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# GC FPD method for the simultaneous speciation of butyltin and phenyltin compounds in waters

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**A method is described for the simultaneous determination of nanogram amounts of mono-, di- and tri-butyltin compounds and mono-, di- and triphenyltin compounds in water. The procedure is based on the conversion of tin compounds to volatile species by Grignard pentylation and analysis using GC with flame photometric detection (GC FPD). The ionic compounds are extracted from diluted acidified (HBr) aqueous solutions by using a pentane–tropolone solution. The extracted organotin compounds are pentylated by a Grignard reagent and purified on a Fluorisil column before analysis by GC FPD. The detection limits are 20 ng $dm^{-3}$ for butyltin compounds and 50 ng $dm^{-3}$ for phenyltin compounds. Recoveries from spiking experiments in tap-water and natural seawater matrices, in which no organotin compounds were detected, were greater than 90% for most of the alkyltin compounds.**

**Keywords: Organotin, tributyltin, dibutyltin, monobutyltin, triphenyltin, diphenyltin, monophenyltin, speciation, gas chromatography, flame photometric detector (FPD), water**

## INTRODUCTION

Worldwide production of organotin chemicals has risen continuously in the last decade, due to the use of numerous organotin derivatives for commercial purposes. Tributyltin compounds [$(C_4H_9)_3SnX$; X = F, Cl, OAc], bis(tributyl) oxide, and triphenyltin compounds [$(C_6H_5)_3SnX$; X = OH, OAc] have been widely used in formulations to combat fungal diseases and as material preservatives and antifouling paints. These provide a great variety of entry pathways into the environment.[1]

On the other hand, environmental degradation causes stepwise loss of organic groups from the tin atom, which results in a variety of species, $R_nSn^{(4-n)+}$ ($n = 0$–4), with lesser toxicities.

Most of the analytical methods used for tin speciation[2–20] are based in the use of chromatography with a pre-column derivatization step, either by hydride generation or by Grignard alkylation, although stannanes are rather labile, thus preventing further clean-up steps.[15] Therefore, alkylation is often preferred over hydride formation, as the resulting tetra-substituted organotin compounds can be purified and concentrated, which is necessary for low-level samples and complex matrices. HPLC has also been considered for the speciation of organotin compounds and there are a number of reports in relation to its uses and possibilities.[21–26] However, for volatile organometallic species or for those that can readily be converted into volatile derivatives, GC is usually the preferred technique, in combination with a selective detector, e.g. FPD, AA or DCP.

Other trends in organotin speciation focus on simpler procedures, e.g. through a direct injection of butyltin chlorides into a GC AA system using an on-column hydride generation method,[17] simultaneous hydridization and extraction into dichloromethane before speciation by GC FPD,[12] or formation of hydride derivatives in a packed reactor inside the injection port of the GC FPD system.[18]

A considerable number of papers consider the characterization and quantification of the more toxic species of tin, especially tributyltin, in different samples and matrices, and the methods have been used for the study of specific environmental problems. Procedures with a pre-column derivatization step by alkylation have been described for the analysis of methyltins,[27] butyltins,[28–33] mixed methylbutyltins[12] and others. However, there are relatively few methods for the sensitive determination of a broad range of organotin compounds in environmental samples.

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Müller has reported the determination of butyltin and phenyltin species on the basis of extraction/ethylation[15] or methylation,[34] and Tsuda[35] has reported using a hydridization process. We have used a modification of the Maguire approach[36] which derivatizes the organotin compounds by Grignard pentylation, and avoids the volatility problems usually present with shorter alkyl groups. In addition, any analytical method for adequate environmental monitoring of organotins must be capable of determining at low concentrations the entire set of species in order to assess their environmental impact. According to Quevauviller and Donard,[37] an Environmental Quality Target value (EQT) was established in the UK at 20 ng $dm^{-3}$ in order to achieve protection of marine life, although more recent studies suggest to that this value should be 2 ng l $dm^{-3}$.

In the present work, we describe a method which allows a sensitive and simultaneous determination of tributyltin (TBT) and triphenyltin (TPhT), as well as their degradation products, dibutyltin (DBT), monobutyltin (MBT), diphenyltin (DPhT) and monophenyltin (MPhT). After extraction into pentane, the organotins are pentylated with a Grignard reagent and analysed by using GC FPD. The method has been applied to spiked tap- and sea-waters with detection limits of 20–50 ng $dm^{-3}$.

