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Improvement in measurement precision with SPME by use of isotope dilution mass spectrometry and its application to the determination of tributyltin in sediment using SPME GC-ICP-MS

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A method is described for the accurate and precise determination of tributyltin (TBT) by species specific isotope dilution mass spectrometry (ID-MS) using solid phase microextraction (SPME) in combination with gas chromatographic (GC) separation and inductively coupled plasma mass spectrometric (ICP-MS) detection. Butyltin compounds were ethylated in aqueous solution with sodium tetraethylborate and the headspace sampled with a polydimethylsiloxane coated fused silica SPME fiber. The analyte was then directly transferred from the fiber to the head of the GC column for desorption following insertion of the fiber through the heated injection port. Reverse spike ID analysis was performed to determine the accurate concentration of a ^{117}Sn -enriched TBT spike using two well characterized natural abundance TBT standards. A concentration of $0.923 \pm 0.005 \mu\text{g g}^{-1}$ (one standard deviation, $n = 5$) as tin was obtained for TBT in National Research Council of Canada (NRCC) marine sediment PACS-2 using the present method, in good agreement with the certified value of $0.98 \pm 0.13 \mu\text{g g}^{-1}$ (as 95% confidence interval). A TBT concentration of $0.93 \pm 0.09 \mu\text{g g}^{-1}$ (one standard deviation, $n = 5$) as tin in PACS-2 was subsequently determined by standard additions calibration using tripropyltin (TPrT) as an internal standard. An eighteen-fold improvement in the precision of TBT concentration measured using ID was observed, clearly demonstrating its superiority in providing more accurate and precise results as compared to the method of standard additions. A detection limit (3s) of 0.09 ng g^{-1} was estimated for TBT in PACS-2 sediment.

Introduction

Tributyltin has been introduced into the marine environment mainly through its usage as an antifouling agent in paints for ships and boats.^{1,2} The toxicity effects of TBT have been observed on a wide range of marine organisms, particularly gastropod molluscs (snails), in which TBT acts as an endocrine disruptor,^{3,4} even at low ng l^{-1} concentration levels in seawater. The growing concerns over the toxicity of TBT and its dibutyltin (DBT) and monobutyltin (MBT) degradation products entering the environment have led to a dramatic increase in interest in the development of accurate and rapid analytical methods for their determination. Butyltin determinations generally involve several analytical steps, including extraction, derivatization (where GC analysis is involved), separation and detection, each of which can contribute to the difficulty of analysis, degrading the accuracy and precision of the results.^{5–7}

Gas chromatography (GC) and high performance liquid chromatography (HPLC) are currently the most commonly used separation techniques. The popularity of GC separation techniques stems from their high resolution and sensitivity. On the other hand, sample preparation for GC analysis is usually time-consuming, and organic solvents used in the liquid–liquid extraction are toxic. In an effort to simplify sample preparation, while retaining the merits of GC, solid phase microextraction (SPME) was introduced by Pawliszyn and co-workers^{8,9} in the early 1990's. Since 1993, following the commercialization of SPME, this sampling technique has enjoyed widespread acceptance as a consequence of its simplicity, relatively low cost and ease with which analytes can be transferred to the GC column. The drawback noted with this technique is the degraded precision (typically 10% RSD). As the volume of the extraction phase provided by

the fiber is extremely small, any irregularity/inhomogeneity in the polymer phase/surface may result in a significant effect on its extraction characteristics.^{10–11} In addition, some level of degradation of the fiber generally occurs during repeated usage, with the result that accuracy and precision achieved with the SPME technique can be compromised. The imprecision of the results obtained with different fibers often makes it necessary to employ an internal standard or method of standard additions.¹¹ More recently, SPME has been applied to the determination of organotin compounds and has evolved as an elegant, solvent-free sample extraction technique.^{12–21} The precision of results obtained using this technique is typically in the range of 5 to 15% RSD for organotin compounds.^{12–21}

