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Isotope dilution analysis as a definitive tool for the speciation of organotin compounds

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Different spike solutions available for the determination of butyltin compounds by isotope dilution analysis are described and applied for the determination of butyltin compounds in PACS-2 certified reference material. Additionally, those spike solutions were evaluated during the course of an interlaboratory exercise organised by the National Research Council of Canada and the Laboratory of the Government Chemist (UK) in order to quantify tributyltin in a pilot sediment. The aim of this project was to evaluate the capabilities of isotope dilution mass spectrometry to reduce the uncertainty in the certification of Reference Materials for the speciation of organotin compounds. All participants were supplied with a ^{117}Sn-enriched TBT solution from the Laboratory of the Government Chemist (UK). In our case, we performed the analysis of the pilot sediment also using a ^{119}Sn enriched spike (mixed mono-, di- and tributyltin) and a ^{118}Sn–^{119}Sn double spike. The use of these additional spike solutions not only allowed the determination of monobutyltin and dibutyltin in the pilot sediment but also the evaluation and correction of possible extraction-derived rearrangement reactions. An excellent agreement amongst our results and between the participants was obtained with a precision of 8.4% RSD at a level of *ca.* 80 ng TBT g^{-1} (as Sn).

Introduction

As it is well known, tributyltin (TBT) is used as a pesticide, fungicide and wood preservative. Due to its use as a biocide additive in paints, aimed at protecting ship hulls from fouling organisms[1] it is widespread today in the marine environment. When TBT is released into the aquatic environment it decays rapidly to less toxic degradation products (dibutyltin and monobutyltin) by the presence of microorganisms (biodegradation) and photolysis.[2] Nevertheless, it can accumulate in sediments, where the degradation processes are much slower, with estimated half-lives of several years.[3] TBT is a highly toxic substance, identified as a priority pollutant in waters by the EU. Its endocrine disrupting power can induce imposex in some gastropods at concentration levels lower than 1 μg m^{-3} (ppt) in seawaters.[4] Additionally, dibutyltin (DBT) and monobutyltin (MBT) are also employed as PVC stabilizers or catalysts and these uses represent more than 60% of the organotin compounds global production.[3] In summary, butyltin compounds are widespread pollutants which have to be monitored today in different environmental compartments.

The reliable quantification of organotin compounds in environmental samples is still a difficult task. The low concentration levels in which these compounds occur in the environment require the use of different derivatisation, extraction and clean-up procedures which are necessary to preconcentrate and separate those compounds from interfering substances. Also, when analysing solid samples, strong leaching procedures have to be applied which assure quantitative extraction of those compounds from the solid. Under those conditions, interconversion reactions may take place adding a new component to the already large uncertainty in the analytical procedure. It is clear that the quality control of speciation analysis must be performed in such a way that it provides verification of the accuracy of the whole analytical measurement procedure. In this sense, the use of Certified Reference Materials (CRMs)[5] is the most common tool employed for this purpose. Of course, the number of "speciated" CRMs has increased over the last years. However, their production in this field of speciation analysis is still very limited and do not cover the needs of testing laboratories[6,7] in the frame of new and emerging regulations and directives.

The production and certification of CRMs is normally a very slow, expensive[6] and complicated process as the strict rules described in ISO guide number 35 have to be followed.[8] As reported by Quevauviller,[9] the certification of matrix CRMs (natural unknown or partially known matrix in which the amount of a certain number of substances are certified) can be carried out by three possible approaches: (1) Certification within one laboratory using a so-called "definitive" method. (2) Certification within one laboratory using two or more independent methods by two or more independent analysts. (3) Certification by many laboratories using one or several different methods, possibly including "definitive" methods.

The first two approaches, even using definitive methods, do not eliminate the risk of systematic errors. Therefore the best way to perform the certification of a CRM is to resort to interlaboratory studies where definitive methods are of great help in identifying and eliminating sources of error.

