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Validation of the Analysis of Organotin Compounds in Biological Tissues Using Alkylation and Gas Chromatography

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Several critical steps in the analytical procedure for organotin compounds in the environment are identified in this paper and solutions are suggested. In particular, an improved procedure for quenching excess Grignard reagent is described. After insight into the nature of losses was obtained, the use of internal standards made it possible to reduce further the method variability. The systematic optimization of the analytical procedure resulted in a well investigated and robust method for analysis of organotin compounds in zebra mussel samples. Organotin compounds (OTs) which enter the environment as a result of their use as biocides and their degradation products are regularly found in environmental samples. Many different analytical techniques are currently being used,[1] but little is known about their accuracy and precision.

Keywords: Organotin, gas chromatography, mass spectrometry, atomic emission, validation, environmental analysis

INTRODUCTION

This presents a considerable challenge for several reasons. The methods have to be very sensitive and selective to be able to detect concentrations at the low environmental target values issued for triphenyltin (TPT) and tributyltin (TBT). In most European countries environmental quality targets of 10 ng l^{-1} for water samples and 1–2 ng g^{-1} for sediment samples are now implemented.[2] For di- and mono-OTs no legal environmental threshold limits have yet been set, but in view of their toxicity and presence in the environment it is desirable to incorporate them in new analytical techniques.

For reasons of efficiency it is desired to extract both non-polar tri-OTs and polar mono- and di-OTs simultaneously. These compounds span a range of hydrophobicity. Techniques employing apolar solvents will extract the polar OTs only to a limited extent.[2] Aggressive digestion techniques, such as those used in heavy-metal analysis, cannot be used, as OTs are not stable under these conditions. Therefore, a non-destructive extraction technique that still allows good extraction of polar compounds has to be used. Extraction schemes employing acetic acid, methanol or diethyl ether, combined with complexing agents, are often employed.[3–8]

For separation, GC has a high separation capability. A derivatization step is required, however, because the high polarity of di- and mono-OTs prevents direct analysis by capillary GC. Analysis by high-performance liquid chromatography (HPLC) is not a viable solution as the great difference in polarity makes chromatography in a single run of non-derivatized mono-, di- and tri-OTs difficult. Moreover sensitive detection of OTs after HPLC is not easily accomplished. For GC, sensitive and selective detectors are nowadays available. In this study an atomic emission detector (AED) and two types of mass-spectrometric detectors (a quadrupole and an ion trap) were used successfully.

For the assessment of accuracy of the analysis of all OTs found in biological matrices, no certified reference materials exist yet. In this study, validation was accomplished by a thorough investigation of the technique. An assessment of the precision of the method was obtained by determining recoveries of spikes and by comparing two different extraction procedures.

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EXPERIMENTAL

Materials and methods

Most materials used in this study have been described previously.[2] Structural formulae of the investigated compounds are also given in Ref. 2. The Grignard reagents methylmagnesium iodide and pentylmagnesium bromide were prepared in the laboratory by reacting 0.4 mol magnesium with an equimolar amount of bromopentane (Merck, Darmstadt, Germany) or iodomethane (Baker, Deventer, The Netherlands) in 200 ml diethyl ether (p.A. quality; Merck). Methylated and pentylated organotin calibrants were synthesized and purified as described earlier.[9]

Degradation effects due to products present after quenching the Grignard reagent were investigated. Freshly prepared Grignard reagent (1 ml methylmagnesium iodide, 2 mol l^{-1}) was diluted with 1 ml diethyl ether (p.A. quality; Merck). After 30 min the Grignard reagent was quenched with 6 ml of either 1 mol l^{-1} sulphuric acid (p.A. quality; Baker), 1 mol l^{-1} ammonium chloride (p.A. quality; Baker) or acetate buffer, pH 5, prepared by mixing equal volumes of solutions of 5×40 mol l^{-1} acetic acid (p.A. quality; Baker) and 3×40 mol l^{-1} sodium hydroxide (p.A. quality; Baker)). Then methylated OT calibrants were added. The mixture was shaken for 3 s, centrifuged and the phases were separated from each other. No clean-up was performed, but in one-half of the experiments the organic phase was washed additionally three times with 7 ml water (HPLC grade; Baker). The effect of the short exposure, and the effect of traces of reagents in the extract on OT recovery, were evaluated by GC MS. Analysis was performed immediately, and again after 1, 3, 5, 9 and 12 days.