Over the past decade, inductively coupled plasma mass spectrometry (ICP-MS) has often been used as a sensitive and selective detector for butyltin determination when coupled to GC^{12,20,22–28} and HPLC.^{29–32} It is well-known that ICP-MS possesses high sensitivity, a large dynamic range and multi-element capability. Moreover, if two interference free isotopes of a given element are found, the isotope dilution (ID) calibration strategy can be applied, which generally provides superior accuracy and precision over other calibration strategies, including external calibration and standard additions. This arises because a ratio, rather than an absolute intensity measurement, is used for quantitation of the analyte concentration.³³ The ID-MS technique is considered to be a primary method of analysis because of its capability for high accuracy and precision.³⁴ Although ID ICP-MS has been widely used for trace element analysis in a variety of sample matrices, its application to species specific determinations has been limited by the commercial non-availability of species specific enriched spikes.³⁵ If these are available, a number of advantages accrue with ID, including: enhanced precision

and accuracy of results as the species specific spike serves as an ideal internal standard; matrix effects are accounted for since quantitation is done by ratio measurements; non-quantitative analyte recovery does not impact on the final results; and species alteration during sample work-up can be assessed. Only recently has this approach been applied to the determination of butyltin^{24–26,31,32,36} and other species, including organolead,^{31–32,37} methylmercury,^{38–39} Cr (III and VI),³⁵ iodide,⁴⁰ methylselenocysteine,⁴¹ and selenite^{40,42} using synthesized species specific spikes.

The objective of this study was to take advantage of the high accuracy and precision offered by ID in combination with the ease of use and efficiency of sampling of SPME coupled with the superior separation and detection power of GC-ICP-MS for organotin determination. A reverse spike isotope dilution approach was performed to quantify the enriched ¹¹⁷Sn TBT solution used for spiking so as to ensure the quality of the final results. The method was applied to the determination of TBT in National Research Council of Canada PACS-2 marine sediment CRM to demonstrate the high accuracy and enhanced precision offered by ID SPME GC-ICP-MS methodology. To the best of our knowledge, this is the first report of use of the isotope dilution technique to overcome the poor precision associated with SPME sampling using GC separation and ICP-MS detection of organotin in environmental samples.

Experimental section

Instrumentation

The ICP-MS used in this work was a Perkin-Elmer SCIEX ELAN 6000 (Concord, Ontario, Canada) equipped with a Gem cross-flow nebuliser. A custom-made quartz sample injector tube (0.9 mm id) was used. A double pass Rytan® spray chamber was mounted outside the torch box and maintained at room temperature. Optimization of the ELAN 6000 and dead time correction were performed as recommended by the manufacturer.

A Varian 3400 gas chromatograph (Varian Canada Inc. Georgetown, Ontario, Canada) equipped with a DB-1 column (1% phenyl, 99% polydimethylsiloxane, 15 m × 0.32 mm × 1.5 µm) was used for butyltin separations. The GC was coupled to the ICP-MS using a home-made interface and transfer line similar to that reported by Bayón *et al.*,²³ essentially consisting of a 1/4 in od. stainless steel Swagelok® “T” mounted on the top of the GC chassis where a conventional detector would normally be located. The lower arm of the “T” was connected to a concentric assembly of a 90 mm length of 15 mm od brass rod, the latter housed inside the heated GC oven and maintained at 300 °C with the use of the detector temperature controller (no additional heating elements required). This concentric rod, threaded at each end, served as a relatively massive heat sink through which the DB-1 column was passed, as illustrated in Fig. 1. The other arm of the “T” was connected, via a stainless steel reducing union, to a 110 cm length of PTFE tubing (0.02 in id × 1/16 in od) which served to conduct the GC effluent to the ICP-MS injector. The side arm of the “T” was used to admit a stream of unheated Ar carrier gas at a flow rate of 0.5 l min^{−1} to aid in the rapid transfer of eluent to the ICP. The PTFE transfer line was subsequently inserted into the quartz torch injector (terminating 15 mm from the injector tip) and secured with an air-tight Swagelok (1/16 in to 1/4 in) fitting to an adapter mounted on the torch box. Typical operating conditions for the GC-ICP-MS system are summarized in Table 1.

A Microdigest model 401 (2.45 GHz, maximum power 300 W) microwave digester (Prolabo, Paris, France), equipped with a TX32 programmer, was used for microwave assisted extraction of butyltins from the sediment sample.

Fig. 1 Schematic diagram of the GC-ICP-MS interface.