Definitive methods, such as isotope dilution mass spectrometry (IDMS), have been scarcely used till now to certify matrix CRMs for speciation analysis (in the case of speciation of organotin compounds only one laboratory used isotope dilution during the certification campaigns of BCR 477 and BCR 710).[10,11] However, IDMS is achieving an increasing importance in this field, as reflected by the number of recent publications[12–22] and can constitute a viable alternative to CRMs for validating speciation procedures. The high accuracy and precision provided by IDMS with one enriched isotope can be used to correct for most of the systematic errors involved in speciation analysis.[23] Additionally, "double spike" (two enriched isotopes) approaches have been already described[13–15] allowing not only the simultaneous determination of the different species but also the correction of possible rearrange-

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ment reactions improving the accuracy of speciation analysis procedures. Therefore, although certification of matrix CRMs through IDMS would not give an estimation of the uncertainty achievable by more classical methods,[9] a certification performed by interlaboratory studies using only definitive methods would be an extremely useful tool in terms of accuracy.

In the case of speciation of organotin compounds in sediments all possible analytical errors can be incurred during the analytical procedure. For example, a large number of extraction procedures have been described but the real efficiency of these methods is generally unknown and hardly comparable.[24] In the last few years we have developed different procedures for the speciation of organotin compounds by IDMS using different species-specific enriched spikes. The use of such spike solutions has allowed not only the accurate, precise and simultaneous determination of mono-, di- and tributyltin in sediment[25,26] and water samples[27] but also the evaluation of different extraction techniques for the analysis of sediments.[28,29] However, specific interlaboratory studies for the quantitation of butyltin compounds by IDMS have not been previously performed. The invitation by the NRCC (National Research Council of Canada) and the LGC (Laboratory of the Government Chemist, UK) to participate in an interlaboratory study for the determination of TBT in a pilot sediment has provided an excellent opportunity to validate in a definitive manner the different organotin spikes prepared in our laboratory. Results obtained with ^{119}Sn MBT, DBT and TBT and with enriched ^{118}Sn and ^{119}Sn spike (synthesised in our laboratory) are compared here with quantitative results obtained using ^{117}Sn TBT (supplied by the LGC for the intercomparison) in our laboratory and in other laboratories around the world.

Experimental

Instrumentation

A Hewlett Packard (Palo Alto, CA, USA) gas chromatograph model 6890, fitted with a split/splitless injector and a HP-5 capillary column (cross linked 5% phenyl-methyl siloxane, 30 m × 0.32 mm × 0.25 μm thickness), was used for the separation of the organotin species. The gas chromatograph was coupled to a HP-4500 inductively coupled plasma mass spectrometer (Yokogawa Analytical Systems, Tokyo, Japan) using the transfer line described in detail previously.[30] For the extraction of the organotin compounds from the sediments with methanol–acetic acid, a high intensity titanium ultrasonic processor (Sonics and Materials Inc., Danbury, USA) and a microwave oven, model 1200 (Milestone, Socisole, Italy), equipped with middle pressure PTFE vessels were used.

Reagents and materials

Tributyltin chloride (96%), dibutyltin dichloride (97%) and monobutyltin trichloride (95%) were obtained from Aldrich (Steinheim, Germany). Stock solutions were prepared by dissolving the corresponding salt in methanol (Merck, Darmstadt, Germany). All organometallic standards solutions were kept in the dark at 4 °C and diluted working solutions were prepared daily before the analysis in methanol. A mixture of acetic acid (Merck) and methanol (Merck) 3:1 was used for the extraction of the organotin compounds from the solid matrix. Ethylation of these species was performed using sodium tetraethylborate (Strem Chemicals, Bisheim, France).

Solid ^{119}Sn-enriched and ^{118}Sn-enriched tin metal were purchased from Cambridge Isotope Laboratories (Andover, MA, USA) and a solution of ^{117}Sn-enriched tributyltin was supplied by the Laboratory of the Government Chemist (Teddington, UK). The synthesis of the ^{119}Sn-enriched mixture of MBT, DBT and TBT has been described in a previous publication[26] and the preparation of the double spike (^{118}Sn DBT and ^{119}Sn MBT and TBT) in ref. 28. Both the PACS-2 CRM and the P-18 pilot sediment were supplied by the Institute for National Measurement Standards of the National Research Council of Canada (Ottawa, Canada).

