1000-fold less sensitive than current state-of-the-art quadrupole or sector-field ICP-MS instruments.

Conclusion

The developed method offers a simple and fast speciation technique for aqueous samples. Instead of using 'conventional' chromatographic approaches, the semi-volatile tin species are separated during the sample preparation/sampling process, permitting a sample analysis throughput of about 150 per hour (not counting the sample preparation time). Although the detection technique in this case was ICP-TOF-MS, the sampling technique can be interfaced to any atomic spectroscopic detector and may also be used with selective GC detectors such as the flame photometric detector (FPD). In this study, results were presented only for TBT: however, the method can be extended to include a number of semi-volatile organometal halide compounds including alkylmercury halides, trimethyl- or triethyllead halides, and various selenium and arsenic compounds. This sample introduction technique combines the advantages offered by GC sample introduction, *i.e.*, clean conditions, no dilution and extreme efficiency, with the sample compatibility of HPLC, namely the possibility to analyse aqueous samples directly without chemical modification/volatilization.

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