## EXPERIMENTAL

### Reagents and standards

All organic solvents were HPLC grade; organotin compounds were obtained from Aldrich and were used without further purification, but analysis did not reveal any detectable impurities. The other chemicals were analytical reagent grade. Water used in all the experiments was distilled and deionized and gave blank readings in all analyses.

Glassware was washed with a detergent solution, then with chromic acid, and soaked with this medium overnight before being rinsed thoroughly with tap-water and then with distilled water.

Standard solutions of $Bu_3SnCl$ (for TBT), $Bu_2SnCl_2$ (for DBT), $BuSnCl_3$ (for MBT), $Ph_3SnCl$ (for TPhT) $Ph_2SnCl_2$ (for DPhT) and $PhSnCl_3$ (for MPhT) (from Aldrich-chemie, Steinheim, Germany) were prepared by dissolving in ether followed by subsequent dilution to give solutions in the working range. Finally, these mixtures were pentylated.

### Derivatization and clean-up

#### Preparation of Grignard reagent

These reagents were prepared according to standard synthetic methods: 25 $cm^3$ of 16% (v/v) pentyl bromide solution in ether was added dropwise to 0.8 g of Mg (0.03 mol), which had previously been heated with a small amount of iodine as catalyst. The mixture was then refluxed with continuous stirring at 40 °C for 1 h.

#### Derivatization

The pentane extract containing the organotin species was added to the ether solution of the Grignard reagent, prepared as described above, and the mixture was refluxed at 40 °C under continuous stirring for 1 h. The mixture was allowed to cool and the excess of reagent was destroyed by careful dropwise addition of about 25 $cm^3$ of 1 mol $dm^{-3}$ sulphuric acid. The organic layer was collected in a round-bottomed flask and the aqueous layer was extracted with 10 $cm^3$ of pentane; both pentane extracts were combined and dried over anhydrous sodium sulphate ($Na_2SO_4$). The resulting extract was reduced in volume to about 2 $cm^3$ at room temperature by rotary evaporation and purified by chromatography on a 7 cm × 1 cm (i.d.) column of Fluorisil (Merck, Darmstadt, Germany), eluting with 5 $cm^3$ of pentane. The pentane extract was then reduced to 2 $cm^3$ and transferred into a microevaporator together with 0.165 μg of dimethyldipentyltin ($Me_2Pe_2Sn$) as internal standard previously derivatized, and concentrated to 0.5 $cm^3$ under a gentle stream of nitrogen in a microevaporator.

### Extraction procedure

A 1000-$cm^3$ portion of the water sample containing the organotin species acidified with 10 $cm^3$ of HBr (Merck) was extracted by shaking vigorously with 300 $cm^3$ of 0.07% (w/v) solution of tropolone (Aldrich) in pentane for 10 min. The organic extract was dried with anhydrous $Na_2SO_4$ and reduce in volume to 5 $cm^3$ in the rotary evaporator. Then the extract was derivatized by pentylation, to be analysed by GC.

### Gas chromatography

A Perkin–Elmer 8140 gas chromatograph (GC) fitted with a split/splitless injector, glass capillary column (Supelco SPB-1 15 m in length, 0.53 mm i.d., film thickness 1.5 μm) and a flame photometric detector were used. The detector was

operated with a 610-nm cut-off interference filter, at a temperature of 250 °C, using hydrogen and air flow rates of 46.5 and 88.0 $cm^3 min^{-1}$, respectively. The injector temperature was set at 250 °C and helium (9.5 $cm^3 min^{-1}$) served as carrier gas using a split ratio of 3.8. Sample aliquots of 5–10 µl were injected and the compounds of interest were eluted with the following temperature programme: initial column temperature 50 °C, heating to 250 °C at 10 °C $min^{-1}$ and isothermal at this temperature for 7 min.

## RESULTS AND DISCUSSION

Usually the procedures for trace analysis of organotin species involve several steps: derivatization, analysis and extraction. It has been necessary to check and develop these steps in detail to meet the speciation requirements considered in this paper.