Procedures

Solid–liquid extraction conditions. A sample weight of 0.35 g of the P-18 pilot sediment, and 0.25 g of the PACS-2 sediment was selected to assure sample to sample homogeneity. Samples were spiked with an appropriate amount of the enriched spike and, immediately, 1 ml of methanol and 3 ml of acetic acid were added in (a) 10 ml glass vials (ultrasonic extraction) or (b) middle pressure PTFE vessels (microwave assisted extraction). When the ultrasonic extraction was used, the samples were introduced in the ultrasonic processor and the titanium finger set 5 mm inside the liquid. The slurries were then exposed to ultrasounds at 50 W for 8 min, left to cool down to room temperature and, finally, 200 μl of the final extract were ethylated as described below. When using microwave assisted extraction the slurries were exposed to microwaves at 150 W for different times (from 30 s to 15 min) and 200 μl of the final extract were also ethylated.

Ethylation, separation and determination by GC-ICP-MS. Ethylation of the tin species was carried out in PFA-stoppered glass test tubes for 200 μl samples. The pH was adjusted to 5.4 with 3 ml of a 1 M acetic acid/sodium acetate buffer and ethylation was performed with 1 ml of 2% w/v sodium tetraethylborate in 0.1 M NaOH. Finally, 1 ml of hexane was added for liquid–liquid extraction. After 10 min of manual shaking the organic layer was transferred to a glass vial and stored at −18 °C until GC-ICP-MS measurement.

Typical operating conditions and features of these determinations by GC-ICP-MS have been described elsewhere.[25,26] Daily optimisation of the ion lenses of the mass spectrometer was performed after the connection of the GC to the ICP-MS, by using $^{38}Ar^{40}Ar^{+}$ and ^{202}Hg signals in the ICP-MS.

Measurement of isotope ratios using GC-ICP-MS. Three replicates of each sample were injected in all experiments. Integration of the chromatographic peaks was carried out using the commercial GC-MS Agilent software supplied with the ICP-MS instrument. Isotope ratios were always computed as peak area ratios. The integration time per isotope selected was 66 ms. Isotopes measured were 118, 119 and 120 when using the ^{119}Sn-enriched spike and the double spike, and 117, 118, 120 when using the ^{117}Sn-enriched tributyltin. In this way, the total integration time, 200 ms, was short enough to be able to follow accurately the chromatographic peak profile. Mass bias was corrected by bracketing of a natural butyltin standard mixture of MBT, DBT and TBT between each triplicate of samples.

Results and discussion

Single isotope spikes composition

Single isotope spikes may contain one or several of the species of interest isotopically labelled with the enriched isotope. These spikes can be extremely useful when no rearrangement or degradation reactions between the species occur during the course of the analytical procedure.

Two single isotope spikes have been synthesised in our laboratory: a ^{118}Sn-enriched dibutyltin[25] and a multispecies

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spike (mono-, di- and tributyltin mixture) enriched in ^{119}Sn.[26] Such spikes, synthesised by direct butylation of enriched metallic tin, had been already successfully applied to the analysis of organotin compounds in sediments.[25,26] Obviously, when using the ^{118}Sn-enriched dibutyltin it is only possible to analyse natural dibutyltin. Conversely, the multi-species-^{119}Sn-enriched spike allows for the simultaneous determination of the three butyltin compounds (*e.g.* it was applied for the development of a routine procedure for the analysis of extremely low levels of butyltin compounds in water samples[27] by direct derivatisation and liquid–liquid extraction). The third single isotope spike available is a ^{117}Sn-enriched tributyltin solution which can be obtained from the LGC, Teddington, UK.

Fig. 1 shows the comparative chromatograms obtained by GC-ICP-MS for both, the major natural tin isotope (mass 120) and each of the enriched isotopes. As can be observed, the isotopic abundance for mass 120 is clearly different from that for the corresponding enriched isotope in all the spikes. The ^{118}Sn enriched spike (Fig. 1a) shows to contain mainly DBT with traces of MBT and TBT. The ^{117}Sn-enriched spike (Fig. 1d) contained both TBT and DBT and the ^{119}Sn-enriched spike (Fig. 1b) contained all three butyltin compounds. The isotopic composition of the different tin species for each spike was the same, within measurement uncertainty, and they are given in Table 1 in comparison with the isotope composition of natural tin.

