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Pentylated Organotin Standards: Guidelines for their Synthesis, Purity Control and Quantification

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Pentylated derivatives of six environmentally important organotin compounds were obtained by using a Grignard derivatization. The purity of these pentylated calibrants was checked by gas chromatography–quartz furnace atomic absorption spectrometry (GC QFAA) and gas chromatography–mass spectrometry ion-trap detection (GC MS-ITD). Through combination of the total tin contents of every pentylated organotin standard, obtained after wet acid destruction of 0.5 ml of the respective calibrant, and the species composition or impurities present in the same standard, a well-defined pentylated organotin standard was obtained which could be used to calibrate GC QFAA and GC atomic emission detection (AED) systems.

In a similar way aqueous organotin standards can be obtained, which can be used in spiking experiments to verify the recovery efficiency of a developed analytical extraction procedure for organotins.

Keywords: Organotin calibrants, pentylation, quantification, gas chromatography–quartz furnace atomic absorption spectrometry

INTRODUCTION

Organotin salts of reasonable purity are mostly commercially available, whereas alkylated (e.g. methylated, ethylated or pentylated) products of these specific organotin salts are not commercially available at all. Additionally, the alkyl group added is dependent on the procedures and detection systems used in the different laboratories. Therefore, every laboratory is forced to synthesize its own derivatized organotin compounds. Their great use as calibration standards for environmental studies necessitates an assessment of the specified purity of the product. Tetra-alkylated tin compounds in a well-chosen organic solvent show an excellent stability and can be used as standards if stored in the dark in a refrigerator.

MATERIALS AND METHODS

Instrumentation

A gas chromatograph (GC)–quartz furnace atomic absorption spectrometer (QFAA) system was assembled with a Varian 3700 gas chromatograph interfaced to a Perkin–Elmer 2380 atomic absorption spectrometer equipped with a quartz T-tube furnace.[1] The optimized operation conditions are described in Table 1. More detailed information about the instrumental system can be found elsewhere.[2]

Reagents

Bu_3SnCl (96%), Bu_2SnCl_2 (95%), $BuSnCl_3$ (95%), Me_3SnCl (99%), Me_2SnCl_2 (97%), $MeSnCl_3$ (97%), Pr_3SnCl (98%) and n-butylmagnesium chloride (2 mol l^{-1}) in tetrahydrofuran were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA). n-Pentylmagnesium bromide (n-PeMgBr) Grignard reagent (1.5–2.5 mol l^{-1} in ether) from Alfa Ventron (Johnson Matthey, Karlsruhe, Germany) was used, as it appeared earlier that it was less prone to butyltin contamination than other brands tested.[3,4] Tributyltin acetate (Bu_3SnOAc; 100%) was received as a gift from the Community Bureau of Reference Materials (BCR) of the European Community, to be used as a calibrant during their round-robin exercises on tributyltin (TBT).

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Table 1 Operating conditions for the megabore column GC QF AA system

Gas chromatograph: Varian 3700	
Injection port temperature	230 °C
Injection volume	4 µl
Carrier gas (Ar) flow rate	6 ml min^{-1}
Oven program	100 °C→ 10 °C min^{-1}→260 °C
Interface	
Transfer line temperature	285 °C
Heating block temperature	305 °C
Atomic absorption spectrometer: Perkin–Elmer 2380	
Atomization temperature	900 °C
Hydrogen make-up gas	350 ml min^{-1}
Air make-up gas	45 ml min^{-1}
Wavelength	286.4 nm
Slit	0.7 nm

With regard to calibration, the quality assurance policy of the present study was largely based on chromatographic and spectrometric analysis. The purity of the individual compounds was assessed by gas chromatography–quartz furnace atomic absorption spectrometry (GC QFAA) and gas chromatography–mass spectrometry ion-trap detection (GC MS-ITD). The total tin content of all concentrated standard solutions was checked periodically by flame AA after an acid destruction method (which is described in detail later in this paper) and by using a 1000 mg l^{-1} inorganic tin standard (Tritrisol 9929; Merck, Darmstadt, Germany) for calibration.

The most frequently used methods for the conversion of ionic alkyltins into gas-chromatographable species are (1) *in situ* hydrization using $NaBH_4$ or ethylation with $NaBEt_4$, and (2) derivatization using Grignard reagents. The Grignard alkylation reaction proceeds quantitatively, leading to stable derivatives when it is carried out in a suitable solvent. Ethylation or pentylation are the usual choice as they allow a simultaneous speciation analysis of methyl-, butyl-, phenyl- and cyclohexyl-tin species.