### Derivatization

Pentylation, obtained by using the Grignard reagent PeMgBr, was chosen for conversion of the different mono-, di- and tri-substituted organotin compounds into the tetra-substituted ones. As Maguire has stated,[36] derivatization with shorter alkyl groups is not suitable for butyltin species as the derivatives are fairly volatile compared with solvents such as hexane, pentane or benzene, and appreciable quantities of the derivatives are lost during routine concentration procedures such as rotary and vortex evaporation of the solvents. In addition, Grignard methylation of environmental samples would exclude the possibility of determining these conversion and degradation products. The same problem is encountered with the series of ethyl derivatives, $Bu_nEt_{4-n}Sn$, when $n \leq 2$, and the series of n-propyl derivatives, $Bu_nPr_{4-n}Sn$, when $n \leq 2$.

The pentylation reaction was carefully studied to check the total conversion of organotin species. Reaction time was a decisive variable, which was established as a 60-min optimum. Lower time reactions did not cause complete derivatization.

### Optimization of the instrumental response

#### Carrier gas

Nitrogen and helium have been tested as carrier gases. Nitrogen causes a drift in the baseline when a temperature programme is used; however, it gives a good response for isothermal conditions. This drift causes a decrease in the reproducibility of the signals. For this reason helium was selected for further experiments. A flow rate through the column of 9.5 $cm^3 min^{-1}$ (with a split ratio of 3.8) was found to be optimum.

**Table 1** Retention times for organotin compounds using different temperature programmes

| Compound | Retention time (min)[a] | | | | |
|---|---|---|---|---|---|
| | a | b | c | d | e |
| $Me_2Pe_2Sn$ | 11.34 | 8.82 | 7.30 | 8.81 | 6.64 |
| $Bu_3PeSn$ | 16.20 | 11.98 | 9.73 | 17.55 | 11.16 |
| $Bu_2Pe_2Sn$ | 17.16 | 12.63 | 10.23 | 19.40 | 12.12 |
| $BuPe_3Sn$ | 18.06 | 13.25 | 10.70 | 21.14 | 13.03 |
| $PhPe_3Sn$ | 20.55 | 15.08 | 12.34 | 25.87 | 15.53 |
| $Ph_2Pe_2Sn$ | 22.66 | 17.03 | 14.26 | 17.57 | 17.57 |
| $Ph_3PeSn$ | 25.99 | 20.37 | 17.56 | 32.97 | 20.93 |

[a] *Conditions*: **a**, initial temperature 50 °C, rate 10 °C $min^{-1}$ up to 250 °C, hold at 250 °C for 7 min; **b**, initial temperature 50 °C, rate 15 °C $min^{-1}$ up to 250 °C, hold for 7 min; **c**, initial temperature 50 °C, rate 20 °C $min^{-1}$ up to 250 °C, hold for 9 min; **d**, initial temperature 100 °C, rate 5 °C $min^{-1}$ up to 250 °C, hold for 3 min; **e**, initial temperature 100 °C, rate 10 °C $min^{-1}$ up to 250 °C, hold for 7 min.

#### Temperature programme

Retention time was assessed by five different temperature programmes, and Table 1 shows the retention times for the different organotin compounds. A good separation was achieved by using an initial column temperature of 50 °C and a heating rate of 10 °C $min^{-1}$, stopping the programme at 250 °C and remaining isothermal at this temperature for 7 min. Under these conditions, the reproducibility of retention times was very good, with a standard deviation of 0.016.

#### FPD performance

Since the photometric detection mechanism is attributed to light emission of the excited organotin species in the detector flame,[38] the response is dependent on flame conditions, which affect the sensitivity. Different hydrogen flow rates were tested from 32.6 to 90.0 $cm^3 min^{-1}$ (Table 2), using in all these experiments a fixed gas flow rate of 87.0 $cm^3 min^{-1}$. There is no signal for 32.6 $cm^3 min^{-1}$ of hydrogen, but the response increases for higher flow values and it is almost constant from 45.0 to 80 $cm^3 min^{-1}$; for this rea-