"Double" spike composition

The double spike was prepared by isolating MBT and TBT from the ^{119}Sn-enriched mixture and mixing them with an appropriate amount of the ^{118}Sn-enriched dibutyltin.[28] Fig. 1c shows the GC-ICP-MS chromatogram of this spike at masses 118, 119 and 120. It can be observed that MBT and TBT are isotopically labelled with the isotope of mass 119 whereas DBT is labelled with that of mass 118. The isotopic composition of this spike is also indicated in Table 1. The mathematical equations developed for this spike[28] allowed both the determination of the correct content of TBT, DBT and MBT in the sediment and the calculation of the decomposition factors F_1 (decomposition of TBT to DBT) and F_2 (decomposition of DBT to MBT).

Selection of the extraction technique for sediments

Both single and double isotope spikes have been applied for the evaluation of different extraction techniques for the analysis of butyltin compounds in sediments in previous works.[25,26,28,29] Comparative results for MBT, DBT and TBT speciation in PACS-2 CRM are summarised in Table 2. As can be observed, the results obtained for DBT and TBT with any of the different spikes tested and extraction techniques used were within the certified range. For the case of MBT, however, the agreement was only good when using mechanical shaking as extraction technique. Higher results were obtained using both ultrasonic, microwave assisted and accelerated solvent extraction. The fact that similar elevated results for MBT in PACS-2 have been reported by other authors[20,22,31] seems to indicate that a re-evaluation of this CRM in terms of MBT is needed. From these results it is apparent also that MBT seems to be bound more strongly that DBT and TBT to the sediment and so harsher extraction conditions are needed to extract MBT quantitatively from the sediment. No significant differences between the single and double spike results observed were apparent using mechanical shaking and ultrasonic extraction.

As stressed before, the double spike procedure allows the evaluation of possible degradation reactions of the species during extraction. Table 2 shows also the decomposition factors

