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Evaluation of Accelerated Solvent Extraction for Butyltin Speciation in PACS-2 CRM Using Double-Spike Isotope Dilution-GC/ICPMS

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Pressurized liquid extraction using the accelerated solvent extractor (Dionex ASE 200) has been evaluated for the determination of mono-, di- and tributyltin (MBT, DBT, and TBT, respectively) in PACS-2 certified reference material. A double-enriched spike containing ^{119}Sn-enriched MBT and TBT and ^{118}Sn-enriched DBT allowed for the simultaneous determination of the three butyltin species and the factors governing species interconversion. The stability of the spike was evaluated by reverse isotope dilution experiments covering more than one year with satisfactory results. Quantitative recoveries using ASE for TBT and DBT were obtained at temperatures above 110 °C. The effect of the extraction time and number of static cycles was evaluated. Results suggest that extraction efficiency was quantitative with extraction times as low as 10 min for all butyltin species at 110 °C. Decomposition reactions were only detected at the higher temperatures assayed (140 and 175 °C) and that was only for the degradation of DBT to MBT (∼4%). The results found for MBT were ∼25% higher than the certified value for the PACS-2 sediment reference material in agreement with previous results obtained by ultrasonic and microwave assisted extraction.

The reduction of sample preparation time and costs for routine environmental analysis has been investigated worldwide in the past few years. New extraction techniques such as microwave[1] and ultrasonic[2] assisted extractions and, lately, accelerated solvent extraction[3] (ASE) have been developed to reduce both extraction time and solvent usage when the leaching of organic compounds from solids is carried out. In the particular case of ASE, extractions are performed at high temperatures (50−200° C) and pressures (5−200 atm) involving short extraction times. Moreover, this modern technique allows for unattended extraction of up to 24 solid samples, providing filtered extracts ready for analysis. All these advantages makes ASE one of the most promising choices in environmental routine analysis, and it has been applied to different organic pollutants in a wide range of environmental matrixes[4] and polymeric samples.[5] Many previous publications have demonstrated the high efficiency of ASE for the extraction of organic pollutants in comparison with that of Soxhlet, sonication,[6] supercritical fluid extraction,[7,8] or microwave-assisted extraction.[9] However, the applications of ASE to the extraction of organometallic compounds are scarce,[10−12] and much work remains to be done to evaluate its efficiency in comparison with other more popular extraction techniques (e.g., microwave- and ultrasonic-assisted extractions) and to assess possible degradation reactions of the analyte species at such high temperatures and pressures. On the other hand, the search for validation approaches in trace element speciation is becoming an urgent need,[13] particularly in environmental issues.

Tri-, di- and monobutyltin (TBT, DBT, and MBT, respectively) are today important target compounds in the environment due to their high toxicity and tendency to accumulate in sediments.[14,15] As favorable sequential degradation of TBT[16,17] into the less toxic DBT, MBT, and Sn(IV) is hindered by the low-oxygenated

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environment of the sediment,[18] the toxic TBT species can remain up to 10 times longer bound to the sediment than in the water column. Therefore, the accurate determination of butyltin species in sediments is mandatory to be able to assess TBT environmental risk in a given area.

