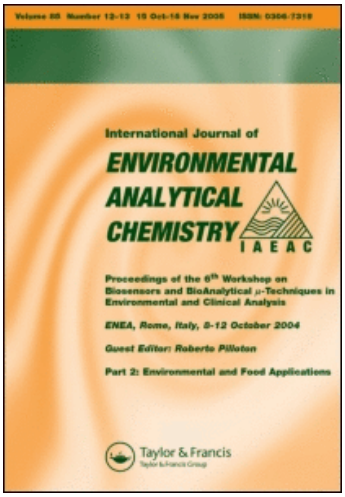

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Reducing blank values for trace analysis of ionic organotin compounds and their adsorption to different materials

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REDUCING BLANK VALUES FOR TRACE ANALYSIS OF IONIC ORGANOTIN COMPOUNDS AND THEIR ADSORPTION TO DIFFERENT MATERIALS

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Organotin compounds (OTC) are highly toxic pollutants strongly affecting many ecosystems. As analytical techniques for OTC have improved in the past, problems with blank values and adsorption to container walls have been revealed. In this study, OTC adsorption to different materials was studied, and different methods such as derivatization, complexation, extraction, UV-light treatment, nitric acid baths, glowing at high temperatures, and rinsing with detergents and distilled water were tested to reduce OTC blank values from chemicals, solutions, and containers of different materials. Rinsing with detergents and distilled water was effective for decontaminating containers of different materials. Glowing at high temperatures was specifically suitable for glassware and chemicals with high melting points. UV-light treatment was suitable only for solutions. However, OTC underwent disproportionation, and tin became methylated under high temperatures and UV-light treatment. Methods combining sodium tetraethylborate and organic solvent extraction had the best decontamination effects among all methods but were not economical. Sodium borohydride provided another alternative but was less effective. However, use of sodium tetraethylborate and sodium borohydride was restricted to aqueous solution and in certain pH ranges. No material was found without adsorption of all OTC in this study. Tributyltin and dibutyltin adsorbed strongly in the Teflons, polyethylene, and silanized glass. Monomethyltin and monobutyltin had strong adsorption in most materials. Different materials should be used for different OTC in adsorption studies. The use of extraction reagents to recover OTC from container walls is suggested to avoid underestimation of OTC concentrations in waters.

Keywords: Organotin compounds; Blank values decomtamination; Adsorption

INTRODUCTION

The highly toxic organotin compounds (OTC) are widely used as fungicides, as stabilizing additives in polymers like polyvinyl chloride, and as antifouling agents in ship paint [1]. OTC are widely distributed and have accumulated in different environmental compartments and animals to different degrees. Consequently, different analytical methods have been developed to determine OTC in the environment and to assess the risks of the environmental condition. As a result of the improvements in instrumental

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techniques in the past, it has been possible to extend the detection limits for the analytical methods for OTC to amounts less than a picogram [2]. With the very high sensitivity of these analytical methods, problems of blank values might occur.

However, the OTC blank-value problem and its solution have seldom been reported in the past. Ceulemans *et al.* [3] were the first to report on problems with blank values. Monobutyl- [2,3], dibutyl-, tributyl, all phenyl-, tripentyl-[2], monooctyl-, and dioctyltin [4] were compounds found to give blank values in different matrixes with varying concentration ranges. One of the relevant sources for OTC contamination to chemicals and water was the use of PVC. Beckera and coworkers evidenced the release of OTC from PVC tubes [5]. In Canada, OTC was found to be present in some household water supplies as a result of the use of PVC pipes to supply the water [6,7]. Owing to the wide application and possible re-emission of OTC, contamination of chemicals, waters, and containers by OTC has been thought to be highly probable. Adsorption of OTC to different materials has been reported [8]. Careless cleaning procedures of containers used for OTC analysis may also result in OTC residues on the container walls. Therefore, reduction in OTC blank values is necessary before beginning OTC trace analyses.

Containers of a suitable material are important for sampling OTC in waters and for OTC-adsorption studies. Adsorption of OTC on the container walls leads to underestimation of OTC concentrations in waters and results in large errors. Carter *et al.* [8] reported the adsorption of TBT to different materials and indicated polycarbonate (PC) as the most suitable material, but knowledge about adsorption of other OTC to different materials was not available.