Clean-up experiments were done using basic alumina (Alumina B—Super 1, basic form; ICN Biomedicals, Eschwege, Germany) (0% and 5% deactivated with water), Florisil (75–150 μm; Merck) and silica gel [63–200 μm; Merck) (0.5% deactivated with water; treated with 22% (w/w) concentrated sulphuric acid; treated with 33% (w/w) 3 mol l^{-1} KOH (p.A. quality; Baker)].

Validation of the extraction procedure was accomplished by comparing acidic extraction and saponification of a zebra mussel homogenate. For the acidic extraction, 2 g homogenate was weighed in a 15 ml centrifuge tube with stopper, spiked with OTs in methanol and allowed to equilibrate for 30 min. It was acidified to pH 1.5–2.2 with approx. 0.3 ml of 1 mol l^{-1} hydrochloric acid. The pH was checked with a pH electrode. Sodium chloride (0.5 g) and 6 ml freshly prepared (less than 3 h old) 0.3% tropolone (Aldrich, Steinheim, Germany) in diethyl ether were added. The mixture was shaken on a vortex mixer for 15 s, sonicated for 5 min and again vortexed. Phase separation was accomplished by centrifugation at 2200 rpm for 3 min. The phases were separated and the homogenate was extracted once more. The combined extract was dried on anhydrous sodium sulphate (Baker) for 30 min.

Extraction using saponification was previously described by Waldock[10] for the determination of butyltins using hydride generation. The method was adapted for all the presently investigated OTs. A portion of 2 g mussel homogenate was spiked with OTs in methanol and allowed to equilibrate for 30 min. Then it was saponified with 6 ml sodium hydroxide (Baker)/methanol (Rathburn, Walkerburn, Scotland)/water (40:100:100, w/v/v) for 20 min at 40 °C. The pH was readjusted to 1.5–2.2 with approx. 3 ml hydrochloric acid (Suprapure, 30%; Merck), using ice-cooling. Sodium chloride (Baker) (2 g) was aded and extraction was performed twice with 12 ml diethyl ether/pentane (nanograde; Malinckrodt, Paris, Kentucky, USA)/tropolone (80:20:0.1, v/v/w). The combined extract was dried on anhydrous sodium sulphate for 30 min.

The extracts were derivatized by methylation. The extracts were concentrated until dry until dry under a gentle stream of nitrogen. Diethyl ether (1 ml) was added and organotin internal standards (triethylMPT, ethylTBT, diethylDPT and ethylTPT) were added. Methylmagnesium iodide (1 ml, 2 mol l^{-1}) was added and the stoppered test-tube was shaken for 3 s. After 30 min the reaction mixture was cooled in an ice bath, 3 ml hexane was added and the excess Grignard reagent was destroyed by carefully adding 6 ml of 1 mol l^{-1} ammonium chloride. The test-tube was shaken (3 s) and centrifuged to obtain a neat layer separation. The organic layer was separated, dried on sodium sulphate (30 min) and reduced in volume to 1–2 ml by evaporation in a stream of nitrogen.

Clean-up was performed within 2 h after the reaction by sorption of the sample on 5 g basic alumina and elution with 15 ml hexane (nanograde; Malinckrodt)/diethyl ether (80:20, v/v). PCB-103 was added to the eluate as an internal standard to check GC performance. The eluate

was reduced in volume to 0.4–0.6 ml, of which 5 µl were injected on the GC column.