In this sense, it is well recognized that the choice of a suitable extraction technique is essential to attain reliable data for organometallic speciation from solid samples.[19] This fact becomes particularly critical for the determination of labile compounds (e.g., butyltin species in very complex environmental matrixes such as sediments). The selection of a powerful hybrid technique (for instance, GC/ICPMS) would allow for highly selective, precise, sensitive, and even rapid species determinations. However, the results obtained will not be accurate if the initial solid−liquid extraction performed is nonquantitative or promotes degradation of the compounds.[20] In fact, a soft extraction technique could lead to incomplete extraction of the organometallic species from the solid while a harsher choice could produce species degradation reactions.[1] In both cases, the speciation results obtained will not reflect the actual speciation existing in the solid sample. Therefore it is of great importance to be able to study this critical step when the potential of new or alternative solid extraction techniques are being investigated. To do so, it is imperative so far to resort to using a "spike" solution containing the different species under scrutiny isotopically labeled with different isotopes in such a way that any rearrangement reaction during extraction would lead to drastic changes in the isotope abundances measured for the different species. So far, this methodology has been successfully applied to the speciation of Cr,[21,22] Hg,[23,24] and Sn[25,26] compounds. In this way, the additional degrees of information provided by this multilabeled−multispecies spike approach would allow us not only to obtain the correct species concentrations but also to calculate the degradation factors from one species into another, if decomposition occurred.[25] Moreover, the possibility of detecting and compensating for species degradation opens the way for using harsher extraction conditions while looking into whether quantitative extraction recoveries of the different species from the solid matrix have been attained. Such extraction studies would be better carried out by applying isotope dilution (ID) methodologies as most errors occurring in speciation analysis can be compensated.[27,28] The high uncertainty usually associated with speciation results using standard calibration strategies would hide possible variations of the extraction efficiencies obtained by operating under different solid−liquid extraction conditions. In fact, the combination of a highly sensitive and multi-isotopic hybrid technique, such as GC/ICPMS, with speciated multilabeled spikes, as mentioned above, has been proved most valuable for validating different solid extraction strategies for trace element speciation in organotin environmental analysis. [25,26]

Accelerated solvent extraction has been previously reported for the extraction of butyltin compounds from solid samples.[10−12] Unfortunately, optimization of experimental extraction conditions was carried out on spiked samples. Moreover, no studies on possible degradation reactions were performed.[10,11] Hence, as an extension of our previous work,[25] we investigate and validate here the use of ASE for the extraction of butyltin compounds from PACS-2 and the corresponding degradation factors under different extraction conditions are calculated. The results will be compared with previous data obtained by the more common ultrasonic- and microwave-assisted solid−liquid extractions.[25]

EXPERIMENTAL SECTION

Instrumentation. A Hewlett-Packard (Palo Alto, CA) 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 coating), 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.[29]

For the extraction of the organotin compounds from the sediments with a methanol−acetic acid mixture, an accelerated solvent extractor (ASE 200, Dionex Corp., Sunnyvale, CA) was used.

Caution: *safety guidelines regarding work with high temperature and pressure should be observed.*

Reagents and Materials. Ethylation of butyltin species was perfomed using sodium tetraethylborate from Galab (Geesthacht, Germany). ^{119}Sn-enriched and ^{118}Sn-enriched tin metal were purchased from Cambridge Isotope Laboratories (Andover, MA). A ^{118}Sn-enriched DBT standard,[27] was used without further treatment and mixed with ^{119}Sn-enriched MBT and TBT[28] (obtained after preparative liquid chromatography as described elsewhere[25]) to obtain the double spike. The isotopic composition and concentration of the different species in this spike was evaluated by reverse isotope dilution analysis. The sediment reference material tested was PACS-2 purchased from NRCC (Ottawa, ON, Canada).

Caution: *butyltin compounds are toxic materials. Sodium tetraethylborate decomposes rapid in the presence of air and light and it is also extremely flammable.*

Procedures. Ethylation, Separation, and Detection by GC/ICPMS of the Tin Compounds. Ethylation of the tin species using sodium tetraethylborate and typical operating conditions used for GC/ICPMS detection have been described elsewhere.[25−28] The daily optimization of the GC/ICPMS was performed, after connection of the GC to the ICPMS, by using ^{202}Hg (present as an impurity in the Ar used to maintain the plasma) and $^{40}Ar_2^+$ signals.