**Table 2** Response of the FPD detector (peak height)[a] for different hydrogen flow rates

| | $H_2$ flow rate ($cm^3\ min^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| Compound | 32.6 | 40.0 | 44.7 | 48.0 | 60.0 | 80.0 | 90.0 |
| $Bu_3PeSn$ | 0 | 2750 | 2815 | 2810 | 2819 | 2790 | 2641 |
| $Bu_2Pe_2Sn$ | 0 | 2920 | 3116 | 3098 | 3120 | 3110 | 2540 |
| $BuPe_3Sn$ | 0 | 2588 | 3115 | 3095 | 3120 | 3125 | 2640 |
| $PhPe_3Sn$ | 0 | 1940 | 2070 | 2074 | 2060 | 2083 | 1990 |
| $Ph_2Pe_2Sn$ | 0 | 1561 | 1650 | 1670 | 1643 | 1655 | 1990 |
| $Ph_3PeSn$ | 0 | 1187 | 1360 | 1353 | 1365 | 1349 | 1290 |

[a] Arbitrary units.

**Table 3** Response of the FPD detector (peak height[a]) for different oxygen flow rates

| | $O_2$ flow rate ($cm^3\ min^{-1}$) | | | | |
|---|---|---|---|---|---|
| Compound | 60.7 | 75.7 | 87.0 | 101.4 | 116.0 |
| $Bu_3PeSn$ | 0 | 2817 | 2810 | 2820 | 1543 |
| $Bu_2Pe_2Sn$ | 0 | 3079 | 3098 | 3084 | 2124 |
| $BuPe_3Sn$ | 0 | 3110 | 3095 | 3083 | 1983 |
| $PhPe_3Sn$ | 0 | 2081 | 2074 | 2085 | 998 |
| $Ph_2Pe_2Sn$ | 0 | 1658 | 1670 | 1674 | 743 |
| $Ph_3PeSn$ | 0 | 1362 | 1353 | 1370 | 527 |

[a] Arbitrary units.

son a 46.5 $cm^3\ min^{-1}$ hydrogen flow rate was selected for further experiments. A similar study was carried out with air flow rates from 60.0 to 116.0 $cm^3\ min^{-1}$ (Table 3), showing a poor response for extreme flow rates, and a stable optimum response for intermediate flow rate values. An air flow rate of 88.0 $cm^3\ min^{-1}$ has been selected.

Tests were made by reversing the hydrogen and air inlets, which had been reported to increase the signal.[36] The results obtained with our detector were similar to the normal configuration but flame-out problems appeared frequently.

We have also tested the influence of injector and detector temperatures. Our recommended injector temperature is in the interval 200–270 °C, in which the peak heights reach a maximum, but they suffer a strong decrease for lower temperature values, specially for the phenyltin compounds which have higher boiling points. The optimum temperature for the detector response has been found to be between 200 and 280 °C.

The detector performance has been tested by using different cut-off interference filters of 394, 525 and 610 nm. The 394 nm filter increases the sensitivity but selectivity is very poor. The sensitivity decreases with the other two filters, although it is higher for the 610 nm filter, which in addition shows a better selectivity due to the excited Sn—H emission bond at this wavelength. This fact made the 610 nm filter more reliable for our analytical purposes.

## Calibration and detection limits

The calibration curves for the different organotin compounds studied using peak heights were linear for tin (as tin atoms) amounts less than 40 ng; this limit increases to 55 ng and 60 ng for DPhT and TPhT, respectively (see fig. 1). The