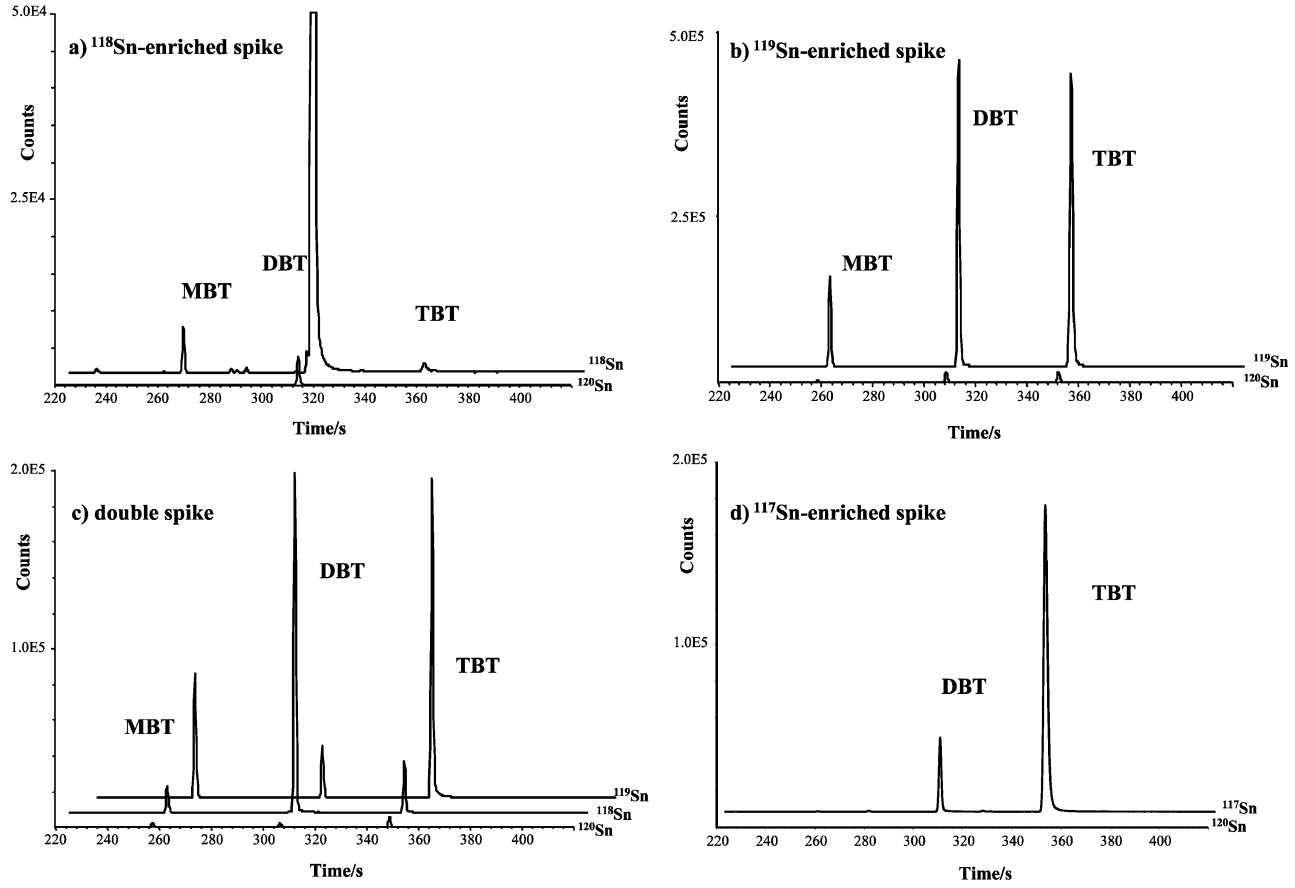

Fig. 1 GC-ICP-MS chromatograms of the spike solutions available for the intercomparison study.

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F_1 (TBT to DBT) and F_2 (DBT to MBT) found for the different extraction techniques tested.[28,29] Ultrasonic extraction and mechanical shaking proved not to promote degradation of the species while degradation factors up to 16% for DBT to MBT and 7% for TBT to DBT were observed when using microwave assisted extraction. Using accelerated solvent extraction, only a maximum of 3% degradation of DBT to MBT was detected. Based on these previous results[28,29] the single isotope spikes were evaluated just by using ultrasonic extraction under routine analytical conditions (8 min of extraction at 50 W) for this intercomparison exercise. The double spike was also tested using microwave assisted extraction at 150 W microwave power with increasing extraction times in order to evaluate the degradation factors for this sediment.

Analysis of the pilot sediment

The international interlaboratory study for the quantitation of tributyltin (TBT) in a pilot sediment was jointly organised by the Institute for National Measurement Standards of the National Research Council of Canada (Ottawa, Canada) and the Laboratory of the Government Chemist (Teddington, UK). Eleven laboratory participants were supplied with a 4 ml volume of ^{117}Sn-enriched TBTCl to be used by those wishing to conduct IDMS calibration. Detailed information about the participants of the round robin and the whole set of results obtained (in each laboratory) can be found in a recent report.[32] Here we will compare our results with the average values obtained by all those participants employing the definitive method of IDMS for quantification (9 laboratories).

The intercomparison exercise for the quantitation of TBT in the pilot sediment was carried out in our laboratory by IDMS using three different spikes: the ^{117}Sn-enriched TBT spike supplied by the LGC, the ^{119}Sn-enriched mixture of MBT, DBT and TBT and the ^{118}Sn-^{119}Sn double spike described before. In this way, the three butyltin species in the sediment could be determined by the additional two spikes for validation purposes. Moreover, the extent of possible rearrangement reactions during the whole speciation procedure could be monitored by the double spike.