In this study, several possible sources of OTC blank values were investigated. The main objectives were to study and evaluate different procedures to remove OTC from chemicals, solutions, and laboratory glassware, and to provide more detailed information about OTC adsorption to different materials.

EXPERIMENTAL

Instrumentation

The GC-ICP-MS coupling consists of a gas chromatograph (HP Model 6890) and an ICP-MS (ELAN 5000, Perkin-Elmer SCIEX, Thornhill, ON, Canada). The design consists of a splitless large-volume solvent injection that is used to analyze low- and high-boiling-point analytes in one run. The thin and flexible transfer line (1.5 m length, 1/16″ o.d., 0.04″ i.d., 'Silcosteel' deactive stainless steel tubing, Restek) is heated by a combination of hot argon and the GC effluent, then passing the transfer line using a T-joint in the GC oven, and by electrical resistance heating. The flow through the transfer line can be reversed to eliminate the solvent peak and to prevent graphite deposition onto the ICP-MS cones after large-volume splitless injection. Operation parameters of this system and further details of the coupling are described by Glindemann *et al.* [9].

Reagents

All OTC were obtained commercially as chloride. Deionized water used throughout the work was purified in a Milli-Q system (Millipore, Milford, MA). Sodium tetra(*n*-propyl)borate ($NaBPr_4$), 98%, was synthesized by Dümichen, Halle. Sodium

tetraethylborate ($NaBEt_4$) was purchased from ABCR, Karlsruhe, and sodium borohydride ($NaBH_4$) was obtained from Merck, Darmstadt. The derivatization reagents were prepared as 2% aqueous solution before each usage by dissolving the reagents in UV-treated Milli-Q water. Acetate buffer was prepared by dissolving 1 mole of sodium acetate in 1 L of water followed by adjusting of the pH to 4 with glacial acetic acid.

Individual stock solutions ($10\,\mu g\,mL^{-1}$ as Sn) of monomethyltin (MMT), monobutlytin (MBT), monooctyltin (MOT), dimethyltin (DMT), dibutyltin (DBT), dioctyltin (DOT), trimethyltin (TMT), and tributyltin (TBT) were prepared in methanol and stored at –40°C in the dark. A multi-compound working solution with a total concentration of $0.1\,\mu g\,mL^{-1}$ as Sn was prepared before each use by dilution of the stock solutions with methanol (Merck, p.a. grade). Triethyltin (TET) used as internal standard was prepared in the same way.

OTC Quantification

The end solutions of different experiments to reduce OTC contamination together with 5 ng of Sn as TET, added as an internal standard, were mixed in a 100-mL glass volumetric flask with Milli-Q water to 85 mL and adjusted to pH 4 with the acetate buffer. Derivatization by 10 mg of $NaBPr_4$ and extraction with 1 mL of cyclopentane were carried out by vigorous shaking for 10 min. The cyclopentane extract was directly analyzed with a coupling of GC-ICP-MS. The procedures for reducing blank values are detailed below:

Nitric Acid Bath

Mixed OTC were spiked in glass bottles containing 10, 20, and 30% nitric acid with $5\,ng\,Sn\,mL^{-1}$ for each species. The glass bottles were covered loosely and incubated in the dark at 20°C in a hood. One millilitre of nitric acid solution was used to analyze the concentrations of spiked OTC with procedures described above.

Safety note: The recommendation for this experiment is for the nitric acid bath to be used as an open system and for this to be put in the hood. Nitric acid undergoes a redox reaction during long-term incubation and forms toxic $NO_{2(g)}$.

UV-light Treatment

Liquid samples like Milli-Q water spiked with OTC concentrations of $100\,ng\,Sn\,L^{-1}$ for each species and acetate buffer were poured into brown glass flasks (1 L, Scott). UV lamps were then dipped into the solution. Fifty millilitres of the solution were used for each OTC quantification.