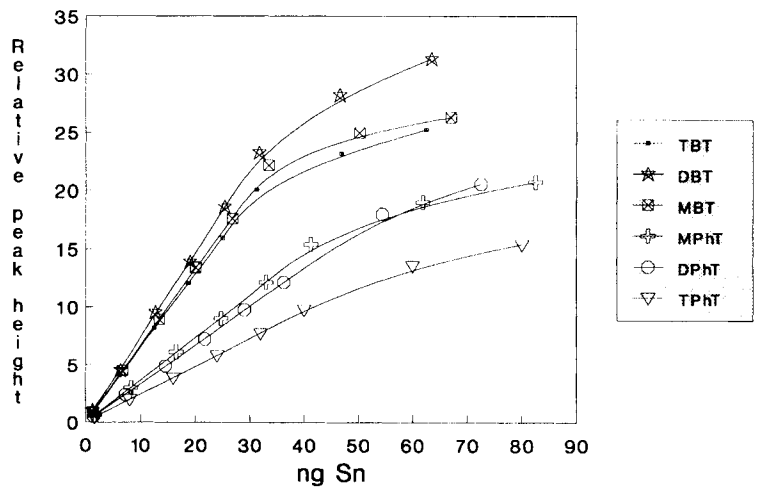


**Figure 1** Calibration curves.

**Table 4** Linear range of response for the different organotins

| Compound | Detection limit (ng)[a] | Maximum limit within linear range (ng) | Correlation coefficient (with internal standard) |
|---|---|---|---|
| $Bu_3PeSn$ | 0.30 | 32 | 0.9999 |
| $Bu_2Pe_2Sn$ | 0.28 | 32 | 0.9999 |
| $BuPe_3Sn$ | 0.32 | 34 | 0.9999 |
| $PhPe_3Sn$ | 0.47 | 42 | 0.9997 |
| $Ph_2Pe_2Sn$ | 0.48 | 55 | 0.9999 |
| $Ph_3PeSn$ | 0.53 | 60 | 0.9999 |

[a]i.e. Absolute limit able to be detected.

determinations were carried out using $Me_2Pe_2Sn$ as internal standard, which improves the precision (Table 4). The minimum detection limits ($3\sigma$ of blank) are also shown in Table 4.

The solutions were analysed at least five times with relative standard deviations lower than 5% when peak height was used. The response of the detector using peak area was usually greater than 5%; for this reason peak height was used throughout.

## Extraction

Extraction of the organotins with a non-polar solvent is a prior step necessary for the derivatization of the species through Grignard alkylation. However, more polar organotin compounds such as monobutyltin and monophenyltin are not extracted into these solvents, and a complexing agent, tropolone, has to be used for a good recovery. In addition, an acid medium is necessary to avoid losses of the organotin species due to adsorption/deposition on the glass wall of the vessels.

We have also studied the influence on the extraction of several variables: pH, type of acid

**Table 5** Influence of pH[a] on extraction (% recovery)

| | pH | | | | | | |
|---|---|---|---|---|---|---|---|
| Compound | 0 | 1.3 | 2.4 | 3.8 | 5.0 | 7.6 | 8.8 |
| $Bu_3PeSn$ | 96 | 98 | 97 | 75 | 76 | 73 | 70 |
| $Bu_2Pe_2Sn$ | 87 | 84 | 84 | 78 | 81 | 75 | 74 |
| $BuPe_3Sn$ | 83 | 60 | 59 | 57 | 59 | 47 | 38 |
| $PhPe_3Sn$ | 88 | 43 | 32 | 33 | 32 | 27 | 24 |
| $Ph_2Pe_2Sn$ | 90 | 100 | 93 | 98 | 85 | 86 | 78 |
| $Ph_3PeSn$ | 93 | 96 | 96 | 95 | 86 | 83 | 80 |

[a]Using HCl.

used, and organic solvent. The extraction of 100 $cm^3$ of spiked water samples [concentration of organotins 1.5 ppb (1.5 ng $g^{-1}$)] at different pH values showed that an acid medium is necessary for a good simultaneous recovery of the six species under study (Table 5); MPhT was the species most affected for this parameter. Hydrobromic acid was the best agent for acidification (Table 6) with recoveries of about 90%; hydrochloric acid also gave good results, but other acids such as $H_3PO_4$, $H_2SO_4$, $HClO_4$, HOAc or $HNO_3$ give lower values for recoveries. The volume of hydrobromic acid added is not decisive, although better results were found for no more than 15 $cm^3$ of this reagent.