First, the ^{117}Sn and ^{119}Sn single-isotope spikes were assayed: the GC-ICP-MS chromatograms of the spiked pilot sediment for each of the two single isotope spikes studied independently are given in Fig. 2: as can be observed in Fig. 2a for the 117 spike and Fig. 2b for the 119 spike inorganic Sn, MBT, DBT and TBT were present in the pilot sediment at measurable quantities. No other organotin compounds were detected in the chromatograms.

The results obtained for MBT, DBT and TBT in the pilot sediment using the ^{119}Sn-mixed spike after ultrasonic extraction

Table 1 Isotopic composition (% abundance) of the spike solutions available

Single isotope spikes				
Isotope[a]	Natural tin	^{118}Sn-DBT	^{119}Sn-MBT, DBT, TBT (average)	^{117}Sn-TBT
116	14.54	0.07	0.03	7.54
117	7.68	0.13	0.11	**92.23**
118	24.22	**98.44**	14.33	0.18
119	8.59	0.69	**82.40**	0.02
120	**32.58**	0.62	3.13	0.03
122	4.63	0.03	< 0.01	< 0.01
124	5.79	0.02	< 0.01	< 0.01

DOUBLE SPIKE			
Isotope	MBT	DBT	TBT
116	< 0.01	< 0.01	< 0.01
117	0.150	0.129	0.118
118	17.13	**86.69**	13.86
119	**79.73**	12.23	**83.08**
120	2.988	0.949	2.936

[a] Isotopes 112, 114 and 115 below 0.01% in all cases.

Table 2 Summary of the results obtained from PACS-2 CRM using different extraction techniques[a]

					Maximum Degradation Factors	
Technique	Spike	MBT	DBT	TBT	F_1	F_2
Mechanical shaking[26]	119-Single	0.51 ± 0.02	1.01 ± 0.03	0.86 ± 0.03	—	—
Mechanical shaking[28]	Double	0.52 ± 0.02	1.06 ± 0.03	0.90 ± 0.03	No	No
Ultrasonic extraction[28]	Double	0.63 ± 0.03	1.04 ± 0.05	0.92 ± 0.02	No	No
Ultrasonic extraction (this work)	119-Single	0.56 ± 0.06	1.02 ± 0.13	0.86 ± 0.11	—	—
Microwave assisted extraction[28]	Double	0.64 ± 0.04	1.06 ± 0.01	0.91 ± 0.06	7%	16%
Accelerated solvent extraction[29]	Double	0.63 ± 0.03	1.00 ± 0.07	0.93 ± 0.03	No	3%
Certified Values		***0.45 ± 0.05***	***1.09 ± 0.15***	***0.98 ± 0.13***		

[a] Uncertainty corresponds to 95% confidence interval.