Glow in Muffin Oven

Glassware was glowed at 540°C for 24 h. Chemicals such as sodium acetate were glowed below their melting points (e.g. 300°C for sodium acetate) for 24 h. After glowing, glassware and chemicals were cooled slowly without opening the Muffin oven. For glassware, mixed OTC as 5 ng of Sn in methanol was well distributed on the container walls. The glass flask was then incubated at room temperature in the dark for 24 h. After glowing, the glassware was filled and extracted with 50 mL of UV-light-treated

Milli-Q water by shaking for 1 h. The extraction solution was analyzed further by the aforementioned procedures. For glowed chemicals, a solution consisting of the glowed chemicals and 50 mL of UV-light-treated Milli-Q water was prepared for further analysis.

Washing Machine

A two-step washing procedure was programmed in the washing machine. At the first step, glassware and containers were washed by detergents and 75°C distilled water for 20 min followed by a rinse with 70°C distilled water for 20 min. At the second step, only 75°C distilled water was applied for washing for 20 min, followed by flushing with 70°C distilled water for 20 min. For testing reduction efficiencies, mixed OTC was spiked to the glass flask similarly to glowing. After the two-step washing, the glassware was filled and extracted with 50 mL of UV-light-treated Milli-Q water by shaking for 1 h. The extraction solution was analyzed further by the aforementioned procedures.

Hydride-generation Method

Five hundred microlitres of 2% $NaBH_4$, prepared fresh in Milli-Q water before use, were added to 85 mL of the target solutions spiked with 5 ng of Sn of each OTC. Extraction with 1 mL cyclopentane was carried out by vigorous shaking for 10 min. For the purging method, a bubbler was equipped to purge hydrogenated OTC with Ar at a rate of 1 L min^{-1}. After cyclopentane was separated or purged for 1 h, the solution was incubated at room temperature in the dark. Further quantification of OTC with $NaBPr_4$ in treated solution was carried out 3 h later using the aforementioned procedures, to prevent derivatization by residual $NaBH_4$.

Ethylation Method

Five hundred microlitres of 2% $NaBEt_4$, prepared freshly in Milli-Q water before use, were added to 85 mL of the target solutions spiked with 5 ng of Sn of each OTC. Extraction with 1 mL of cyclopentane was carried out by vigorous shaking for 10 min. After cyclopentane was separated, the solution was incubated at room temperature in the dark. Further quantification of OTC with $NaBPr_4$ in treated solution was carried out 3 h later using the aforementioned procedures, to prevent derivatization by residual $NaBEt_4$. Figure 1 shows a typical chromatogram from a blank sample treated using the ethylation method.

Complex Reagents Extraction Method

0.1 g of sodium diethyldithiocarbamate (NaDDTC), 8-quinolinol or tropolone, and 1 mL of cyclopentane were added to 85 mL of the target solutions spiked with amounts of 5 ng of Sn for each species. After vigorous shaking for 10 min, cyclopentane was removed. Further quantification of OTC with $NaBPr_4$ in treated solution was performed 3 h later by the procedures described above.

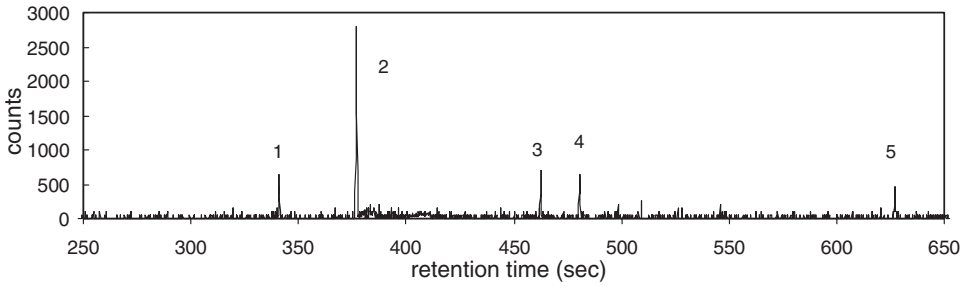

FIGURE 1 Chromatogram for a blank sample treated by the ethylation method: (1) dimethyltin; (2) triethyltin as internal standard; (3) monobutyltin; (4) dibutyltin; (5) dioctyltin.