Apparatus

GC MS was carried out on a Varian Saturn II ion trap detector (ITD) (Varian, Walnut Creek, CA, USA) and on an HP 5971A quadrupole mass-selective detector (MSD) (Hewlett–Packard, Waldbronn, Germany). Atomic emission detection was performed on an HP 5921 AED. For GC an HP 5890 or a VARIAN 3400 was used. The GC column was a DB5-MS column 30 m × 0.2 mm i.d., film thickness 0.2 µm (J&W Scientific, Folsom, CA, USA). A retention gap of 2 m × 0.53 mm i.d. deactivated fused silica was used in all cases (Chrompack, Middelburg, The Netherlands). Helium column flow was 40 cm s^{-1} at 60 °C. The temperature programme was from 70 °C (1 min) at 30 °C min^{-1} to 120 °C, then at 5 °C min^{-1} to 260 °C, then at 30 °C min^{-1} to 285 °C (13 min).

RESULTS AND DISCUSSION

Introduction

In organotin analysis involving alkylation combined with GC, the following procedure is commonly used: the sample is extracted using a complexing agent to allow simultaneous extraction of the mono-, di- and tri-OTs. After concentration, the extract is derivatized by a Grignard reagent. The excess Grignard reagent is then destroyed by a dilute acid solution.[3,4,6–8] The alkylated OTs are extracted and after a clean-up step the extract is injected on the GC.

First experiments using methods described in the literature revealed that no statistical control was achieved. Within-day precision was reasonable, but between-day variations were high. Therefore the method was studied systematically to find the cause of the variations. In this study, the whole OT analysis procedure was tested, starting with the end of the procedure.

Calibrants

Calibrants of alkylated OTs are not commerially available. Therefore pentylated and methylated organotin calibrants were prepared in our own laboratory.[9] Purified alkylated OTs are stable[6] and are necessary if methods are to be evaluated thoroughly.

Detection

Detectors were evaluated for sensitivity and for selectivity using calibrants and real sediment samples. Both mass-spectrometric detectors showed good sensitivity (1–10 pg as tin) and selectivity. Quantitation was achieved by using optimized *m/z* values for each OT (included in Table 2 below), while for AED the Sn 303 channel was used. The ion trap has the advantage that full-scan mass spectra are available for positive identification of the compounds, while with quadrupole MS only a few *m/z* values can be monitored if good sensitivity is required. Selectivity on the selected masses appeared to be good for even the most complex samples. The AED showed a similar sensitivity. The detector proved to be extremely selective and gave chromatograms with only very few non-OT peaks for the most complex sample matrices.[2] Linearity was from the detection limit up to 1 ng for the Saturn II and up to more than 10 ng for the MSD and the AED.

Chromatography

Environmental samples generally are concentrated many times before injection, in order to achieve low detection limits. For real samples this implies that high amounts of matrix compounds are injected, which may interfere with column performance. It was observed that the response of OTs can be quickly affected, even when the peak shapes seemed normal. Control standards were incorporated in the series of measurements. Deterioration of the column was apparent, as is illustrated in Fig. 1(A). It is clear that no meaningful results can be obtained for the samples injected in this sequence. It was found that by using splitless injection combined with a 2 m retention gap as a guard column, the effect of the harmful matrix compounds could be greatly reduced. For reliable analysis of the high-molecular-weight compound fenbutatin (FBT), however, on-column injection is preferred. Therefore an improved clean-up procedure was developed to remove the interfering compounds before injection. In all the series of measurements control standards were included to monitor the column performance.

Clean-up

Different clean-up column materials were tested by eluting derivatized sample extracts. The results were evaluated in terms of whether coloured