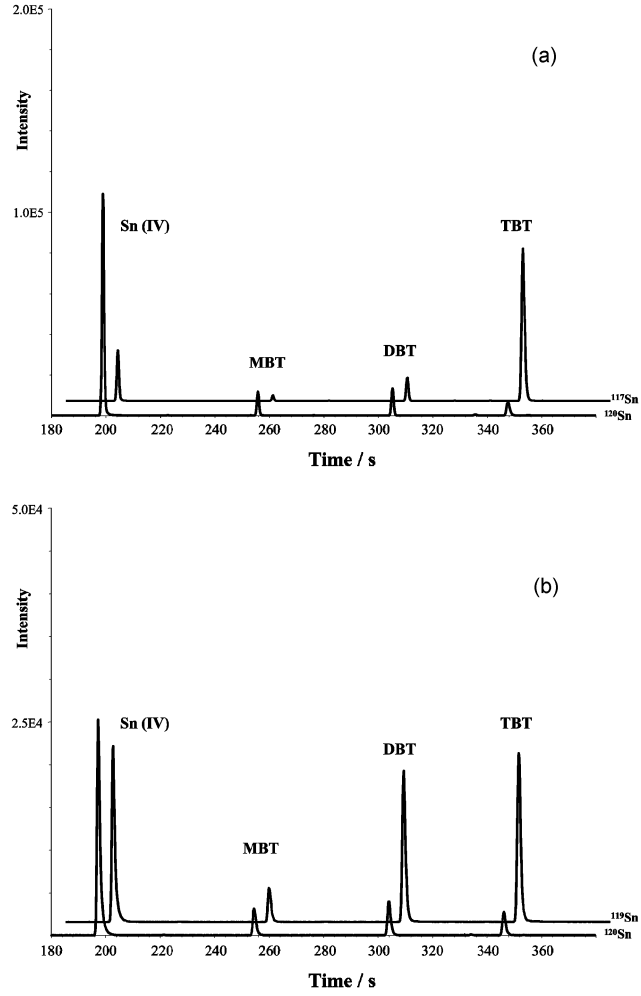

Fig. 2 (a). Pilot sediment spiked with LGC ^{117}Sn-enriched spike. (b). Pilot sediment spiked with our ^{119}Sn-enriched spike.

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with a methanol–acetic acid mixture are given in Table 3. Ten independent sample extractions were performed in four different days and every sample was injected three times in the GC-ICP-MS system. The combined standard uncertainties for each sample extraction were calculated following the ISO guide[33] and are also given in Table 3 (an example of the calculation of the uncertainty for replicate 1 is given in Table 4 and will be discussed later). The total combined uncertainty on the measurements was calculated by combining the uncertainty for each sample replicate with the uncertainty in the average (standard deviation of the ten replicates divided by square root of 10) which may come from lack of homogeneity of the material or lack of reproducibility in the extraction procedure. The contribution of the uncertainty of each replicate to the total uncertainty was computed using the law of propagation of errors. The combined standard uncertainty on the average was calculated using the equation:

$$U(C_s) = \sqrt{\frac{s(\bar{x})^2}{10} + \sum \frac{s(x_i)^2}{10}} \quad (1)$$

where $s(\bar{x})$ is the standard deviation of the average of the ten measurements and $s(x_i)$ is the uncertainty of each individual measurement. The obtained values were multiplied by 2 (for a coverage factor of 2) and are included in the last line of Table 3. In our case, the contribution of the uncertainty in each individual measurement was much smaller than the standard deviation of the mean of the 10 independent measurements. For example, for TBT the standard deviation of the 10 replicates was 1.30 and, after including the uncertainty for the individual measurements, it increased to only 1.40. The same occurred for MBT and DBT indicating that the uncertainty in the individual measurements was not the main source of uncertainty of the total analytical procedure.

The uncertainty budget was calculated for all samples. As an illustration the results calculated for "replicate 1" are given in Table 4 (the calculation of the concentration of the spike and its uncertainty was performed by reverse isotope dilution analysis as described previously).[26] As can be observed, the most important contributors to the total uncertainty were the uncertainty in the concentration of the spike and the measurement of the ratio R_m in the sample extract blend. For MBT the uncertainty of the spike concentration was most important while for DBT the measurement of the ratio R_m in the blend was the predominant factor. For TBT both the uncertainty in the spike and the measurement of R_m were the predominant sources of uncertainty. However, when comparing the individual uncertainty values with the uncertainty of the mean we see that the main source of uncertainty seems to be sample preparation (or sample homogeneity).

Table 5 compares final results obtained in our laboratory (for organotins speciation in the pilot sediment) with the three different spikes employed. In this table the uncertainty is expressed only as standard deviation to be able to compare all results as no uncertainty budgets were available for the double spike. As can be observed, the values obtained in our laboratory for TBT (employing two different solid–liquid extraction techniques) are well in agreement with each other and with the mean of the participants. The data given for the double spike were obtained after microwave assisted extraction using different extraction times from 0.5 to 15 min. No significant differences were observed even for the lower extraction time of 0.5 min for all three butyltin species. Finally, the results obtained from all laboratories by IDMS showed an excellent agreement among them since the standard deviation obtained from all results reflect differences up to ±6.9 ng g^{-1} at the very low TBT levels (80.4 ng g^{-1}) of the pilot sediment, being the precision of the determination 8.4% RSD (1*s* data). This value is comparable to that obtained in the certification of PACS-2 CRM (a sediment containing 10 fold higher TBT concentrations).