As discussed earlier[3,5] the use of n-pentyl derivatives of the organotin halides as calibrants for the determination of ionic alkyltin compounds by the hypenated techniques has several advantages. It leads to less volatile analytes than ethylation, which, on one hand, facilitates further preconcentration and clean-up steps but, on the other hand, can account for condensation problems in the interface during GC QFAA analysis. Seven unsymmetrical tetra-alkylated tin standards of the type R_nSnPe_{4-n} (R = Me, Bu or Pr, $n = 1$, 2 or 3) and two symmetrical alkyltin standards of the type R_4Sn (R = Bu or Pe) were analysed. These were prepared by reacting the organotin halides with a 2 mol l^{-1} solution of n-pentylmagnesium bromide in diethyl ether or a 2 mol l^{-1} solution of n-butylmagnesium chloride in tetrahydrofuran. The standards were subsequently taken through a quantification procedure as outlined in the previous paragraph. Figure 1 shows the strategy followed for the preparation and quantification of organotin standards.

Synthesis and quantification of pentylated organotin standards in octane

In the early development stage of the speciation procedure it was still unclear which would be the most suitable solvent for injecting the pentylated organotin compounds after extraction and derivatization, into the hyphenated techniques used. After preliminary trials with hexane, nonane and benzene, octane (boiling point 125–127 °C) was found to fulfil optimally the GC QFAA requirements (low volatility, suitable solvent peak position in the chromatogram, high recovery and sensitivity of analytes, convenience in use). Nonane, having similar characteristics to octane, could not be used, as its solvent peak overlapped with the retention time of Me_3SnPe.

Grignard pentylation of the organotin salts

Such pentylated standards are not commercially available and therefore had to be synthesized in our laboratory. They were prepared in separating funnels by direct pentylation in octane solutions (10 ml) of an exactly weighed amount of the respective organotin salt, by adding an excess of pentylmagnesium bromide (PeMgBr) in diethyl ether (5 ml of a 2 mol l^{-1} solution). The reaction