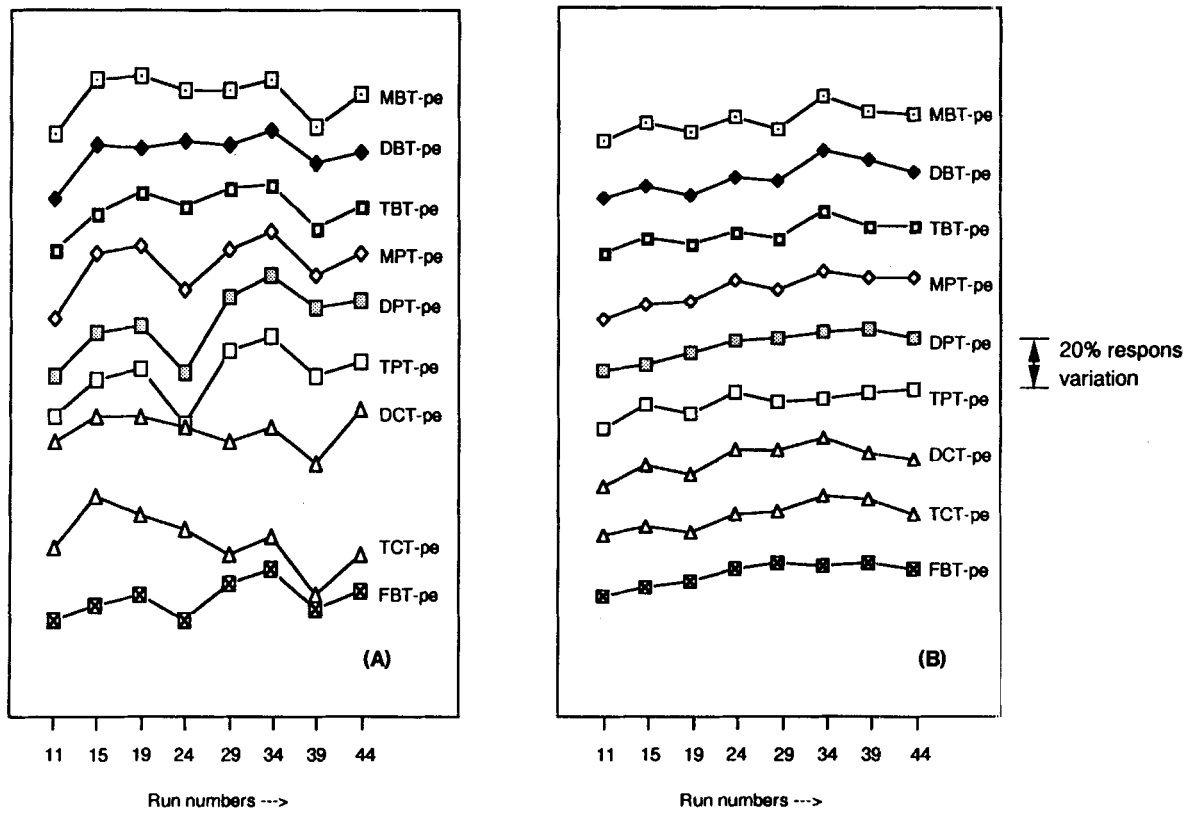

Figure 1 (A) Response variations of a control standard mixture injected repeatedly between real water samples. In this case GC column performance was seriously affected by the sample matrix. (B) Response variations of a control standard mixture injected between real samples using an optimized clean-up procedure.

bands could be separated from the organotin fraction, and whether GC column performance was affected. With the sulphuric acid- and potassium hydroxide-treated columns it was not possible to elute any OTs; they are irreversibly sorbed or degraded on the column. The other materials all achieved some separation between interfering compounds and the OTs. Fully activated basic alumina and elution with 15 ml hexane/diethyl ether (80:20) was most effective and was therefore used in all further work. As can be seen from Fig. 1(B), the response of control standards was fully maintained when using the optimized clean-up procedure.

Exposure of methylated OTs to the derivatization reagents

Results for replicates of real samples still showed large variability in some cases. Therefore it was checked whether products present after quenching of the Grignard reagent were able to destroy previously derivatized methylated OTs. In the literature sulphuric acid, hydrochloric acid and ammonium chloride solutions have been used for quenching. Experiments were carried out using mixtures of Grignard reagent with three quenching solutions.