Adsorption of Organotin Compounds to Different Materials

Five nanograms of Sn of each OTC were spiked with 50 mL of artificial rainwater (NH_4NO_3 11.64 mg L^{-1}, K_2SO_4 7.85 mg L^{-1}, Na_2SO_4 1.11 mg L^{-1}, $MgSO_4 \cdot 7H_2O$ 1.3054 mg L^{-1}, $CaCl_2$ 4.32 mg L^{-1}) filled in bottles of different materials. The bottles were shaken in the dark at $20 \pm 1^{\circ}C$ for 24 h. Then, the whole solution was transferred into a glass volumetric flask and quantified using the aforementioned procedures.

RESULTS AND DISCUSSION

Sources of Blank Values

In our case, methyltin and butyltin species were found in commercial sodium acetate (Tables I and IV), which was commonly used for acetate buffer, and the contents of OTC differed among the samples. MBT and DBT were the principal species, with contents up to several nanograms of Sn per gram. In comparison with NaOAc of analytical grade, NaOAc of super-pure grade was less contaminated. In our Milli-Q water, MBT, and DBT were found with concentrations of several nanograms of Sn per litre. The concentrations of other OTC in Milli-Q water were below detection limits.

This investigation provided further evidence for the existence of OTC blank values in chemicals and laboratory water. Therefore, different procedures to reduce OTC contamination from water (solutions), chemicals, and containers needed to be tested and developed.

Derivatization reagents ($NaBH_4$, $NaBEt_4$, $NaBPr_4$) probably contain OTC blank values. However, decontamination of derivatization reagents was not suggested here, because such reagents are usually unstable, and complicated treatment might introduce more blank values and decrease derivatization efficiencies [3]. Small amounts of reagents should be used for analysis to reduce the risk of blank values from reagents.

Reducing OTC Blank Values

Derivatization and Extraction

The addition of derivatization reagents followed by organic solvent extraction eliminated OTC contaminants in the solution to different extents depending mainly on the properties of the derivatization reagents (Table II). The method combining $NaBEt_4$

TABLE I Blank values of organotin compounds in different matrixes[a]

	DMT	*MBT*	*DBT*	*TBT*
NaOAC 1[b] ($ng\,Sn\,g^{-1}$)	< DL	0.26 ± 0.063	0.20 ± 0.021	< DL
NaOAC 2 ($ng\,Sn\,g^{-1}$)	0.010 ± 0.0011	0.39 ± 0.025	0.38 ± 0.032	< DL
Milli-Q water ($ng\,Sn\,L^{-1}$)	< DL	0.18 ± 0.09	1.01 ± 0.17	< DL

[a]Mean values and SDs for three replicates are presented. < DL: below detection limit. All decontamination was done by ethylation method. To determine OTC in NaOAc, about 4 g NaOAc was dissolved in the 50 ml Milli-Q water and pH was always adjusted to 4 for propylation procedures.
[b]Super pure grade with purity 99.9%.

TABLE II Percentage of remaining spiked organotin compounds after reducing blank values (%)[a]

Method	*TMT*	*DMT*	*MMT*	*TBT*	*DBT*	*MBT*	*DOT*	*MOT*
$NaBEt_4$	< DL	0.73	2.59	< DL	< DL	2.09	< DL	4.09
$NaBH_4$	32.4	12.1	12.9	15.0	8.12	4.57	32.2	8.57
$NaBH_4$ purge	0.76	1.08	0.96	12.3	8.20	9.15	40.8	25.6
NaDDTC	103	87.9	103	6.14	5.73	8.19	12.3	71.5
Tropolone	104	33.1	101	8.52	6.44	52.5	8.92	12.3
8-Quinolinol	92.9	9.74	98.7	9.28	6.18	43.4	12.0	7.77

[a]Mean values are presented. $N = 3$; all SDs were below 5%. < DL: below detection limit.

and cyclopentane extraction exhibited the best elimination efficiencies, and more than 99% of most spiked OTC was removed. However, around 2–4% of the spiked mono-substituted OTC (MMT, MBT, and MOT) species were still found in the solution. In the case of derivatization with $NaBH_4$, about 80–90% of most spiked OTC were eliminated from the solution, but species such as TMT and DOT were still left in the solution for *ca.* 30%. In comparison with extraction, purging with Ar after derivatization with $NaBH_4$ notably improved the elimination rates of all methyltin species to 99%. For butyltin species, around 90% of the spiked materials could be eliminated, whereas, the DOT and MOT elimination rates reached only 60 and 75%, respectively.