Table 1 GC and ICP-MS operating conditions

GC	
Injection mode	Splitless
Injection volume	1 µl solvent or SPME injection
Injector temperature	250 °C
Column	DB-1 (15 m × 0.32 mm × 1.5 µm)
Carrier gas	He at 26 psi
Oven program	50 °C (1 min) to 250 °C at 15 °C min ^{−1}
Detector temperature	300 °C
ICP-MS	
Rf power	1200 W
Plasma Ar gas flow rate	15.0 l min ^{−1}
Auxiliary Ar gas flow rate	1.0 l min ^{−1}
Nebulizer Ar gas flow rate	0.50 l min ^{−1}
Sampler cone (nickel)	1.00 mm
Skimmer cone (nickel)	0.88 mm
Lens voltage	8.25 V
Scanning mode	Peak hopping
Points per peak	1
Dwell time	40 ms
Sweeps per reading	1
Readings per replicate	6500
Number of replicates	1
Dead time	55 ns

A manual SPME device, equipped with a fused silica fiber coated with a 100 µm film of polydimethylsiloxane (Supelco, Bellefonte, USA), was used for sampling of the ethylated butyltins from the headspace above the aqueous solutions.

A 10 µl liquid sampling syringe (Hamilton Company, Nevada, USA) was used for the injection of isooctane butyltin standard solutions for the optimization of GC-ICP-MS response.

Reagents and solutions

Acetic acid was purified in-house by subboiling distillation of reagent grade feedstocks in a quartz still prior to use. Environmental grade ammonium hydroxide was purchased from Anachemia Science (Montreal, Quebec, Canada). OmniSolv® methanol (glass-distilled) was purchased from EM Science (Gibbstown, NJ, USA). High purity de-ionized water (DIW) was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp, Iowa, USA). Sodium tetraethylborate solution, 2% (m/v), was prepared daily by dissolving NaBEt₄ (Strem, Bischoff, France) in DIW. A 1 mol l^{−1} sodium acetate buffer was prepared by dissolving an appropriate amount of sodium acetate (Fisher Scientific, Nepean, Ontario, Canada) in water and adjusting the pH to 5 with acetic acid.

Tributyltin chloride (96%) and tripropyltin chloride (95%) were purchased from Alfa Products (Danvers, MA, USA). Individual stock solutions of 1000–1500 $\mu\text{g ml}^{-1}$ as tin were prepared in methanol and kept refrigerated until used. The concentrations of TBT standards were characterized as described previously³⁶ and then used for reverse spike ID analysis of a ^{117}Sn enriched TBT spike. The natural abundance TBT working standard solutions (2.05 and 1.99 $\mu\text{g ml}^{-1}$) were prepared by diluting the stock solutions with methanol. A 1.00 $\mu\text{g ml}^{-1}$ tripropyltin (TPrT) solution was prepared by diluting the stock solution in methanol for use as an internal standard.

A ^{117}Sn enriched TBT stock solution (97% purity), with isotopic compositions and uncertainties provided at a nominal concentration of 90.5 $\mu\text{g g}^{-1}$ in methanol, was provided by the Laboratory of the Government Chemist (LGC, Teddington, UK). A working solution containing 0.40 $\mu\text{g ml}^{-1}$ as tin was prepared by volumetric dilution of the stock in methanol. From previous experience, although the uncertainty contribution from volume measurements is usually larger than the uncertainty arising from mass, but the overall uncertainty contributions from dilutions by volume remain insignificant compared to the total combined uncertainty characterising the overall procedure.³⁶ Thus, for simplicity in sample preparation, all dilutions were conducted by volume. The concentration of this spike solution was verified by reverse spike isotope dilution against the natural abundance TBT standard.

The marine sediment CRM PACS-2 (NRCC, Ottawa, Canada) was used as a test sample for method development. This material is certified to contain $0.98 \pm 0.13 \mu\text{g g}^{-1}$ TBT (as tin).

Sample preparation and analysis procedure

Experiments for isotope dilution determination of TBT in PACS-2 and reverse spike isotope dilution for quantitation of the ^{117}Sn enriched TBT solution were conducted on two consecutive days. During day 1, six reverse spike isotope dilution calibration samples were prepared in a clean room (class-100) to minimize any possible contamination, and were analyzed using GC-ICP-MS. In brief, a 0.150 ml volume of ^{117}Sn enriched TBT spike solution and 0.250 ml of 2.05 $\mu\text{g ml}^{-1}$ (or 1.99 $\mu\text{g ml}^{-1}$) natural abundance TBT solution were accurately pipetted into a vial. After 10 ml of 1 mol l^{-1} NaAc buffer solution, 1 ml of 2% NaBEt₄ and 2 ml of isooctane were added, the mixture was manually shaken for 5 min. After separation of the phases, the isooctane layer was transferred to a small glass vial. A mass bias correction solution was prepared in the same way using 0.25 ml of 2.05 $\mu\text{g ml}^{-1}$ natural abundance TBT standard. All samples were immediately injected onto the GC for ICP-MS analysis following extraction and derivatization.