GC/ICPMS Isotope Dilution Procedure. Isotope ratios were always computed as peak area ratios. Integration of the chro-

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matographic peaks was carried out using the commercial GC/MS Agilent software supplied with the ICPMS instrument. Data acquisition parameters were optimized previously.[30] The integration time per tin isotope selected (118, 119, and 120) was 66 ms in order to obtain a total integration time of 200 ms. Under such conditions, the chromatographic peak profile could be followed accurately and peak area ratios showed good precision. Mass bias was corrected for by injecting a solution containing a mixture of the three natural butyltin species before and after every three spiked samples.

The equations for the computation of the concentrations (taking into account the possible sequential degradation reactions occurring throughout the speciation procedure) and the stepwise decomposition factors of TBT to DBT (F_1) and DBT to MBT (F_2) were described in detail in a previous paper.[25] In summary, nine mass balance equations can be postulated (three tin isotopes for each butyltin species) which are then reduced to six isotope ratio equations (120/119 and 120/118 for all three species) containing five unknowns, the three species concentrations, and two degradation factors (TBT to DBT, F_1, and DBT to MBT, F_2). By solving this equations system the degradation-corrected concentrations for MBT, DBT and TBT and F_1 and F_2 can be calculated.

Extraction Conditions for Accelerated Solvent Extraction. A cellulose filter (Dionex) was placed into an 11-mL stainless steel extraction cell, supplied with the instrument, making sure that it was in full contact with the cell. Afterward, the cells were partially filled with a dispersing agent (Varian, Palo Alto, CA). Sediment samples of at least 0.25 g (to ensure sample-to-sample homogeneity) were weighed directly into these cells and spiked with appropriate amounts of the "double-enriched-isotope spike". Both, sample and spike were accurately weighted using a precision balance (Mettler Toledo AT200, Barcelona, Spain). Finally, the cells were completely filled with the dispersing agent, hand-tight capped, and placed in the cell carousel. This carousel rotated the sample cell into position for transfer to the oven chamber (where it was eventually sealed under pressure). The ASE instrument automatically mixed the selected solvents in the method editor and carried them to the cell, which was then pressurized and heated within 5−8 min to the selected extraction temperature (up to 175 °C). Once the cell reached the selected temperature, the samples were extracted with one static cycle of 5, 10, or 15 min or three static cycles of 5 min according to the method created. Finally, the extracts were collected in cleaned 50-mL glass vials and the cell was flushed and purged by nitrogen gas. Table 1 shows in detail the extraction conditions operated in the ASE instrument. A 1-mL aliquot of each final extract was eventually ethylated and subjected to the speciation procedure by GC/ICPMS.

Table 1. Operating Conditions Used in the Optimization of the ASE Extraction Procedure

cell conditions	
cell size	11 mL
pressure	1750 psi (120 atm)
temperature	50, 80, 110, 140, and 175 °C
preheat time	0 min
heat time	5−8 min (depending on the selected *T*)
static time	5, 10, and 15 min
purge time	60 s
static cycles	1 and 3
solvents	
solvent mixture	90% MeOH−10% AcOH
flush volume	60%
final volume	∼25 mL

Table 2. Isotopic Composition of the Double-Spike Solution[a]

Sn isotopes	natural tin	MBT ($n = 5$)	DBT ($n = 5$)	TBT ($n = 5$)
118	24.22	17.13 ± 0.23	86.69 ± 0.49	13.86 ± 0.21
119	8.59	79.73 ± 0.27	12.23 ± 0.43	83.08 ± 0.21
120	32.58	2.988 ± 0.058	0.949 ± 0.061	2.936 ± 0.066

[a] Uncertainty corresponds to the 95% confidence interval ($n = 5$).

RESULTS AND DISCUSSION

Characterization and Stability of the Spike Solution. The isotopic composition of the double-spike solution was measured by means of five GC/ICPMS replicate injections and corrected for mass bias by using a mixed natural standard. All 10 tin isotopes were measured and the results obtained for the three selected Sn isotopes (120, 119, 118) are presented in Table 2. As can be observed, the isotopic abundances exhibited by all butyltin species are different from those of the natural tin, allowing the adequate application of the isotope dilution analysis procedure. Moreover, the large difference between the isotopic composition of tin in DBT and that of TBT and MBT would allow for decomposition reactions corrections (i.e., drastic modifications in the species isotope ratios are brought about by decompositions and they could be accurately detected by GC/ICPMS[25]).