The higher elimination rates provided by using $NaBEt_4$ may contribute principally to the higher hydrophilicity of ethylated OTC, which can be extracted by organic solvent better than hydrogenated species. For further quantification with $NaBPr_4$, one advantage in using $NaBEt_4$ over $NaBH_4$ is the similarity of pH conditions for derivatization as compared with $NaBPr_4$. The pH value for the best derivatization efficiency with $NaBEt_4$ was around 5, which was not far from the ideal derivatization pH with $NaBPr_4$ [10]. However, derivatization with $NaBH_4$ was more efficient under more acidic conditions [11]. Yields of derivatization with $NaBEt_4$ were less reduced than with $NaBH_4$. Adjusting the pH with untreated acid or base was not recommended because such addition of acid or base might have introduced some other OTC contamination. Elimination of OTC contaminants by hydride generation followed by purging with Ar was suitable for more volatile hydrogenated species, such as methyltins. The less volatile hydrides like TBT-H suffered from condensation [12] and therefore left more residue reseeded in the solution.

By combining an OTC complexing agent, such as NaDDTC, tropolone, and 8-quinolinol, together with cyclopentane extraction, reduction in most spiked methyltin species failed. However, about 90% of spiked butyltin and octyltin species were elim-

inated. Generally speaking, the spiked di-substituted OTC was better eliminated using these methods, whereas mono-substituted OTC had the most residues in the tested solution.

All methods based on complexing agents exhibited very low elimination rates of spiked OTC. The elimination rates of OTC from solutions depended on the polarity of the individual OTC. Thus, highly hydrophilic species like methyltins and MBT were poorly removed from solution. The combination of derivatization ($NaBH_4$ or $NaBEt_4$), complexing agents (tropolone, NaDDTC, or 8-quinolinol), and organic solvent extraction did not increase the elimination rates of spiked OTC significantly compared with derivatization and extraction (data not shown). The use of complexing agents did not improve the extraction efficiency.

Without considering elimination efficiencies, the decontamination methods described above were convenient for solutions, containers, and stir bars, but are essentially applied in conjunction with aqueous solutions. For the use of both $NaBEt_4$ and $NaBH_4$, the pH of solutions is restricted in certain ranges. $NaBH_4$ can be stored easily and is much cheaper than $NaBEt_4$. Therefore, decontamination with $NaBEt_4$, the most powerful method demonstrated here, was specifically recommended for OTC quantification with $NaBPr_4$ due to the similarity of their derivatization conditions and for ultra-trace analysis. $NaBH_4$ provides a cheaper alternative to reduce most OTC contaminants but is less effective. The use of $NaBH_4$ accompanied with purge gas is suitable for denominating methyltin species. The use of complexing agents for reducing OTC contaminants is not recommended.

Glowing

Over 99% of the OTC spiked to glassware was successfully removed with glowing for 24 h at 540°C (Table III). Only MBT, DOT, and MOT (2.92, 14.3, and 27.3 left residues) could not be completely removed. In the case of NaOAc, most OTC blank values could be reduced with glowing at 300°C (Table IV). Disproportionation of OTC was observed here for all species at the high temperature.

TABLE III Percentage remaining compounds of 5 ng of Sn spiked OTC after reducing blanks (%)[a]

Method	*TMT*	*DMT*	*MMT*	*TBT*	*DBT*	*MBT*	*DOT*	*MOT*
Glowing	0.21	0.12	< DL	0.42	0.27	2.92	14.3	27.3
Washing machine	< DL	0.29	< DL	0.41	0.16	2.32	4.05	1.73

[a]$N = 3$; mean values are presented, and all SDs were below 5%. < DL: below detection limit.