With the Grignard–sulphuric acid mixture, serious degradation occurred for the methyl derivatives of MBT, DBT, TBT, MPT, DCT and TCT, while DPT, TPT and FBT were not affected. The effects for methylTBT, trimethylMPT and methylTPT ($n=2$) are shown in Fig. 2(A). The duplicate experiments showed large differences in some cases. This is probably caused by whether or not traces of acid are still present in the final extract. MPT in one experiment showed only moderate losses, whereas in the duplicate there appeared to have occurred a fast degradation and most MPT was lost within a few hours. In one TBT experiment, 33% of the original amount was destroyed within one day, whereas the duplicate showed a loss of 68% in one day. A washing step with water was added, in order to remove traces of acid from the final extract. This approach was

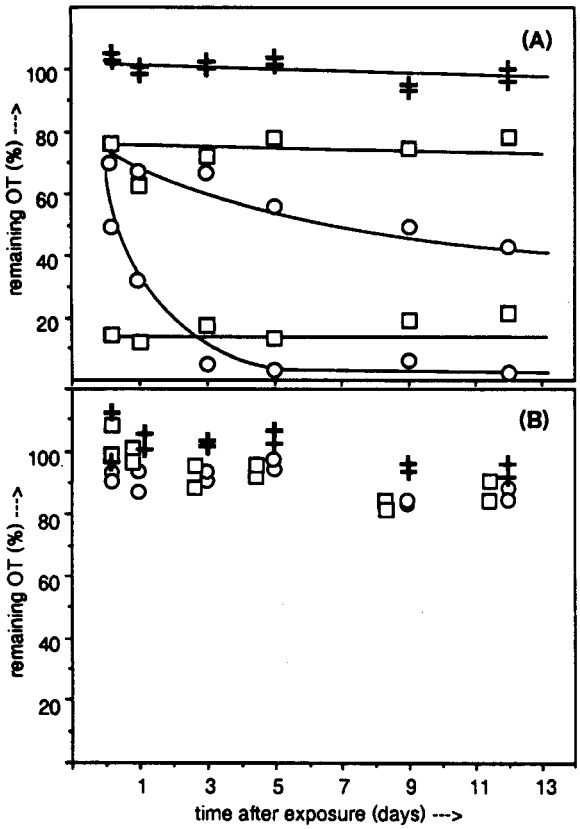

Figure 2 (A) Recovery of methylated TPT (+), MPT (□) and TBT (○) followed during 12 days after a short exposure to the MeMgI–sulphuric acid mixture. (B) As in (A), but after exposure to the MeMgI–ammonium chloride mixture. Recoveries are >80% for all compounds.

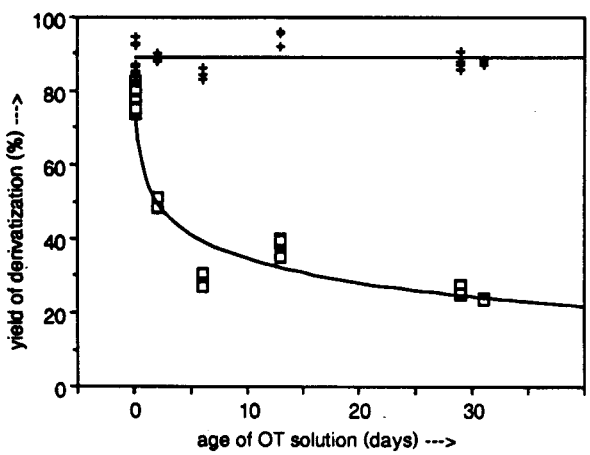

Figure 3 Derivatization yields of TPTCl (+) and $MPTCl_3$ (□) derivatized at different times after preparation of the standard solution in toluene.

not successful as recoveries did not improve significantly.

With Grignard–buffer mixtures, recoveries were >50%, while Grignard–ammonium chloride mixtures gave recoveries >80% for all compounds after 1–12 days (both without a washing step). Results are given in Fig. 2(B). Quenching with ammonium chloride was adopted for all further work.

