Determination of Butyltin Compounds in Environmental Samples by Isotope Dilution GC-MS

Application

Environmental

Authors

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Abstract

A GC-MS with electron impact ionization was used for the development of a speciation method for the simultaneous determination of monobutyl-, dibutyl-, and tributyltin in environmental samples (waters, sediments, and biota). The method is based on the use of a mixed spike containing ^{119}Sn-enriched monobutyltin (MBT), dibutyltin (DBT), and tributyltin (TBT) for isotope dilution analysis. The mixed ^{119}Sn-enriched spike was applied to the simultaneous determination of MBT, DBT, and TBT in waters, sediments, and mussel tissue samples with satisfactory results. A single injection allows the concentration of all three butyltin compounds in the sample to be computed quickly using standard spreadsheet software.

Introduction

Recently, the EU has included TBT in the list of compounds to be measured regularly in fresh waters. Thus, analytical methods for the determination of organotin compounds should provide enough sensitivity, selectivity, and accuracy to be applied routinely by testing laboratories. Most reported methods so far combine a separation technique such as gas chromatography (GC) hyphenated to element-specific detection systems, including atomic absorption spectrometry (AAS), flame photometric detection (FPD), mass spectrometry (MS), or inductively coupled plasma mass spectrometry (ICP-MS).

Isotope dilution (ID) methodologies, on the other hand, can produce superior accuracy and precision compared to more common calibration strategies provided that the first solid-liquid extraction step is quantitative or true isotope equilibration between the added spike and the analyte is achieved. Since quantitation is done by ratio measurements, subsequent nonquantitative analyte recoveries do not affect the final results. Identification for trace element speciation has been widely applied using ICP-MS for detection after HPLC or GC separation. However, ICP-MS is an expensive and not generally available instrument and similar results can be obtained with standard GC-MS instrumentation using electron impact ion sources. This application describes this analytical method, which could be applied routinely by testing laboratories.

Experimental

Reagents

Tributyltin (TBT) chloride (96%), dibutyltin (DBT) dichloride (96%), and monobutyltin (MBT) trichloride (95%) were obtained from Aldrich (Steinheim, Germany). Stock solutions were prepared by dissolving the corresponding salt in a 3:1 mixture of acetic acid (Merck, Darmstadt, Germany) and methanol (Merck). All organometallic standards solutions were kept in the dark at –18 °C and diluted working solutions were prepared by weight daily before the analysis. Acetic acid (Merck) and methanol (Merck) were used for the extraction of the organotin compounds from the solid matrices. Ethylation of the butyltin species was performed using sodium tetraethylborate (Galab, Geesthacht, Germany).

The spike solution (^{119}Sn-enriched butyltin mixture) was obtained from ISC-Science (Oviedo, Spain), diluted by weight with a mixture of methanol and acetic acid (3:1), and stored in the dark at –18 °C. Table 1 shows the isotopic composition as well as the concentration of the butyltin species in the spike solution.

Table 1. Isotope Composition and Concentration of MBT, DBT, and TBT in the ^{119}Sn-Enriched Butyltin Mix (Uncertainty Corresponds to 95% Confidence Interval)

Isotopic composition					
Isotopes	116	117	118	119	120
Abundance (%)	0.029	0.114	14.33	82.40	3.127
Uncertainty	0.008	0.005	0.12	0.15	0.032

Concentration (µg Sn / g)		
MBT	**DBT**	**TBT**
0.121 ± 0.005	0.748 ± 0.009	1.019 ± 0.017

Reference materials tested were PACS-2 purchased from National Research Council of Canada (NRCC) (Ottawa) and CRM 477 obtained from Bureau Communautaire de Référence (BCR). Sea and fresh water samples were spiked with natural abundance butyltin compounds to check for recovery.

Instrumentation

Chromatographic analysis was performed with an Agilent Technologies gas chromatograph model 6890N, fitted with a split/splitless inlet and an HP-5MS capillary column (cross-linked 5% phenyl methyl siloxane, 30 m × 0.25 mm id × 0.25 µm coating). The gas chromatograph was equipped with an Agilent mass spectrometric detector model 5973 Network MSD (quadrupole based).