The sediment extraction procedure used in this study has been described elsewhere.^{29,36} Three sample blanks and five samples of PACS-2 were prepared at the same time. In brief, 0.5 g PACS-2 spiked with 0.250 ml of a ^{117}Sn enriched TBT and 10 ml of acetic acid were heated in a Prolabo microwave digester at 60% power for 3 min. The contents were transferred to centrifuge tubes and centrifuged at 2000 rpm for 5 min. Only a 50 μl volume of the supernatant (due to the high sensitivity of SPME GC-ICP-MS) was transferred to a 50 ml glass vial for quantitation. After 10 ml of 1 mol l^{-1} NaAc buffer solution, 0.05 ml ammonium hydroxide, 10 ml of DIW and 1 ml of 2% NaBEt₄ were added, the vial was capped with a PTFE coated silicon rubber septum. The SPME needle was inserted through the septum and headspace sampling was performed for 10 min. During the extraction, the solution was vigorously stirred with a Teflon coated magnetic stir bar. The collected analyte was then desorbed from the SPME fiber onto the GC column.

A one minute desorption time at an injector temperature of 250 °C ensured complete desorption from the fiber.

Following injection of the sample onto the GC, data acquisition on the Elan 6000 was manually triggered. Both ^{117}Sn and ^{118}Sn were simultaneously monitored. The mass bias solution was introduced between samples to permit a mass bias correction factor to be determined. At the end of the chromatographic run, the acquired data were transferred to an off-line computer for further processing using in-house software to yield both peak height and peak area information. In this work, only peak areas were used to generate $^{118}\text{Sn}/^{117}\text{Sn}$ ratios, from which the analyte concentration in the sediment was calculated.

Results and discussion

GC-ICP-MS interface and optimization of GC-ICP-MS

An easily removable interface has earlier been designed by Bayón *et al.*²³ for coupling GC with ICP-MS and has been successfully applied for butyltin speciation. The interface used in this study, with small modifications (without any additional heating blocks for the interface), is similar to that reported by Bayón *et al.*,²³ as described earlier in the experimental section. Optimisation of the ELAN 6000 and dead time correction were first performed as recommended by the manufacturer using a standard liquid sample introduction system. The plasma was then extinguished and the spray chamber and nebulizer assembly replaced with the transfer line and its adapter. The final optimization of lens voltage, rf power and Ar carrier gas flow for dry plasma conditions was quickly performed by monitoring the ^{120}Sn intensity over the last portion of the chromatographic run during the column cleaning cycle (holding temperature at 270 °C) following injection of 1 μl of a 1000 ng ml^{-1} butyltin standard in isooctane.

It is worth noting that the length of the transfer line had little effect on either the butyltin peak shape or sensitivity due to the very short residence time of the analyte in the transfer line under the chosen flow rate of Ar carrier gas. Therefore, for ease of handling of the GC-ICP-MS, a 110 cm long PTFE tube was used for the final work. A significant influence of the distance between the injector tip and the end of the transfer line on the resulting sensitivity was, however, observed. Optimum sensitivities for all three butyltins were achieved at distances between 10 and 20 mm, sensitivities decreasing at greater or shorter distances. A 15 mm distance was therefore chosen for this study. As shown in Fig. 2, good resolution and peak profiles for all three ethylated butyltins were obtained under optimized conditions using this home-made interface and transfer line. The peak widths for the butyltin compounds ranged between 2 and 4 seconds at 10% height, comparable to those obtained by conventional GC detectors under the given temperature programme.

Reverse isotope dilution for the quantitation of ^{117}Sn enriched TBT spike solution

More accurate and precise results can be obtained if isotope dilution and reverse ID experiments are performed the same day, following the sequence developed by Watters *et al.*,⁴³ wherein a spiked sample and reverse spike isotope dilution sample are bracketed between mass bias drift correction solutions. Unfortunately, this cannot be achieved in the same day due to the time required for all measurements. Thus, reverse ID analysis was conducted first on the first day. To achieve best accuracy and precision for the ratio measurement, the mass bias correction solution was repeatedly injected onto the GC-ICP-MS between reverse spike ID samples. The following equation was used to calculate the concentration

Fig. 2 Chromatogram of a mixed natural abundance standard solution obtained by GC-ICP-MS; 100 pg each of TBT, DBT and MBT injected in 1 μ l iso-octane.