Another conclusion at this point is that the smaller OTs are more sensitive to degradation than the bulkier molecules and that OTs containing aromatic groups are more stable than OTs with cyclohexyl groups. As OTs with larger alkyl groups are less sensitive to degradation, pentylation may be more favourable than methylation. However, Grignard reagents with larger alkyl groups are less reactive than those containing small organic groups and thus quantitative derivatization may not always be achieved.

Derivatization of OTs

Müller[3] assumed that it is necessary to generate OTS with halogen counter-ions, before alkylation by a Grignard reagent can be performed. Because OTs in solutions may readily alter their counter-ions, this may be a source of variation in the results. First the effect of the counter-ions on derivatization efficiency was investigated. To this end, solutions of OTs with Br^-, Cl^-, CH_3COO^- and OH^- as counter-ions were subjected to the derivatization procedure. The same yields were found, regardless of the counter-ion (Table 1). The conclusion is that it is not necessary to generate halogenated OTs prior to the Grignard reaction. This is in accordance with Davies and Smith,[11] who described the alkylation reaction for

Table 1 Derivatization yields for OT-salts containing different anionic groups

	Anionic group			
	Cl^-	Br^-	OH^-	OAc^-
Bu_3SnX	77 ± 7 ($n=6$)	—	—	69 ± 10 ($n=3$)
Ph_3SnX	85 ± 7 ($n=6$)	—	—	—
Cy_2SnX	—	78 ± 8 ($n=6$)	—	—
Cy_3SnX	—	—	85 ± 4 ($n=6$)	—

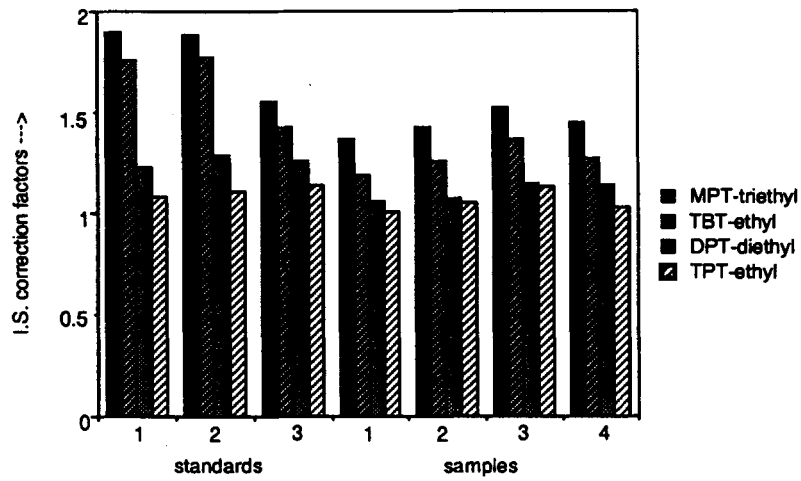

Figure 4 Typical internal-standard correction factors obtained with the optimized method. Three clusters of correction factors obtained with spike standards added to diethyl ether and four clusters obtained with non-spiked real zebra mussel samples are shown.

tin as a transmetallation reaction which is not dependent on the associated anion.

The influence of the age of the Grignard reagent was checked but no effect on the yields was observed for reagents up to 40 days old. Subsequently, the influence of fresh and old spike solutions on recovery was investigated. Spike solutions containing OT salts in toluene were stored for different periods of time and then derivatized. Solutions of organotin salts of more than a few hours old gave low derivatization yields for the mono-OTs; di-OTs gave stable recoveries for 2–5 days, while tri-OTs gave high and stable yields for at least one month. In Fig. 3 results are given for the methylation of MPT and TPT. Possibly polymerization reactions convert the OTs to products that cannot be derivatized, as was suggested by Soderquist and Crosby.[12] For all subsequent recovery studies, standards of OT salts in toluene were prepared freshly just before the spikes were derivatized and, in the case of spikes added to real samples, equilibration of the spike with the sample matrix was restricted to 30 min.