TABLE IV Contents of organotin compounds (in pg Sn g^{-1}) in sodium acetate before and after glowing at 300°C for 3 h[a]

Method	*TMT*	*DMT*	*MMT*	*TBT*	*DBT*	*MBT*	*DOT*	*MOT*
NaOAc 3	< DL	65.1	2.44	< DL	1030	3470	3.21	348
NaOAc 3[b]	2.10	< DL	5.28	8.83	21.3	9.23	6.31	116

[a]$N = 3$, All SDs were under 5%. < DL: below detection limit. Detection limit: 0.3 pg Sn g^{-1}, based on 4.05 g of NaOAc in 50 mL of solution.
[b]Sample NaOAc 3 after glowing at 300°C for 3 hours.

The high residue rates of MBT, MOT, and DOT were reflected in the higher Sn–C bond dissociation energy of lower substituted OTC and OTC with longer-chained alkyl groups [13]. Generally speaking, the glowing method is limited to containers of materials withstanding high temperatures (over 300°C), like glassware and chemicals with high melting points. Glowing at these high temperatures successfully eliminated most OTC contaminants except MBT, MOT, and DOT. OTC disproportionate at these high temperatures but at a much lower level of content in relation to original blank values.

Washing Machine

The two-step washing by the washing machine cleaned up over 99% of most OTC spiked (Table III). Only MBT, MOT, and DOT showed residue rates higher than 1%. Washing with detergents and hot distilled water removed OTC efficiently without any OTC disproportionation observed. It is suitable for containers of all materials.

UV-light Treatment

MBT and DBT blank values decreased pronouncedly after 10 h of UV-light treatment in 1 M NaOAc solution (Fig. 2), and then concentrations of MBT and DBT increased slightly when the treatment lasted for longer times (e.g. 20 h). The blank values of methyltin species were very low before UV-light treatment, but their concentrations increased with increasing time for UV-light treatment. The spiked OTC in water showed similar results as the MBT and DBT contaminants in NaOAc solution (Fig. 3). Concentrations of all OTC species decreased sharply at the initial stage of UV-light treatment, but increased again with long-term UV-light treatment. Lower substituted OTC as intermediates were not observed in either of the UV-light treatment experiments.

Past studies have demonstrated that OTC decay under UV light [14] and the ability of UV light to decompose OTC was here shown again. The UV-light treatment is facilitated to reduce the OTC contaminants in solutions. The increase in methyltin species during UV-light treatment (Fig. 2) suggests disproportionation of dimethyltin species and the Sn-methylation in the solution. The methyl groups for Sn-methylation might transfer from the UV-decomposed OAc groups or butlytin species. The slight increase in butyltin species in Figs. 2 and 3 and methyltin species in Fig. 3 was more likely to be

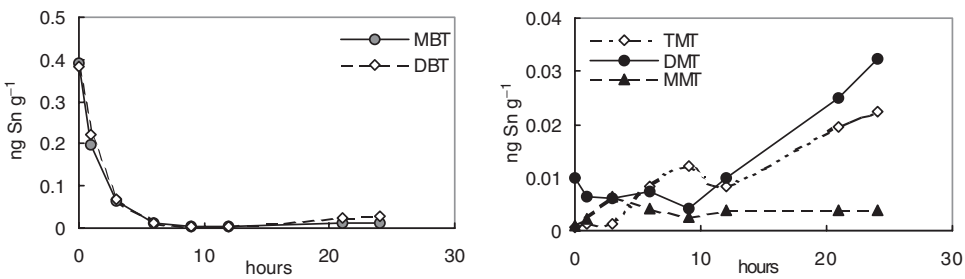

FIGURE 2 Concentrations of butyltin and methyltin species as Sn in 1 M sodium acetate solution treated with UV light (15 W). Mean values are given, and all SDs were below 5%.