Table 4 Uncertainty budget for replicate 1 in the analysis of the pilot sediment using the ^{119}Sn enriched spike

	Relative standard uncertainties of		
	MBT	DBT	TBT
Concentration of spike	0.024	0.019	0.0084
Abundance of ^{120}Sn natural	0.0028	0.0028	0.0028
Abundance of ^{119}spike	0.0018	0.0018	0.018
Sample weight	0.0005	0.0005	0.0005
Spike weight	0.0005	0.0005	0.0005
R_{sp}	0.0005	0.0020	0.0040
R_s	0.0014	0.0004	0.0002
R_m	0.012	0.045	0.013
$U(C_s)/C_s$	0.0271	0.0486	0.0164
Combined uncertainty $U(C_s)$	**2.5**	**5.2**	**1.2**

Table 5 Final results obtained in the analysis of the pilot sediment using three different spike solutions (mean ± std dev)

	MBT	DBT	TBT
^{117}Sn-enriched TBT (n = 11)	—	—	72.5 ± 5.4
^{119}Sn-enriched MBT,DBT,TBT (n = 10)	93.9 ± 4.5	105.1 ± 3.6	75.6 ± 4.1
Double spike (n = 5)	101.5 ± 3.1	108.8 ± 2.2	78.3 ± 5.4
Mean of the participants	—	—	*80.4 ± 6.9*

Table 3 Final results obtained in the analysis of the pilot sediment using the ^{119}Sn-enriched spike

	MBT		DBT		TBT	
Replicate	Result/ng g^{-1} as tin	Combined standard uncertainty	Result/ng g^{-1} as tin	Combined standard uncertainty	Result/ng g^{-1} as tin	Combined standard uncertainty
1	90.3	2.5	106.4	5.2	72.9	1.2
2	93.6	3.9	106.0	2.7	80.1	2.3
3	90.7	2.3	104.2	2.5	71.3	1.5
4	87.9	2.6	101.4	2.2	76.3	1.8
5	90.9	2.9	99.4	2.1	72.9	1.9
6	91.3	2.8	106.1	2.2	73.3	1.0
7	101.8	3.4	112.3	2.4	84.8	2.5
8	97.7	2.7	104.2	2.1	75.2	1.0
9	98.1	2.5	108.3	2.2	75.9	1.0
10	97.3	3.0	102.7	2.2	72.8	1.1
Average	**93.9**		**105.1**		**75.6**	
Combined standard uncertainty (k = 2)	**3.4**		**2.9**		**2.8**	

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Table 6 Degradation factors obtained in PACS-2 CRM and in the pilot sediment using microwave assisted extraction with the double spike

	F_1(%)		F_2(%)	
Extraction time/min	PACS-2[28]	Pilot sediment	PACS-2[28]	Pilot sediment
0.5	0.6	0.6	0.3	1.8
2	1.3	0.9	1.6	1.7
8	2.4	1.6	3.9	1.9
12	4.5	4.6	9.5	2.0
15	6.9	5.7	16.1	2.9

The use of the double spike allowed the calculation of the degradation factors obtained by applying the mathematical equations previously developed.[28] The degradation factors found here for the pilot sediment are compared with those obtained previously, under similar extraction conditions, for the PACS-2 sediment[28] in Table 6. As can be observed, the degradation factors F_1 (which reflect the decomposition of TBT to DBT) were similar in both sediments while the degradation factors F_2 (which reflect the decomposition of DBT to MBT) in the pilot sediment were clearly lower than those obtained in PACS-2. The relevance of these findings and their relation with the influence of the matrix of the sediment on the final quantitative speciation results deserves further investigation.

Conclusions

The capabilities of isotope dilution analysis in the species-specific spiking mode for the speciation of butyltin compounds have been demonstrated in our laboratory for the last three years,[25–29] in other laboratories around the world[17,19–22] and during this interlaboratory study.[32] As IDMS will correct for TBT degradation reactions, regardless of the spike or extraction technique used, all spikes tested performed well for the determination of TBT and so the developed method could be considered as a definitive method for TBT. However, the use of double or even triple spikes (each species enriched in a different isotope) will be required for future intercomparison studies where all three butyltin species need to be determined and species interconversion could be a source of error.

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