Determination of each butyltin species in the double spike was performed by reverse isotope dilution analysis, as described in our previous publication[25] where the species stability in this spike was studied over three months. Here the stability evaluation time has been extended to more than one year, by performing additional reverse ID experiments. Three independent reverse spiking experiments were carried out for each individual tin species and the overall results obtained for the stability of the double spike are presented in Figure 1 (including previous data). The average concentrations (boldface line) observed and the 95% confidence intervals (dashed lines) of the isotopically enriched species are included in this figure. The results demonstrate that adequate stability for the three butyltin species can be safely assumed at least throughout the time period evaluated so far (442 days).

Extraction of Butyltin Species from PACS-2 Using ASE. Our previous studies using microwave-assisted extraction and ultrasonic extraction for organotins in sediments were performed using a 75% acetic acid−25% methanol solvent mixture.[25,27,28] However, solvent composition selected for ASE was 10% acetic acid−90% methanol (as weak acids are recommended by the manufacturer not to exceed this range) without further optimization.

It is well known that temperature plays a crucial role in optimizing the extraction efficiency using ASE. However, labile

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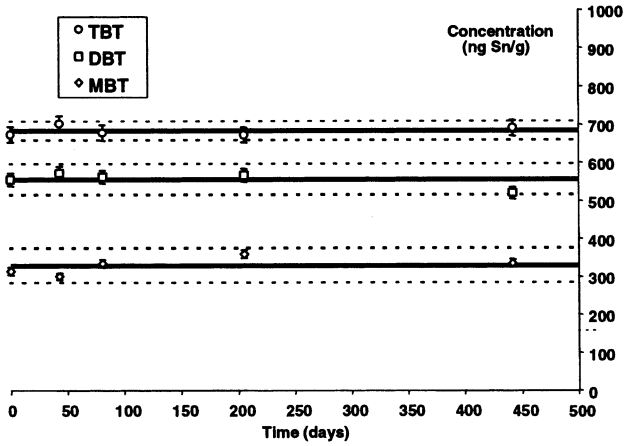

Figure 1. Reverse isotope dilution analysis of the doubly labeled spike using natural standards. Five independent spiking experiments were carried out covering 442 days to check for stability. Uncertainty bars correspond to the 95% confidence interval. Boldface and dashed lines correspond to the mean concentration and 95% confidence interval for each species, respectively.

species such as butyltin compounds might suffer from possible degradation reactions under such harsh conditions. Thus, different aliquots of PACS-2 sediment samples were spiked with the double spike under increasing extraction temperatures, ranging from 50 to 175 °C. A static extraction cycle of 5 min was selected for all the experiments, and speciation by GC/ICPMS was carried out in each experiment. Degradation-corrected concentrations for TBT, DBT, and MBT were calculated and they are presented in Figure 2a and b, respectively. Figure 2b collects the results for MBT and also includes previous MBT determinations[25] obtained by microwave, ultrasonic, and mechanical extraction[25] (for eventual comparisons). As can be observed in Figure 2, for all three butyltin compounds, the recoveries observed from the solid increased with the extraction temperature.

To assess the overall precision associated with the whole procedure, a duplicate was performed at 110 °C and both samples were analyzed twice by GC/ICPMS. As expected,[27,28] the precision ($n = 4$) was within 2% for the three tin species (0.73, 0.81, and 2.0% for TBT, DBT, and MBT, respectively). This result confirms once again the capability of isotope dilution analysis to provide highly precise speciation results (regardless of the extraction technique used).