Helium was employed as the carrier gas with a constant flow of 1.2 mL/min. The column temperature was initially held at 60 °C for 1 min, increased at 30 °C/min to a final temperature of 300 °C. Injection was performed using a split/splitless inlet in splitless mode. The transfer line and ion source temperatures were at 280 °C and 230 °C, respectively. Electron impact ionization was performed at an electron energy of 70 eV. A mass range from *m/z* 40 to 400 was recorded in the full-scan mode to check for spectral interferences. The measurement of isotope ratios for each butyltin compound was performed on the M-29 molecular ion (loss of an ethyl group) using 10-ms dwell-time per mass. Five *m/z* values were used for the selective ion monitoring (SIM) mode for each butyltin compound. Daily optimization of the GC-MS conditions was performed using the "autotune" option of the software supplied with the GC-MS instrument. For this purpose, perfluorotributylamine (PFTBA) was used as the tuning compound for all GC-MS autotunes, because it provides ions at 31, 50, 69, 100, 131, 219, 264, 414, 464, 502, 576, and 614 amu. Using this option, mass calibration and sensitivity optimization over the entire mass range was performed using the *m/z* 69, 219 and 502.

Procedures

Extraction and Derivatization of Organotin Compounds from Sediments

Approximately 0.2 g of sample was spiked with a diluted solution of the ^{119}Sn-enriched mixture of MBT, DBT, and TBT. A 4-mL mixture of acetic acid and methanol (3:1) was immediately added. The resulting slurry was exposed to ultrasound (30 W) for 8 minutes. A volume of 200 µL of the extract was derivatized as described below.

Extraction and Derivatization of Organotin Compounds from Mussel Tissue

Approximately 0.2 g of sample was spiked with a diluted solution of the ^{119}Sn-enriched mixture of MBT, DBT, and TBT. A 4-mL mixture of acetic acid and methanol (3:1) was immediately added. The resulting slurry was heated in a water bath at 37 °C for 1 hour. A volume of 250 µL of the extract was derivatized as described below.

Derivatization of Sn Compounds

Ethylation of the tin species was carried out in 7 mL clear glass vials with screw caps (Supelco, Bellefonte, PA). The pH was adjusted to 5.4 with

4 mL of 1 M acetic acid/sodium acetate buffer. Ethylation was performed using 0.5 mL of 2% w/v sodium tetraethylborate in 0.1 M NaOH. After 10 min of manual shaking, the organic layer was transferred to a glass vial and stored at –18 °C until measurement. The organic layer was then evaporated under a gentle stream of nitrogen to approximately 10 µL. Finally, 1 µL was injected in the GC instrument.

Extraction and Derivatization of Organotin Compounds from Water Samples

A sample of 100 mL of seawater is measured in a precleaned all-glass volumetric flask and mixed with a diluted solution of the mixed ^{119}Sn-enriched spike. In order to correct for volumetric errors, the amounts of sample and spike added were controlled gravimetrically. The spiked sample was shaken manually and left to equilibrate for 15 min prior to derivatization. Then, 1 mL of acetate buffer, to adjust the pH to 5.4, and 100 µL of a 2% w/v sodium tetraethylborate in 0.1M NaOH were added for the ethylation of the organotin compounds. Finally, 1 mL of hexane was introduced into the flask in such a way that it remained in the narrow neck of the flask. All these procedures can be performed under clean-room conditions to reduce the blank levels. The volumetric flasks were shaken manually for 10 min, the phases allowed to separate, and most of the organic layer was transferred to a 2-mL chromatographic vial with the help of a Pasteur pipette. Then, the hexane phase was evaporated under a gentle stream of nitrogen to approximately 10 µL. Finally, 1 µL of this volume was injected in the GC instrument.

Results and Discussion

Isotope Ratio Measurements by GC-MS

While elemental isotope ratios can be easily obtained with ICP-MS, in GC/MS the isotopic pattern in molecular ions is different from that of the naturally occurring elements due to the contributions from the organic groups attached to the metal because of the presence of ^{13}C. The contribution of ^{13}C to the observed m+1 and m+2 ions can be calculated in a fairly straightforward way, by applying equations 1 and 2:

$$I_{m+1} = I_m \cdot nX_{13_C} \quad (1)$$

$$I_{m+2} = I_m \cdot 1/2 \cdot n(n-1)^2 \cdot X^2{}_{13_C} \quad (2)$$

where x_{13_C} is the relative abundance of ^{13}C with respect to ^{12}C (0.0111/0.9899), n is the number of C atoms in the molecular ion and I is the intensities of the ions m, m+1 and m+2, respectively. The contributions to m+1 and m+2 of the butyltin compounds were corrected by monitoring five molecular ions for each analyte, corresponding to the ^{116}Sn, ^{117}Sn, ^{118}Sn, ^{119}Sn, and ^{120}Sn isotopes. The measured signal intensities at the different masses were corrected taking into account the ^{13}C contributions to m+1 and m+2. The intensity (I) correction equations used were:

$$^{116}Sn = {}^{116}I \quad (3)$$

$$^{117}Sn = {}^{117}I - x(^{116}Sn) \quad (4)$$

$$^{118}Sn = {}^{118}I - x(^{117}Sn) - y(^{116}Sn) \quad (5)$$

$$^{119}Sn = {}^{119}I - x(^{118}Sn) - y(^{117}Sn) \quad (6)$$

$$^{120}Sn = {}^{120}I - x(^{119}Sn) - y(^{118}Sn) \quad (7)$$

Where x is the contribution factor m+1 and y the contribution factor m+2. The contributions of ^{114}Sn and ^{115}Sn can be neglected owing to their very low natural abundances, and therefore the signal intensity measured for ^{116}Sn can be considered free of m+1 and m+2 contributions. The selected molecular clusters for the measurement of MBT, DBT, and TBT by GC-MS and the contribution factors x and y are given in Table 2. The selected molecular cluster for TBT (*m/z* = 287 to 291) in the sample, spike, and mixture can be observed in Figure 1.

Table 2. Monitored Masses and Contribution Factors for MBT, DBT, and TBT

Corresponding tin isotope	MBT ($BuEt_2Sn^+$)	DBT (Bu_2EtSn^+)	TBT (Bu_3Sn^+)
116	231	259	287
117	232	260	288
118	233	261	289
119	234	262	290
120	235	263	291
x (M + 1)	0.088	0.110	0.132
y (M + 2)	0.0038	0.0060	0.0086

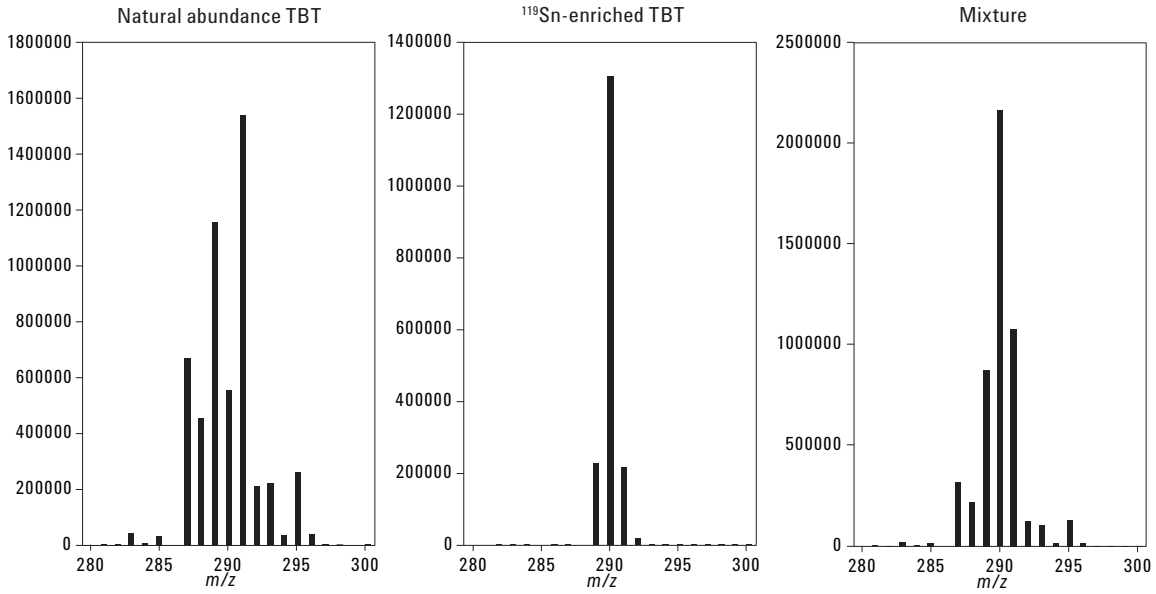

Figure 1. TBT mass spectra for the selected molecular clusters (*m/z* = 287 to 291) in the sample, spike, and mixture.

Analytical Characteristics of the Method

The analytical characteristics of the method are listed in Table 3. Method detection limits were calculated as three times the standard deviation of the blanks after measuring the concentration of MBT, DBT, and TBT in nine blank replicates by isotope dilution analysis following the methodology given in the procedures. The reproducibility of the method was studied by analyzing a natural seawater sample containing approximately 10 ng/kg of TBT. Recovery studies for seawater analysis were performed at three different levels to cover the range of concentrations that could be found in the real samples. The two high levels were obtained by addition of a natural MBT, DBT, and TBT standard to a real sample of coastal seawater (low content of butyltins) and the low level by addition of the natural standard to an artificial seawater sample. As can be observed, quantitative recoveries were obtained for all compounds at all concentration levels studied.