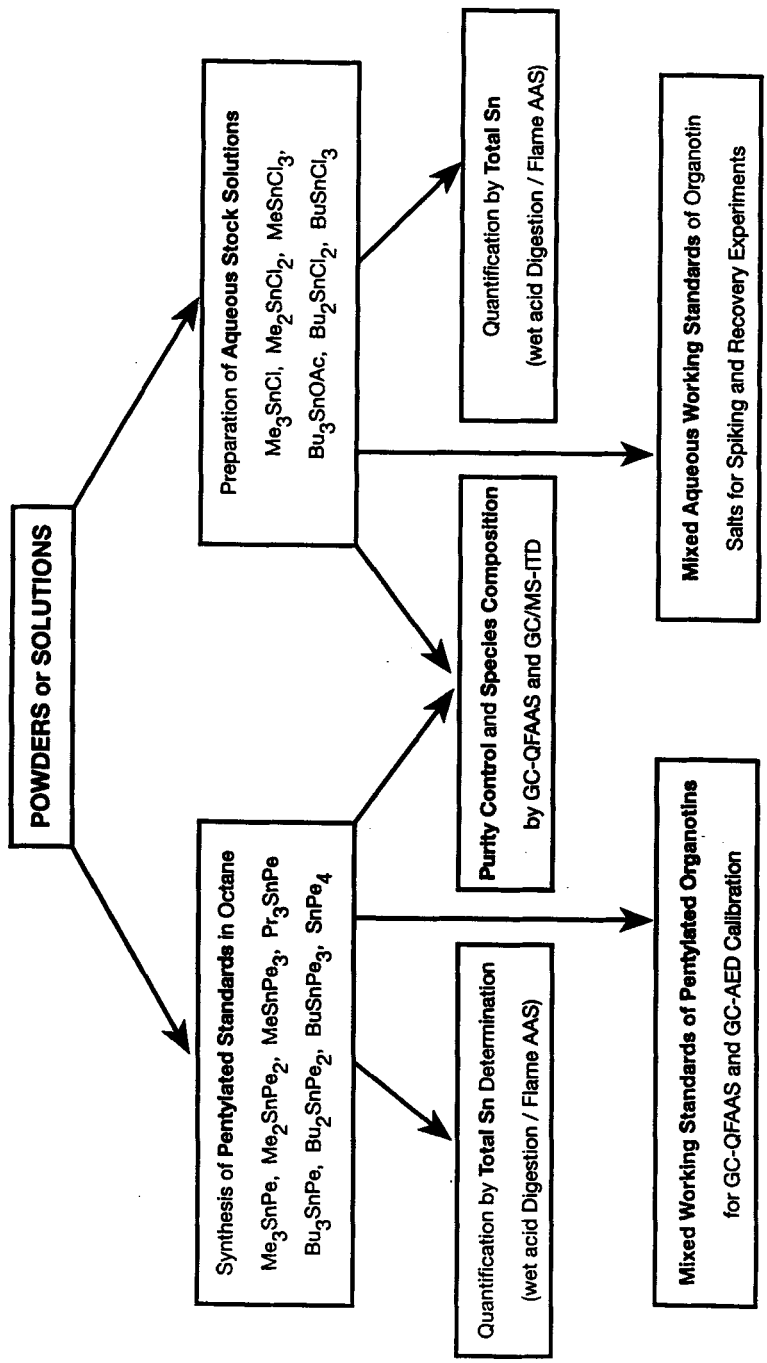

Figure 1 Schematic layout followed for the preparation and quantification of organotin standards.

Table 2 Organotin impurities in the pentylated standard stock solutions in octane, as determined by GC QFAA

	Percentage organic tin							
Standard	Me_3SnPe	Me_2SnPe_2	$SnBu_4$	$MeSnPe_3$	Bu_3SnPe	Bu_2SnPe_2	$BuSnPe_3$	$SnPe_4$
Me_3SnPe	98.59	1.41	—	—	—	—	—	—
Me_2SnPe_2	—	97.72	—	1.30	—	—	—	0.99
$SnBu_4$	—	—	100	—	—	—	—	—
$MeSnPe_3$	—	0.89	0.52	98.59	—	—	—	—
Bu_3SnPe[a]	—	—	2.56	1.52	89.65	3.76	—	2.51
Bu_3SnPe[b]	—	—	—	—	100	—	—	—
Bu_2SnPe_2	—	—	—	—	—	99.32	0.68	—
$BuSnPe_3$	—	—	—	—	—	—	100	—
$SnPe_4$	—	—	—	—	—	—	—	100

[a] Original salt Bu_3SnCl. [b] Original salt Bu_3SnOAc.

mixture was gently swirled around for 10 min at room temperature and subsequently treated with 15 ml of a 0.5 mol l^{-1} sulfuric acid solution to destroy the excess of Grignard reagent. After rinsing the organic layer (twice) with 30 ml of deionized water, a small stream of nitrogen gas was blown through the solution for 20 min to remove the excess of diethyl ether. Since, for the most volatile species (Me_3SnPe) synthesized during this study, no evaporation losses were observed, it was assumed that this treatment would not lead to losses of any of the less volatile pentylated organotin compounds.

Finally, the octane solution was transferred to a 25 ml flask and the original funnel was rinsed twice with 5 ml of octane, which was added to the earlier octane solution. Additionally, octane was added to make up the volume to 25 ml. Similarly, Bu_4Sn was prepared by the reaction of Bu_3SnCl with n-butylmagnesium bromide in tetrahydrofuran. Additionally, these pentylated alkyltin derivatives can be further purified by column chromatography as described by Stäb *et al.*[6]

The pentylated standards in octane were stored in a refrigerator at 4 °C and a working calibration standard (prepared from them) was used in all further experiments. For all these individual standards, the theoretical concentration or balanced amount was confirmed by a quantification based on acid digestion and subsequent flame AA measurement. This theoretical concentration corresponds with the amount of inorganic tin present in the balanced amount of the respective organotin salt used. The purity was monitored by GC QFAA and GC MS–ITD analysis. All reagents were of analytical grade, and the water was deionized and further purified through a Millipore Milli-Q system.

Since some of the alkyltin salts are not pure, the exact concentration of the stock solutions are still not known. Each standard may contain other alkyltin compounds (e.g. degradation products) and eventually some inorganic tin species as impurities. Therefore a species composition of every standard stock solution needed to be carried out by GC QFAA.