On the other hand, it should be pointed out that concentrations obtained at 110 °C, for all three tin compounds, were statistically indistinguishable from those obtained at 140 and 175 °C (assuming the same uncertainty for 140 and 175 °C experiments as that experimentally obtained for 110 °C). Thus, it can be assumed that quantitative recoveries of organotin species from the solid matrix were attained using ASE at 110 °C. Figure 2 shows that the use of 50 or 80 °C resulted in nonquantitative recoveries. The certified value for MBT in PACS-2 seem to be low as can be clearly observed in Figure 2b. These ASE data compare well with previous independent data obtained for MBT in PACS-2 using alternative solid extraction procedures[25] and confirm the convenience of PACS-2 reevaluation for organotins content.

Three different static extraction times (5, 10, and 15 min) at 110 °C were investigated with ASE, and the results obtained are summarized in Table 3. As can be observed, extraction times

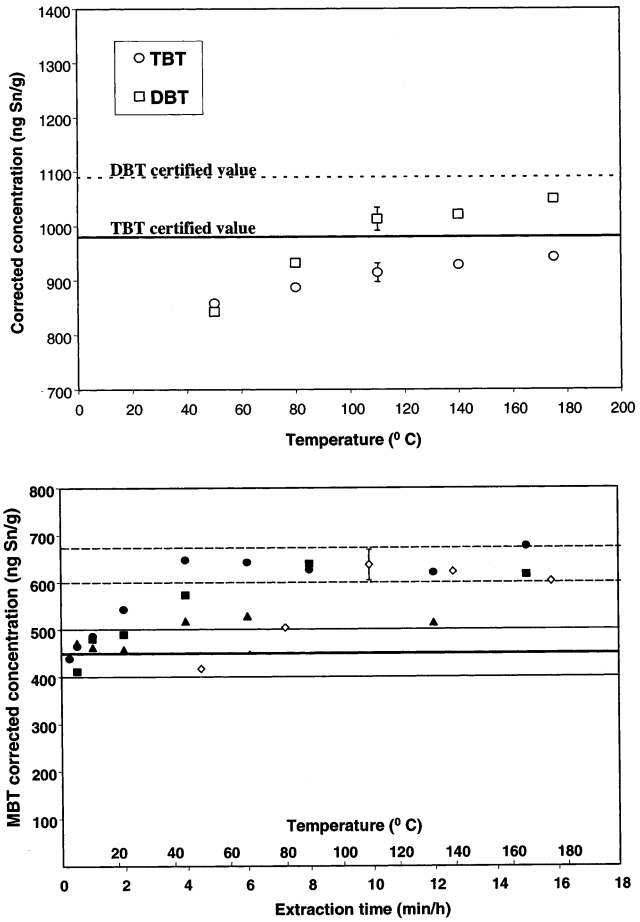

Figure 2. Isotope dilution GC/ICPMS results for the PACS-2 sediment using ASE. (a) corresponds to TBT and DBT and (b) corresponds to MBT values obtained using ASE (rhombus), microwave (circles), ultrasonic (squares), and mechanical shaking (triangles). Dashed lines in this figure correspond to the 95% confidence interval for the plateau points of microwave (≥4 min), ultrasonic (≥8 min), and ASE (≥110 °C). Error bars for ASE at 110 °C correspond to the 95% confidence interval.

Table 3. Effect of Time and Number of Cycles on the Butyltin Speciation Results in PACS-2 Reference Material Using ASE at 110 °C[a]

extraction time (min)	TBT	DBT	MBT
5	0.92 ± 0.02	1.01 ± 0.02	0.64 ± 0.03
10	0.93	0.97	0.64
15	0.93	1.00	0.61
3 × 5	0.96	0.96	0.64
reference value	0.98 ± 0.13	1.09 ± 0.15	0.45 ± 0.05

[a] Concentration expressed as microgram of Sn per gram of sediment. Uncertainty corresponds to 95% confidence interval.