of the ^{117}Sn enriched TBT spike:

$$C_y = C_z \frac{m_z}{m'_y} \frac{B_{xz} R'_n - A_{xz}}{A_y - B_y R'_n} \frac{AW_y}{AW_{xz}}$$

where C_y is the ^{117}Sn enriched TBT concentration ($\mu\text{g ml}^{-1}$) as tin in the spike; C_z is the TBT concentration ($\mu\text{g ml}^{-1}$) as tin in the natural abundance TBT standard; m_z is the volume (ml) of natural abundance TBT standard used; m'_y is the volume (ml) of spike used to prepare the blend solution of spike and natural abundance TBT standard solution; A_y is the abundance of the reference isotope (^{118}Sn) in the spike; B_y is the abundance of the spike isotope (^{117}Sn) in the spike; A_{xz} is the abundance of the reference isotope in the sample or in the standard; B_{xz} is the abundance of the spike isotope in the sample or in the standard; R'_n is the measured reference/spike isotope ratio (mass bias corrected) in the blend solution of spike and natural abundance TBT standard; AW_y is the atomic weight of the analyte in the spike; and AW_{xz} is the atomic weight of analyte in the sample or standard. A concentration of $0.4075 \pm 0.0034 \mu\text{g ml}^{-1}$ as tin (one standard deviation, $n = 6$) was obtained for the ^{117}Sn enriched TBT spike solution. This value was later used to quantitate the TBT concentration in PACS-2.

Results for TBT in PACS-2 using ID SPME GC-ICP-MS

As noted earlier, ID ICP-MS is capable of compensating for any loss of analyte during sample manipulation, suppression of ion sensitivities by concomitant elements present in the sample matrix and for instrument drift. In order to achieve accurate and precise results, an interference free isotope pair must be available for ratio measurements, care must be taken to avoid any contamination during the process, and an optimum measurement procedure must be used to achieve accurate ratio measurements.

Equilibration between the added spike and the endogenous analyte in the sample is a prerequisite for achieving accurate results using isotope dilution techniques. Results would be biased low if equilibration between the spike and the sample was not achieved during the ratio measurements (with the spike being recovered with greater efficiency). Although direct proof of equilibration being achieved between the spike and the sample remains elusive, the effect of sample mass on spike recovery can be used to help elucidate this process.

Experiments on spike recovery were fully reported previously.^{29,36} Despite the difference in the spike recoveries obtained (100% at sample weight of 0.5 g and 83% at 2.0 g), there was no significant difference in TBT concentrations measured in PACS-2 using standard additions calibration. These data suggest that the added spike fully mimics the analyte in the sample during the microwave extraction process, as equilibration between the added spike and the endogenous TBT in the sample has been achieved.

In a subsequent experiment, the $^{118}\text{Sn}/^{117}\text{Sn}$ ratio from TBT was measured in an unspiked PACS-2 extract using SPME GC-ICP-MS to investigate possible interferences from $^{102}\text{Pu}^{116}\text{O}^+$ and $^{102}\text{Pd}^{116}\text{O}^+$, $^{101}\text{Pu}^{116}\text{O}^+$ and $^{234}\text{U}^{2+}$ on the isotopes selected for measurement. A mass bias corrected ratio of 3.163 ± 0.024 (one standard deviation, $n = 5$) obtained in unspiked PACS-2 is not significantly different from the expected natural abundance ratio of 3.154. This observation confirmed that no significant spectroscopic interference on either isotope arises from the sample matrix, permitting accurate results to be obtained using the chosen isotope pair.

The final analysis of TBT in PACS-2 was performed using SPME GC-ICP-MS with isotope dilution calibration. As shown in Fig. 3, good separation of all three major butyltin species present in the PACS-2 sediment was achieved under the chosen experimental conditions. All sample blanks and spiked samples were analyzed immediately after they were prepared. To achieve optimum accuracy and precision for the ratio measurement, the mass bias correction solution was repeatedly introduced between spiked samples. The mass bias correction factor was calculated using the expected ratio divided by the ratio measured in the TBT mass bias correction solution. The following equation was used for the quantitation of TBT in PACS-2:

$$C_x = C_y \frac{m_y}{wm_x} \frac{A_y - B_y R_n}{B_{xz} R_n - A_{xz}} \frac{AW_{xz}}{AW_y}$$

where C_x is the TBT concentration ($\mu\text{g g}^{-1}$) as tin based on dry mass; C_y is the concentration ($\mu\text{g ml}^{-1}$) as tin of ^{117}Sn enriched TBT in the spike; m_y is the volume (ml) of spike used to prepare the blend solution of sample and spike; m_x is the mass (g) of sample used; w is the dry weight correction factor; A_y is the