Recovery and reproducibility

In order to have further control on every extraction performed, a mixture of four internal standards (triethylMPT, ethylTBT, diethylDPT,

Table 2 Analytical figures of merit for the determination of OTs in zebra mussels

Compound	Quantitation mass, *m/z*	Recovery[a] (%)		Detection limit (ng g^{-1})
		Spike to diethyl ether ($n=6$)	Spike to mussel ($n=13$)	
MBT	165	83 ± 22	69 ± 18	6
DBT	205	93 ± 12	93 ± 23	4
TBT	247	77 ± 7	79 ± 25	2
MPT	227	59 ± 9	58 ± 12	5
DPT	289	83 ± 8	72 ± 17	2
TPT	351	85 ± 7	83 ± 18	6
DCT	233	78 ± 8	84 ± 14	20
TCT	301	85 ± 4	88 ± 19	20
FBT	401	92 ± 5	82 ± 16	8

[a] Spike level: 0.2 µg of individual OT added to 1 ml diethyl ether or 2 g wet mussel homogenate respectively.

ethylTPT) was added just before the derivatization reaction was carried out. By monitoring internal-standard correction factors, irregularities in individual extractions can easily be identified.

Figure 4 shows a bar graph of internal-standard correction factors obtained for the work-up of three OT-salt standards and four zebra mussel samples. It can be seen that correction factors are generally higher for derivatization of OT-salt solutions than for real samples. The sample matrix showed some protective properties that keep the degradation, and subsequently correction factors, down. This is in line with earlier findings.[2,13] Furthermore, correction factors are higher for the smaller OTs, which implies that the losses caused by the procedure are not the same for different OTs. It is evident that the adoption of ammonium chloride for quenching of excess Grignard reagent did not eliminate all degradation. Therefore the results were corrected for losses by using the internal standard with the closest retention time. In this case (with methylation), MBT, DBT and MPT were corrected for by triethylMPT; TBT was corrected for by ethylTBT; DPT and DCT were corrected for by diethylDPT, and TPT, TCT and FBT were corrected for by ethylTPT. Other possible internal standards such as triethylMBT and diethylDBT were not used because they elute at the same retention time as dimethylDBT and the internal standard, diethylDPT, respectively.

The extraction efficiencies were determined for spikes of OT salts added to diethyl ether and added to mussel homogenate, using the internal-standard procedure as described (Table 2). The recoveries of the spikes added to diethyl ether were generally good (77–93%), which indicated that derivatization efficiencies are high and that the internal standards corrected well for remaining losses. Only for MBT and MPT a rather high RSD (27%) and a rather low recovery (59%), respectively, remained. Recoveries for spikes added to different mussel samples were in good accordance with the spikes added to diethyl ether. It is clear that reliable determination of all nine OTs investigated is very feasible with the optimized technique.

Method validation

To validate the extraction procedure, results obtained with the saponification procedure were compared with those from the acidic procedure. Mussel homogenates from 10 different locations were determined by the two techniques and the results of butyltins and phenyltins were checked, after correction for recovery and normalization, for systematic differences using a paired *t*-test. For TPT this is elaborated in Table 3. In Table 4 the results are given for all OTs. For TPT, significantly (albeit only slightly) higher results were found when using the saponification procedure (28% higher). For the other compounds no significant differences were found at the present level of precision attained. The difference found for TPT may be due to enhanced extraction of strongly bound TPT using saponification. Because the difference is only small, both techniques may be considered adequate. The acidic extraction procedure has the advantage that it is much faster. The fact that two fundamentally different extraction techniques do give similar results supports the validity of the methods.

Blank values were determined by extracting 2 ml water as if it was a mussel sample. Values were well below the detection limits given in Table 2. Finally, the repeatability of the method was determined by analysing a mussel homogenate internal reference material (IRM). During a series of 100 analyses this was done regularly. A control-chart type of presentation (not enough

Table 3 TPT concentrations from 10 mussel samples, employing acid extraction and saponification

Concentrations were corrected for recovery (acid extraction, 83%; saponification, 71%). After this the results were normalized (for all samples to have equal weight, irrespective of the OT concentrations) and tested using a paired *t*-test. The *t*-test yielded a probability of 0.001, which means that the two extraction techniques give significantly different results for TPT.