Table 3. Analytical Characteristics of the Method for the Analysis of Seawater Samples

			MBT	DBT	TBT
Limit of detection (3 σ) (ng/Kg)			0.2	0.1	0.2
Limit of quantification (10 σ) (ng/Kg)			0.8	0.5	0.7
Reproducibility (% RSD) (n = 9)			1.4	1.6	2.8
Recoveries (%)					
Sample Concentration (ng/Kg)					
Artifical seawater	2	(n = 3)	98 ± 7	101 ± 2	102 ± 9
Seawater	20	(n = 3)	103 ± 3	97 ± 2	104 ± 1
Seawater	100	(n = 3)	101 ± 2	98 ± 2	101 ± 3

Analysis of reference materials

Mono-, di- and tributyltin were determined in two reference materials: a sediment (PACS-2) and a mussel tissue (CRM 477), by the proposed ID procedure. Three independent spiking experiments were made on each certified reference material and each sample was injected three times in GC-MS systems. The overall results obtained for the two reference materials by GC-MS are summarised in Table 4 (PACS-2) and Table 5 (CRM 477).

The concentration values for TBT and DBT obtained for PACS-2 (Table 4) were within the certified range (890 ± 105 ng/g for TBT and 1047 ± 64 ng/g for DBT). Values found for MBT were substantially higher than the original certified value (450 ng g^{-1}) at the time the analyses were made. Recently, PACS-2 was recertified for MBT and the new "recommended value" for MBT is 600 ng/g – close to the values found by our method. The corresponding results obtained for CRM-477 certified mussel tissue (Table 5) show an excellent agreement between the certified and found values for each individual butyltin species.

Table 4. Determination of MBT, DBT, and TBT in PACS-2 Using the 120/119 Isotope Ratio for Quantitation; data in ng/g as Sn

Replicate	MBT	DBT	TBT
1	623 ± 2	1022 ± 7	872 ± 9
2	605 ± 4	971 ± 10	863 ± 2
3	617 ± 17	996 ± 1	849 ± 10
Average	**615 ± 9**	**996 ± 25**	**849 ± 10**
RSD (%)	1.5	1.5	1.5
Certified values	*600**	*1047 ± 64*	*890 ± 105*

**information value only due to lack of independent methods*

Table 5. Determination of MBT, DBT, and TBT in CRM- 477; data in ng / g as Sn

Replicate	MBT	DBT	TBT
1	1154 ± 9	761 ± 7	816 ± 6
2	1173 ± 18	766 ± 3	817 ± 2
3	1207 ± 19	787 ± 4	841 ± 2
Average	**1178 ± 27**	**772 ± 14**	**825 ± 14**
RSD (%)	2.3	1.9	1.7
Certified values	*1014 ± 182*	*786 ± 61*	*902 ± 78*

Conclusions

A fast, precise, and accurate method for the simultaneous determination of mono-, di-, and tributyltin in water, sediments, and mussel tissue has been developed. The detection at masses corresponding to ^{116}Sn and ^{117}Sn permits one to correct for the m+1 and m+2 contributions of ^{13}C on the ^{118}Sn, ^{119}Sn, and ^{120}Sn masses with simple mathematical equations. A single injection allows the concentration of all three butyltin compounds in the sample to be computed quickly without the need for time-consuming calibration, standard addition or recovery correction procedures. The method corrects for all possible errors in the speciation of butyltin compounds, provides extremely low detection limits, and is fast and simple to apply by non-trained personnel. The price of the enriched spike is no longer a limitation as a single determination in water samples requires less than 2 ng of the enriched compounds. In brief, the proposed ID-GC-MS technique appears to be a practical alternative to other measurement procedures, such as GC-AED or GC-FPD. The results obtained by this method are similar to those obtained by GC-ICP-MS.

The advantages provided by the proposed methodology are not only the less expensive instrumentation and high-quality analytical results, but also a drastic minimization of the time required both in the sample preparation steps and in the analytical measurement. Using such isotope dilution analysis methods and a GC-MS equipped with an autosampler, more than 15 samples can be analyzed by one operator per day from sample reception to analysis report. These advantages have been demonstrated in practice with the implementation of the proposed methodology in several routine testing laboratories and its subsequent accreditation according to the requirements of UNE-EN ISO/IEC 17025 by the Spanish National Accreditation Body.

References

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