Analysis of purity by GC QFAA and CG MS-ITD

The first step in the quantification was the determination of the proportions of the different organotin compounds within one particular standard stock solution. The purity of the prepared pentylated organotin standards was verified by GC QFAA analysis. Whereas some of the standards proved to be 100% pure, others were found to be mutually contaminated at a concentration level of 0.5–4%. To detect any impurities present, a relatively large amount of each standard (corresponding to an absorbance of 0.500–1.000) was injected into the GC QFAA system and the absorbance of the different peaks recorded. The purity of all standards was found to be well in excess of 95%. Table 2 contains a survey of the observed impurities, expressed relative to the total amount of organotin in the chromatogram (and thus corrected for the different sensitivities of the species). The (mutual) impurities were taken into account by the calculation of the concentration in the mixed dilute working standard.

Table 2 clearly shows that Bu_3SnCl obtained from one commercial source was impure and

Table 3 Experimental conditions used in GC MS-ITD

Gas chromatograph: Hewlett–Packard 5890	
Injector temperature	260 °C
Injection volume	0.2 µl
Column	25 m × 0.32 mm × 0.4 µm CP-Sil 5CB
Column flow rate	1.5 ml min^{-1}
Oven program	100 °C→15 °C min^{-1}→260 °C (3 min.)
Transfer line temperature	250 °C
Mass spectrometer: Finnigan MAT series 800 with ion trap detector	
Mode	Full scan
Scan range	100–350 amu
Scan time	1 s
Multiplier	1400 V
Mass defect	100 mmu per 100 amu

contained several other organotin species, whereas Bu_3SnOAc, which we received from BCR as a calibrant, is quite pure. Hence this Bu_3SnOAc was used for preparing tributyltin standard stock solutions. Additionally, the stock solutions of the various pentylated organotins were analyzed by gas chromatography–mass spectrometry ion-trap detection (GC MS-ITD) [7]. The instrumentation and experimental conditions used are summarized in Table 3

As an example in Fig. 2 the total ion chromatogram of Me_3SnPe is shown, it indicates the presence of one contaminant (Me_2SnPe_2). Dismutation reactions are not likely to be responsible for the presence of such impurities. A more likely reason is that the pentylated impurities arise from any degradation products formed or orignally present in the commercial, theoretically pure organotin salts. All compounds and contaminants were identified by the mass spectra generated. The relative impurities were calculated on the basis of peak heights and confirmed the results already obtained by GC QFAA, given in Table 2. Figures 3 and 4 show the mass spectra of Me_3SnPe and Me_2SnPe_2. Identities of *m/z* ions for spectra shown in the figures are given in Table 4. As is expected on the basis of data for the other pentylated compounds, the molecular ion is not visible and typical tin isotope patterns are seen on loss of the pentyl group (*m/z* 165 $[Sn_{120}-Pe]^+$) or one methyl group (*m/z* 221 $[Sn_{120}-Me]^+$) for the Me_3SnPe species.

Determination of the total tin content

The next step in the quantification procedure is the determination of the total tin content of the basic stock solutions, by means of an acid destruction. Many authors recommend a wet oxidation for the destruction of the organic material by different combinations of sulfuric acid with nitric acid,[8–11] perchloric acid[12,13] and either 30% hydrogen peroxide[14] or 50% hydrogen peroxide

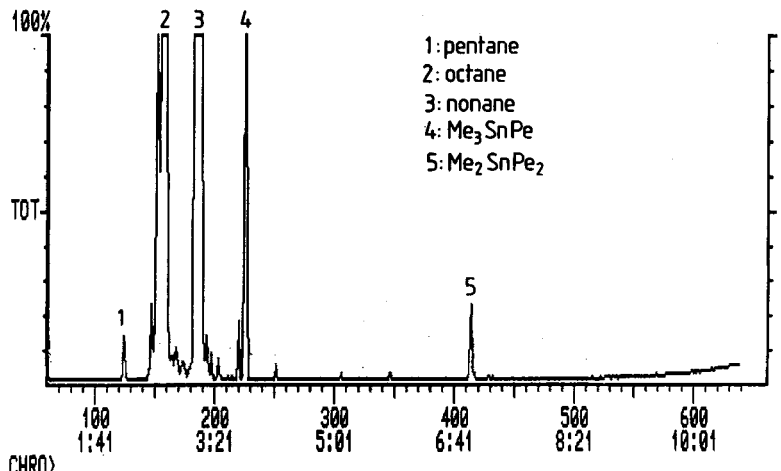

Figure 2 GC MS-ITD total ion chromatogram of Me_3SnPe.