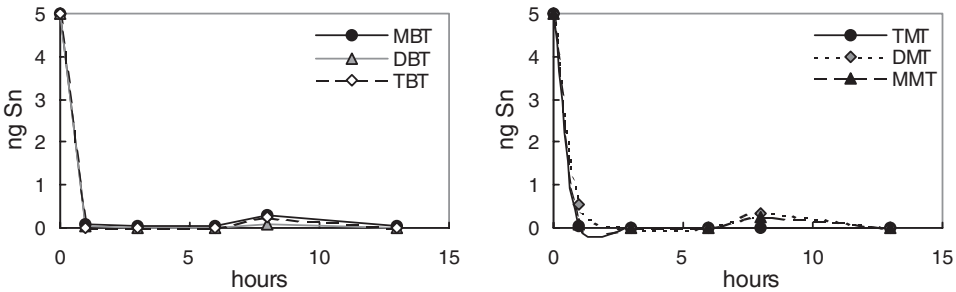

FIGURE 3 Amounts of spiked butyltin and methyltin species in water treated with UV light (750 W). The initial spiked amounts were 5 ng of Sn for each species. Mean values are given, and all SDs were below 5%.

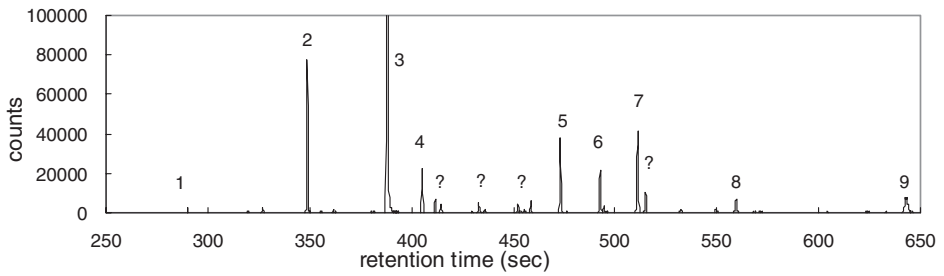

FIGURE 4 Chromatogram for a 100 ng Sn L^{-1} OTC spiked solution with UV (750 W) treatment after 8 h: (1) trimethyltin; (2) dimethyltin; (3) triethyltin as internal standard; (4) monomethyltin; (5) monobutyltin; (6) dibutyltin; (7) tributyltin; (8) monooctyltin; (9) dioctyltin.

re-alkylation by UV-decomposed alkyl groups in the solution. This hypothesis was supported by some unidentified peaks, which might be methylbutyltin species, after UV treatment (Fig. 4).

Nitric Acid Bath

Among all tri-substituted OTC, TPhT decomposed fastest in a 30% nitric acid bath (Fig. 5a). It took about 2 weeks to reduce the spiked TPhT below the detection limit. Degradation of TMT in 30% nitric acid was very slow, and especially at the beginning of the incubation. It took about 5 weeks to decompose most of the TMT in the solution. To eliminate most spiked TBT in solution, about 4 weeks were needed. TPhT decompose remarkably more rapidly in a bath with 30% nitric acid than with 10 and 20% nitric acid (Fig. 5b). More than 3 months was required to eliminate spiked TPhT thoroughly in a 10 and 20% nitric acid bath. No apparent reduction in TBT and TMT was found with 10 or 20% nitric acid (data not shown). Lower substituted OTC as intermediates were observed at all nitric acid concentrations (data not shown).

A 10 to 30% nitric acid bath was broadly used to clean up containers for OTC analysis [15]. It was presumed that nitric acid decomposes OTC by its high oxidation potential. In this investigation, decomposition of the spiked OTC in the nitric acid bath was demonstrated. The decomposition rates depended on the concentrations of nitric acid and the substitution of OTC species. Although the nitric acid bath could be used for cleaning containers of different materials, the OTC degradation rates were very low.