higher than 5 min or three cycles of 5 min each did not provide higher recoveries related to the certified value. In comparison with previous reported ASE extractions of butyltin compounds,[10−12] the conditions finally selected here, (5 min of heating time plus 5 min of static time at 110 °C) involve an important time saving: Arnold et al.[10] and Chiron et al.[11] required 30 min of extraction time consisting of 5 min of heating time plus five cycles of 5 min each. Moreover, the methodology finally selected did not require the

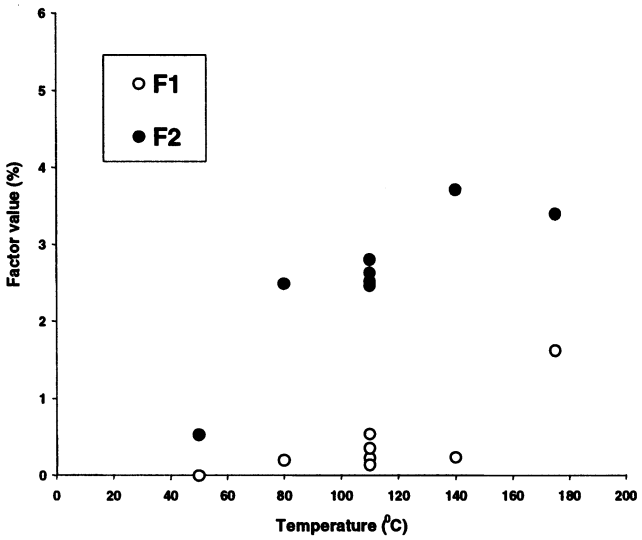

Figure 3. Decomposition factors (%) calculated after ASE extraction at different temperatures and extraction times for PACS-2. F_1: TBT to DBT. F_2: DBT to MBT.

use of complexing agents (e.g., tropolone or triethylamine) to obtain similar recoveries for MBT as those previously reported by Chiron et al., using ASE for PACS-2 analysis.[11] The use of isotope dilution analysis might be responsible for the short extraction time needed here as there is no need for quantitative recovery of the butyltin compounds in the extract once isotope equilibration has been reached. In fact, if there are losses due to incomplete washing of the extraction cell with fresh solvent, this will not affect the results obtained by isotope dilution analysis but it will affect classical calibration strategies.

Degradation Factors Obtained Using ASE. Figure 3 shows the values of F_1 and F_2 found for ASE as a function of extraction temperatures. At 110 °C, the different extraction times and cycles investigated have been included for comparison in the graph. As can be seen, F_1 values were close to 0 under all extraction conditions except for the highest temperature assayed, indicating that TBT is resistant to thermal degradation to DBT. However, as we reported previously using other extraction techniques,[25] F_2 values were significantly higher than F_1 and increased with temperature above 50 °C; for instance, values up to 3−4% were obtained at the maximum temperatures tested (140 and 175 °C). It is worth noting that the values of calculated F_1 or F_2 decomposition factors corresponding to four different extraction time conditions at 110 °C were quite similar. In other words, the static temperature plays the main role in the occurrence of butyltin degradation reactions during extraction from the sediment matrix rather than extraction times.

Comparison of ASE with Other Extraction Techniques[25] for Butyltin Analysis in Sediments. From the above results, it seems that using the ASE technique at temperatures over 100 °C for 10 min (5 min of heating time + 5 min of one static cycle) provides quantitative recoveries for the three butyltin species determined (including MBT). It is most interesting to compare the quantitative results obtained using different extraction techniques in our laboratory during the last two years with the reference values of organotin species in PACS-2. Table 4 collects such data for four extraction techniques providing supposedly quantitative recoveries. As can be observed, the results for TBT and DBT using all four extraction techniques are in complete agreement with the certified values and so they also very similar between them. Indeed, taking into account the 16 experiments carried out using the four independent techniques, operated at different conditions, the obtained overall precisions of 3.5 and 2.4% RSD for DBT (1.03 μg/g) and TBT (0.92 μg/g), respectively, can be considered excellent.