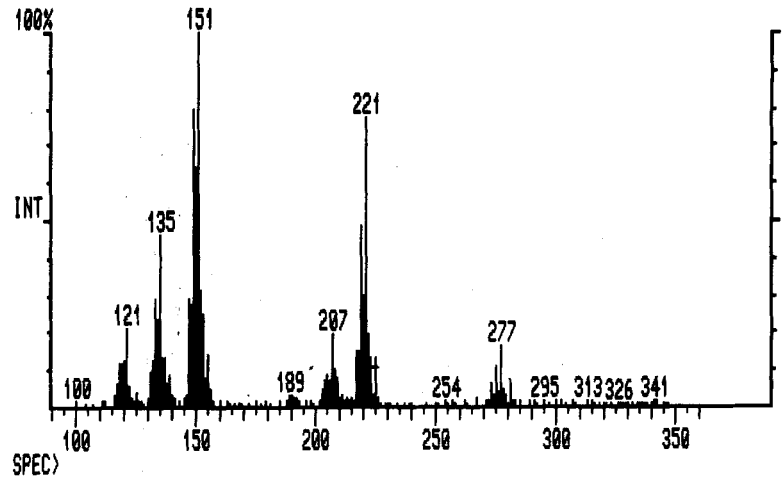

Figure 3 ITD scan no. 227: Me_3SnPe peak.

(H_2O_2),[15,16] before the final tin determination. Manicke and Lauth[14] recommended the use of a H_2SO_4–H_2O_2 mixture, which after total oxidation gave a clear solution. They noticed that in their case the addition of nitric acid to the mixture did not have much influence on the destruction. It was decided to use a modified version of their procedure on each of the individual basic stock solutions.

After 500 µl of the respective pentylated organotin standard (stock solution) and 1 ml of suprapure sulfuric acid (96%) had been placed in a 50 ml Erlenmeyer flask, it was fitted with a condenser, 2 ml of nitric acid (65%) was added through the opening at the top of the condenser. The destruction unit was installed in a fume hood to remove the fumes (NO_2, SO_2 and SO_3) which appeared during gentle heating of the flask on a hotplate. The solution fizzled and turned brown, then 3 ml of 30% H_2O_2 was added through the condenser. The solution was boiled for 30 min and, after cooling, the condenser was rinsed with ultrapure water (deionized and further purified through a Millipore Milli-Q system) and removed. The mixture was then gently heated until finally a sulfuric acid (H_2SO_4) fraction remained. If after drying this fraction was not clear, H_2O_2 was added again and the process repeated until a transparent solution was obtained after drying. To the residual sulfuric acid fraction 1 ml of hydrochloric acid (HCl) (1 mol l^{-1}) and 3 ml of doubly deionized water were carefully added and the solution was transferred to a 10 ml flask. Again 3 ml of doubly deionized water was added to the Erlenmeyer flask, and after swirling, poured into the 10 ml

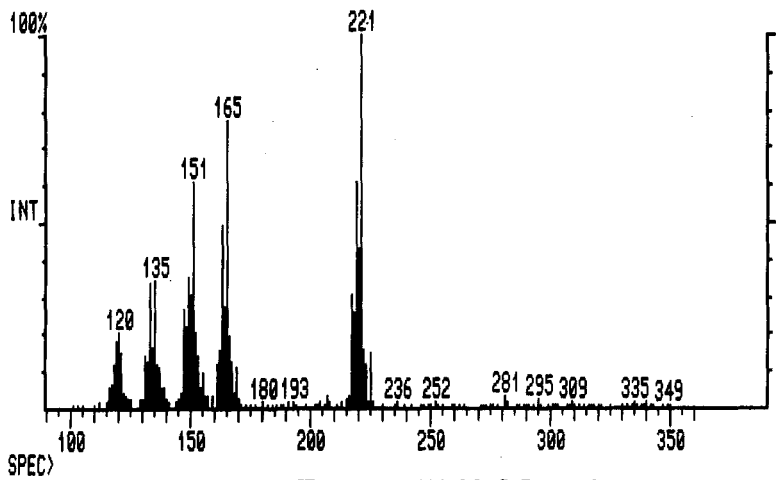

Figure 4 ITD scan no. 414: Me_2SnPe_2 peak.