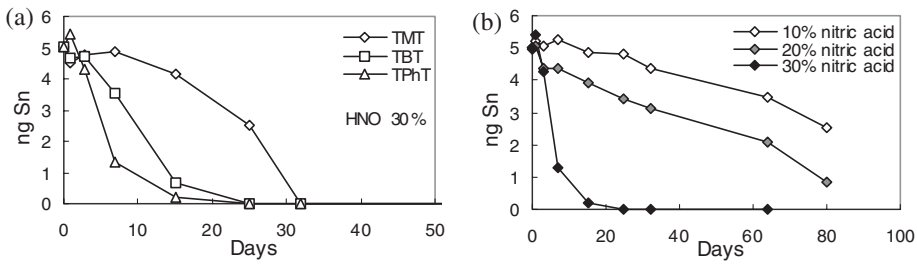

FIGURE 5 Remaining amounts of spiked organotin compounds in nitric acid. The initial spiked amount for each species was 5 ng of Sn. Mean values are given, and all SDs were below 5%. (a) Tri-substituted organotin compounds with different alkyl groups in 30% nitric acid. (b) Triphenyltin in 10, 20, and 30% nitric acid.

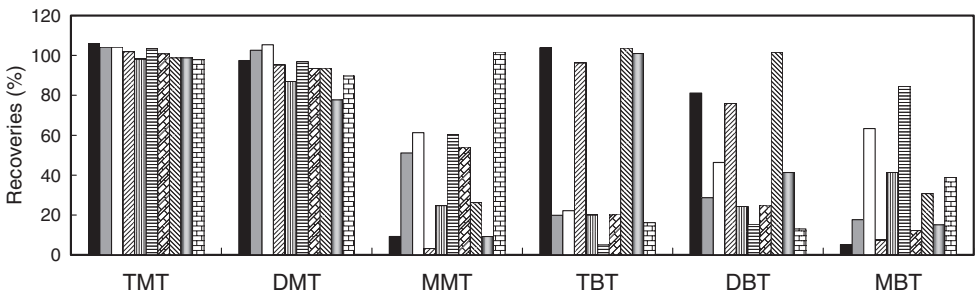

FIGURE 6 Recoveries (%) of organotin compounds from bottles of different materials. Mean values of three replicates are shown, and all SDs were below 5%. ■ polycarbonate; ▒ Teflon PFA; □ Teflon FEP; ▨ polyethyleneterephthalate G copolymer; ▥ polypropylene; ▤ low-density polyethylene; ▩ high-density polyethylene; ▧ aluminium; ◧ glass; ▦ silanized glass.

Thus, reduction of OTC contaminants using nitric acid baths was only suggested for long-term incubation and at best with highly concentrated nitric acid.

Adsorption of Organotin Compounds to Different Materials

Only a small degree of adsorption of TMT and DMT to all materials tested here was found (Fig. 6). TBT adsorbed in negligible amounts to PC, polyethyleneterephthalate G copolymer (PETG), aluminium and glass. Strong adsorption ($>80\%$) was observed in both Teflons, both polyethylene (PE), and silanized glass. No apparent adsorption of DBT to aluminium was found. Around 80% of the spiked DBT adsorbed to PC and PETG, and $<50\%$ of the spiked DBT was recovered from the other materials. MMT exhibited a small degree of adsorption only to silanized glass, but showed $>40\%$ adsorption to the other materials. MBT was poorly recovered from most materials and the lowest degree of adsorption (about 20%) was observed in the low-density PE.

The extents of adsorption to different materials increased remarkably with the increase in charges and hydrophobicity of OTC. Adsorption of ionic OTC to materials seems to be governed mainly by electrostatic and hydrophobic interactions. According to the results presented here, no material is suitable for all OTC. Different materials should be applied for different OTC, especially for MMT and butyltin compounds. When quantifying ionic OTC, underestimation of some species through adsorption

to the sampling container walls seems to be unavoidable. Measurement of OTC *in situ* or application of extraction reagents such as tropolone to recover possibly all OTC in waters is recommended.

CONCLUSIONS

To reduce OTC blank values of containers, rinsing with detergents and distilled water was found to be the most simple, available, and efficient method. For chemicals with high melting points, glowing at high temperatures is suggested to reduce OTC contaminants. Solutions can be decontaminated using UV-light treatment for an appropriate time or by using derivatization reagents followed by extraction or purging.

Adsorption of OTC to container walls is inevitable. Therefore, the use of extraction reagents to recover OTC in the sampling container is suggested to avoid underestimating OTC concentrations in waters.

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