	Concentration (ng g^{-1} dry wt)		Normalized concentration	
Sample	Acid extraction	Saponification	Acid extraction	Saponification
1	59	60	0.494	0.506
2	152	190	0.444	0.555
3	57	79	0.417	0.583
4	66	82	0.443	0.557
5	815	878	0.481	0.519
6	281	458	0.380	0.620
7	2206	2437	0.475	0.525
8	43	59	0.417	0.583
9	414	547	0.431	0.569
10	107	158	0.403	0.597

Table 4 Comparison of acid extraction and saponification as extraction techniques for 10 randomly chosen samples and concentrations and relative standard deviation (RSD) for an internal reference material

	Comparison of acid extraction and saponification		Internal reference material for acid extraction	
Compound	*t* Value	Probability	Concentration ($ng\ g^{-1}$)	RSD (%) ($n = 11$)
MBT	1.408	0.202	18	33
DBT	0.709	0.496	26	32
TBT[a]	1.312	0.222	152	16
MPT	0.302	0.771	8.2	29
DPT	1.472	0.175	23	34
TPT	6.285	0.0001	82	15
DCT	—	—	<20	—
TCT	—	—	<20	—
FBT	—	—	<8	—

[a] TBT was tested without previous correction for recovery because the recovery values for the saponification extraction were unreliable for this compound.

data have been obtained to construct a real control chart) of the extraction of TBT and TPT from an internal reference mussel sample is presented in Fig. 5 and RSDs are included in Table 4.

CONCLUSIONS

Systematic checking of an existing analytical method, starting from the end of the procedure, is the best way to trace back weaknesses in existing methods, and was performed in this study for the analysis of organotins in zebra mussels. Critical steps were identified. They included the verification of calibrants, GC column performance and the Grignard quenching procedure. Different detectors (quadrupole and ion-trap mass spectrometry, atomic emission detection) can be used successfully for OT analysis. The use of well chosen internal standards helped to improve the reproducibility of the optimized method. The present technique offers several means to monitor its performance. Internal-standard correction factors, responses of control standards injected between real samples, the quality of ion-trap mass spectra, and results from the internal reference material all proved to be valuable tools.

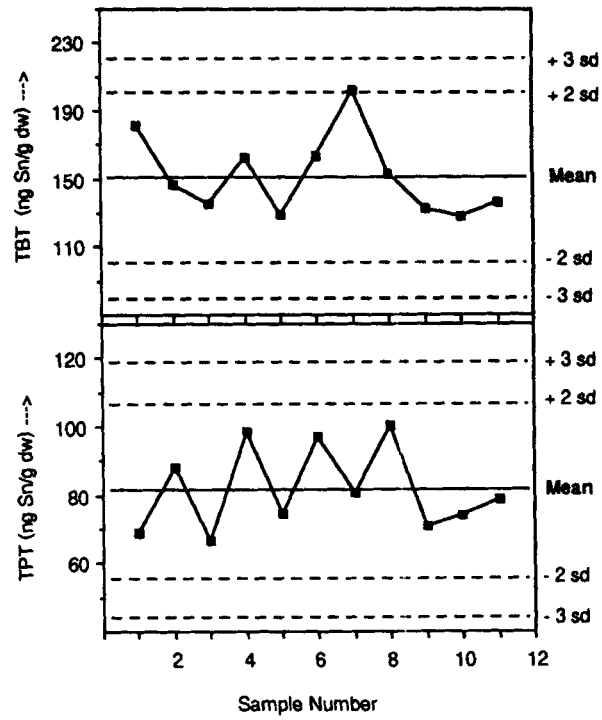

Figure 5 Shewhart-type control chart for the analysis of TPT and TBT in zebra mussel internal reference material.

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