Table 4 Mass-spectral peaks containing ^{120}Sn

Trimethylpentyltin (Me_3SnPe)		Dimethyldipentyltin (Me_2SnPe_2)	
m/z	Origin	*m/z*	Origin
120	Sn^+	120	Sn^+
135	$SnMe^+$	135	$SnMe^+$
150	$SnMe_2^+$	150	$SnMe_2^+$
165	$SnMe_3^+$	191	$SnPe^+$
191	$SnPe^+$	206	$SnMePe^+$
206	$SnMePe^+$	221	$SnMe_2Pe^+$
221	$SnMe_2Pe^+$	262	$SnPe_2^+$
236	$SnMe_3Pe$	277	$SnMePe_2^+$
		292	$SnMe_2Pe_2$

flask. Finally, the volume in the flask was adjusted with Milli-Q water. All solutions were measured by flame AA (PE 3030 instrument) on the day that they had undergone destruction.

The addition of nitric acid to the sample mixture (in an Erlenmeyer flask without condenser) initially resulted in a violent fizzling reaction and gave rise to the development of a fine spray (**SAFETY POINT**). The losses resulting from this effect were avoided through the use of a condenser. In this way the volatile components and the spray are brought back to the reaction mixture together with the condensed solvent vapors. After the destruction step, hydrochloric acid was added to the residual sulfuric acid fraction to increase the stability of the aqueous solutions, as it was observed that solutions stored for one day, without the addition of hydrochloric acid (HCl), showed the appearance of a white deposit (probably SnO_2) at the bottom of the flask. All destruction processes for the aqueous organotin salt solutions as well as for the pentylated alkyltin standards, were performed five times, and the average total tin concentration is given in Table 5. Three blank determinations were also performed with our procedure: during the flame AA measurements no tin signal was recorded.

The stock solutions in octane are now fully quantified, with a knowledge of the amount of inorganic tin present in the solution (Table 5) and the fractions of the different species (Table 2). By suitable dilution in octane or hexane, mixed working standards can be prepared for the GC QFAA and GC AED calibration[17] which contain between 1 and 2.5 ng μl^{-1} as tin (Sn) for each of the pentylated butyl- and methyl-tin compounds, $SnBu_4$, $SnPe_4$ and the internal standard Pr_3SnPe. Throughout the whole study no degradation of these standards was observed; even the dilute mixed working standard remained stable for at least eight months if stored in a well-sealed glass volumetric flask in the refrigerator and opened only for a short time during use.

Table 5 Total tin content of the pentylated organotin standards in octane

	Total tin (mg per 25 ml nonane)		
Species	Balanced amount[c] (mg)	Found (mg)	Yield (%)
Me_3SnPe	93	88.9	95.6
Me_2SnPe_2	126	112.7	89.4
$MeSnPe_3$	183	154.4	84.4
$SnBu_4$	135	130.4	96.6
Bu_3SnPe[a]	126	121.4	96.4
Bu_3SnPe[b]	122	116.0	95.1
Bu_2SnPe_2	130	125.5	96.5
$BuSnPe_3$	135	110.8	82.1
$SnPe_4$	150	91.6	61.1

[a] Original salt Bu_3SnCl. [b] Original salt Bu_3SnOAc. [c] The amounts of tin present in these basic stock solutions, which are calculated from the balanced amounts of the respective pentylated organotin salts.

Preparation of the aqueous organotin salt standard stock solutions

Organotin standards obtained in powder form can, as they age, partly degrade with the formation of other alkytlin species as degradation products and finally inorganic tin. Hence, it is of great importance to develop a procedure which permits one to check the purity and stability of these standards as a function of time.

Preparation

In the first place, individual standard stock solutions of each of these alkyltin salts (Me_3SnCl, Me_2SnCl_2, $MeSnCl_3$, Bu_3SnCl, Bu_3SnOAc, Bu_2SnCl_2, $BuSnCl_3$) were prepared by dissolving an accurately measured quantity of each methyltin species in doubly deionized water or, for the butyltin species, in an ethanol–water (96/4, v/v) mixture.[18] When stored in the dark in a refrigerator (4 °C), these stock solutions were stable for at least six months without measurable concentration changes.