Fig. 3 Chromatogram obtained with sampling of an ethylated extract of ^{117}Sn TBT spiked PACS-2 using SPME GC-ICP-MS. First black trace: ^{118}Sn , the ^{117}Sn trace was shifted 25 s for clarity.

abundance of the reference isotope (^{118}Sn) in the spike; B_y is the abundance of the spike isotope (^{117}Sn) in the spike; A_{xz} is the abundance of the reference isotope in the sample or in the standard; B_{xz} is the abundance of the spike isotope in the sample or in the standard; R_n is the measured reference/spike isotope ratio (mass bias corrected) in the blend solution of sample and spike; AW_y is the atomic weight of the analyte in the spike; and AW_{xz} is the atomic weight of the analyte in the sample or in the standard. A TBT concentration of $0.923 \pm 0.005 \mu\text{g g}^{-1}$ (one standard deviation, $n = 5$) as tin was obtained in PACS-2, in good agreement with the certified value of $0.98 \pm 0.13 \mu\text{g g}^{-1}$ (as 95% confidence interval) as tin.

For convenience, SPME sampling was conducted in a regular fumehood. An average concentration of $0.00041 \pm 0.00003 \mu\text{g g}^{-1}$ (one standard deviation, $n = 3$), obtained from three sample blanks, is insignificant compared to the TBT concentration in PACS-2. This confirmed that contamination was effectively under control during sample preparation. The blank was subtracted from the gross TBT concentration measured in PACS-2.

The detection limit for the ID SPME GC-ICP-MS technique was calculated using three ^{117}Sn TBT spiked sample blank measurements. A value of 0.09 ng g^{-1} was estimated, based on three times the standard deviation of measured concentrations normalized to a 0.5 g sample and a 0.05 ml subsample of the acetic acid extract. It is worth noting that this detection limit could, in principle, be improved 200-fold if the entire 10 ml extract was used.

It is of interest to determine the absolute amount of TBT sampled by the SPME fiber under the chosen experimental conditions. Based on a comparison of intensities obtained from a TBT standard in iso-octane injection and the SPME sampling in a PACS-2 extract, as shown in Figs. 1 and 2, this was estimated to be 250 pg. In other words, about 10% of the total TBT in the extract (2450 pg) was removed by the SPME fiber.

Results for TBT in PACS-2 using standard additions calibration with SPME GC-ICP-MS

A subsequent comparative analysis of PACS-2 sediment was undertaken using the method of standard additions for calibration with SPME GC-ICP-MS. A 10 min headspace sampling time did not permit extraction equilibrium to be reached, but this period was sufficient to yield acceptable intensities. The linearity of the calibration curve was tested under the chosen experimental conditions. Additions of approximately 1- and 2-fold of the TBT concentration in the sediment were made. A spike of 50 ng of TPrT was added to all samples as an internal standard. Quantitation of TBT was based on the ratios obtained from the intensity of ^{118}Sn of TBT peak area divided by TPrT peak area. The correlation coefficient of the standard additions calibration curve for TBT in the concentration range of $0 \sim 3 \mu\text{g g}^{-1}$ was 0.99998. The final analysis of the PACS-2 sediment was performed using five replicate samples based on only one addition. Each spiked sample was prepared by adding approximately the same mass of TBT as expected in the PACS-2 subsample. A mean concentration of $0.93 \pm 0.09 \mu\text{g g}^{-1}$ (one standard deviation, $n = 5$) was obtained, in good agreement with the certified value.

As expected, the precision of 0.54% RSD for TBT measured in PACS-2 using isotope dilution SPME GC-ICP-MS was significantly better than the precision of 9.7% RSD obtained using standard additions calibration. An 18-fold improvement was achieved, clearly demonstrating the superior capability of the ID technique for improvement of the precision of SPME sampling for TBT determination in PACS-2.

Conclusion

An accurate and precise method has been developed for the determination of TBT in sediment using ID SPME GC-ICP-MS. A significant improvement in the precision of TBT determination in PACS-2 using ID, as opposed to standard additions calibration, was obtained, clearly demonstrating its superior capability in overcoming the generally poor precision associated with the SPME sampling technique. The described method should be well suited not only for butyltin certification work, but for improvement in the methodology used for organometallic speciation in general when SPME sampling is used.

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