Table 4. Comparison of Accelerated Solvent Extraction (ASE), Mechanical Shaking, and Microwave- and Ultrasonic-Assisted Extraction for Butyltin Speciation in PACS-2 Certified Reference Material[a]

extraction technique	TBT	DBT	MBT
mechanical shaking[25] ($t \geq 4$ h)	0.90 ± 0.03	1.06 ± 0.06	0.52 ± 0.02
ultrasonic[25] ($t \geq 8$ min)	0.92 ± 0.02	1.04 ± 0.05	0.63 ± 0.03
microwave[25] ($t \geq 4$ min)	0.91 ± 0.06	1.06 ± 0.01	0.64 ± 0.04
ASE ($T \geq 110$ °C)	0.93 ± 0.03	1.00 ± 0.07	0.63 ± 0.03
reference value	0.98 ± 0.13	1.09 ± 0.15	0.45 ± 0.05

[a] Concentration expressed as microgram of Sn per gram of sediment. Uncertainty corresponds to 95% confidence interval.

With regard to MBT, Figure 2b shows that MBT concentration values found increased with harsher conditions: in fact, while mechanical shaking provided a value (0.52 ± 0.02 μg/g, Table 4) agreeing well with the certified PACS-2 value (0.45 ± 0.05 μg/g), ultrasonic (0.63 μg/g), microwave (0.64 μg/g), and ASE (0.63 μg/g) values turned out to be significantly higher than the certified one. Summarizing, the use of different extraction techniques (physical basis) in combination with different solvent mixtures (chemical basis) led to the same MBT result, demonstrating again the validity of the methodology developed. Other authors have also previously reported higher concentrations for MBT in PACS-2 sediment both using complexing agents only (0.620 μg/g)[31] or in conjunction with ASE (0.634 μg/g).[11] All these results seem to indicate that the MBT species is bound more strongly to the sediment matrix than DBT and TBT and so its quantitative extraction demands for more aggressive conditions. The double-spike approach used in this work allows for solid extraction recovery evaluation of the labile MBT without worrying about degradation reactions, taking place with hasher conditions, because application of the equations developed previously[25] correct for them.

On the other hand, it should be noted that microwave-assisted extraction provided higher degradation factors (up to 7 and 16% for F_1 and F_2, respectively, at the harshest conditions assayed) than those obtained using ASE (degradation factors below 4% even at 175 °C).

CONCLUSIONS

Analytical extraction of butyltin compounds from sediment matrixes is an involved issue as we need to attain quantitative recoveries from one side while preventing degradation of the species from the other. The "doubly isotopically labeled" methodology[25] has certainly demonstrated to be the best approach so far to cope with this difficult task. It allows us to investigate

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conditions for quantitative recoveries from the solid of the analyte species, while degradation reactions (possibly brought about by the use of harsher extraction conditions) can be corrected and degradation factors evaluated by the isotope dilution analysis.[25] In this study of ASE efficiency to extract butyltin species from PACS-2 sediment, the double spike has demonstrated that extraction time did not seem to influence neither recoveries nor degradation reactions. However, static extraction temperature could eventually influence the degradation factors (Figure 3). A time of 5 min of heating followed by 5 min of a single static cycle at 110 °C was enough to reach maximum recoveries for the three butyltin species (even MBT) under scrutiny.

In brief, ASE has proved to be at least equivalent, in terms of quantitative speciation of organotins in sediment samples, to more common solid extraction methodologies. However, ASE generates in ∼10 min a filtered extract from a sediment sample ready to be derivatized and injected in the GC/ICPMS. In any case, the main advantage of ASE in routine laboratories is the possibility to perform up to 24 unattended solid sample quantitative extractions. The analytical performance of ASE demonstrated here for organotins speciation in environmental samples points to its definitive implementation for routine environmental analysis of organometallics in clear competition with other well-established solid extraction techniques.

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