Determination of total tin

A destruction method quite similar to that for pentylated standards was used. In a 50 ml Erlenmeyer flask, 2 ml of the respective organotin salt standard (stock solution) and 0.5 ml of supra-

pure sulfuric acid were placed. Again, after the Erlenmeyer flask had been fitted with a condenser, 2 ml of nitric acid (65%) and 3 ml of H_2O_2 (30%) were added through the top of the condenser. The solution was boiled for 30 min on a hotplate and, after cooling, the condenser was rinsed with ultrapure water and removed. The mixture was then gently heated until finally a sulfuric acid fraction remained. To the residual sulfuric acid fraction, 0.5 ml hydrochloric acid (1 mol l^{-1}) and 3 ml of doubly deionized water were carefully added, the solution was transferred to a 5 ml flask and the volume was adjusted with Milli-Q water. This solution was measured with flame AA (PE 3030 instrument). The results are shown in Table 6.

From the total tin present in the aqueous stock solutions and with the relative species composition given in Table 2, it is possible to evaluate the contribution of every stock solution (organotin salts) towards the aqueous working standard. The concentration of the individual standard stock solutions in water or a mixture of ethanol and water (96:4) ranged between 44.5 and 66.5 mg (100 ml)$^{-1}$ as tin. Working standards, obtained by further dilution in water, were prepared immediately before use in extraction recovery experiments, and contained between 3 and 6 μg ml^{-1} as tin of each species.

Comparison of pentylated standards

After the intercomparison exercises on tributyltin (TBT) organized by the BCR, it became clear that there was a great demand for quantified standards or guidelines on how to prepare quantified derivatized standards. It was decided between Dr J. Stäb (University of Amsterdam, The Netherlands) and our group that we would exchange our pentylated butyltin standards and cross-check them. The same derivatization technique (PeMgBr) was used by both laboratories[6,19] but at the University of Amsterdam the pentylated organotin compounds were further purified by column chromatography,[6] as already mentioned. Each laboratory analyzed the other laboratory's standards using the instruments available, i.e. GC MS with mass-selective detection in Amsterdam, GC QFAA at the University of Antwerp. The results obtained are shown in Table 7. This interlaboratory exchange clearly demonstrated that the pentylated standards prepared in both laboratories were well quantified. There was a negligible difference (less than 1%) for TBT and DBT, whereas for MBT it was 1.6%, which could be attributed to a small dilution error for MBT in the mixed working standard.

Table 6 Total tin determination for the aqueous organotin salt standards

Species	Total tin (mg per 100 ml water)		
	Balanced amount* (mg)	Found (mg)	Yield (%)
Me_3Sn^+	69.1	67.3	97.4
Me_2Sn^{2+}	47.8	46.6	97.5
$MeSn^{3+}$	67.7	62.1	91.7
Bu_3Sn^{+a}	52.2	49.9	95.6
Bu_3Sn^{+b}	58.4	57.8	99.0
Bu_2Sn^{2+}	47.9	45.3	94.6
$BuSn^{3+}$	54.1	52.5	97.0

[a] Original salt Bu_3SnCl. [b] Original salt Bu_3SnOAc. [c] The amounts of tin present in these basic stock solutions, which are calculated from the balanced amounts of the respective organotin salts.

Table 7 Comparison of pentylated butyltin standards prepared in different laboratories for OT_1MB001 (Amsterdam's standard)

Species present	Concentration (μg ml^{-1} as tin)		
	Value given by Amsterdam	Value found in this work	Yield (%)
Bu_3SnPe	6.60	6.62	100.34
Bu_2SnPe_2	6.97	7.02	100.71
$BuSnPe_3$	7.45	7.57	101.62

SUMMARY

These studies dedicated to standardization have yielded information of a dual nature. Firstly, pentylated standards of six environmentally important organotin compounds could be obtained by using a straightforward Grignard procedure. The purity of these derivatives was checked by GC QFAA and GC MS-ITD. No attempts were made to purify these pentylated compounds further, since concentrations could easily be calculated when the impurity is known.

As a result of the first point, we then obtained a well-defined standard to calibrate the GC QFAA and GC AED system (pentylated alkyltins in octane or hexane) respectively. In a similar way an aqueous standard was obtained, which can be

used to verify the recovery efficiency of the developed analytical procedures. Equally important, however, is the availability of an independent method to monitor and correct any concentration changes in these standards.

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