Several non-polar solvents such as pentane, hexane, toluene and heptane were tested in combination with tropolone (at 0.05%, w/v) to extract the organotin species from 100 $cm^3$ of water acidified with HBr, using single and multiple (up to three extractions). In Table 7 we see the results obtained, which show good recoveries when two successive extractions were tried; a single extraction was insufficient, but three extractions do not cause any significant improvement. Pentane, hexane and heptane give the best

**Table 6** Influence of type of acid on extraction (% recovery)

| | Acid[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | $H_2SO_4$ | $HClO_4$ | HOAc | HCl | HBr | $HNO_3$ | $H_3PO_4$ | Without acid |
| $Bu_3PeSn$ | 89 | 70 | 88 | 96 | 95 | 85 | 80 | 73 |
| $Bu_2Pe_2Sn$ | 36 | 45 | 71 | 87 | 92 | 57 | 65 | 80 |
| $BuPe_3Sn$ | 4 | 6 | 35 | 83 | 88 | 5 | 10 | 71 |
| $PhPe_3Sn$ | 0 | 2 | 8 | 88 | 91 | 3 | 0 | 12 |
| $Ph_2Pe_2Sn$ | 95 | 87 | 93 | 90 | 87 | 92 | 75 | 85 |
| $Ph_3PeSn$ | 80 | 65 | 75 | 93 | 94 | 48 | 83 | 88 |

[a] Configured to obtain a pH value about 0.

**Table 7** Influence of organic solvent on extraction (% recovery)

| | Organic solvent | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pentane | | | Hexane | | | Toluene | | | Benzene | | | Heptane | | |
| Compound | *a*[a] | *b* | *c* | *a* | *b* | *c* | *a* | *b* | *c* | *a* | *b* | *c* | *a* | *b* | *c* |
| $Bu_3PeSn$ | 80 | 95 | 91 | 90 | 95 | 93 | 85 | 87 | 84 | 83 | 88 | 85 | 81 | 93 | 89 |
| $Bu_2Pe_2Sn$ | 83 | 92 | 88 | 88 | 91 | 89 | 85 | 81 | 78 | 82 | 79 | 81 | 86 | 96 | 88 |
| $BuPe_3Sn$ | 65 | 87 | 90 | 75 | 88 | 89 | 75 | 78 | 73 | 73 | 80 | 88 | 72 | 88 | 77 |
| $PhPe_3Sn$ | 64 | 89 | 89 | 70 | 91 | 84 | 78 | 75 | 70 | 82 | 83 | 79 | 64 | 86 | 74 |
| $Ph_2Pe_2Sn$ | 75 | 87 | 91 | 81 | 92 | 90 | 72 | 67 | 59 | 79 | 75 | 78 | 63 | 85 | 84 |
| $Ph_3PeSn$ | 79 | 93 | 92 | 88 | 95 | 91 | 52 | 57 | 55 | 72 | 70 | 69 | 54 | 78 | 73 |

[a] *a*, *b* and *c*: one, two and three extractions with 25 $cm^3$ of organic solvent, respectively.

results but the high boiling point of heptane makes the usual concentration step difficult, and pentane is more volatile than hexane; for these reasons pentane was selected in our approach. In these conditions the extraction of organotins is not difficult; it is sufficient to agitate the separating funnel for 1 min for total recovery.

## Analysis of organotin species in tap-water and seawater

The extraction procedure described previously has been adapted to the characteristics of the real samples which are analysed in environmental studies. The low levels of organotin species in natural waters makes necessary the use of higher sample volumes (1000 $cm^3$), introducing changes in the extraction method, especially in relation to the volume of organic phase and the amount of tropolone. We have tested the influence of different volumes of pentane, from 100 to 400 $cm^3$, in a single extraction, with optimum results for 300 $cm^3$. The amount of tropolone dissolved in the organic phase has to be reduced when a higher volume of the organic solvent is involved, because this compound eventually concentrates in the microevaporator, when the volume of the organic phase is reduced to about 0.5 $cm^3$, and it could cause some problems in the chromatogram due to dismutation processes.[17] It was determined that the optimum amount of tropolone was 0.02 g in 1000 ml of pentane since lower concentrations do not give good recoveries for monobutyltin and monophenyltin. In this way it is possible to obtain the following detection limits (ng $dm^{-3}$ as tin): MBT 22, DBT 20, TBT 19, MPhT 52, DPhT 45, TPhT 55, for a volume of sample of 1000 $cm^3$.

A clean-up step is necessary to remove the excess of tropolone and other impurities present in real samples, which can damage the gas chromatography column. For this purpose a purification of the organic phase by chromatography on

**Table 8** Concentration[a] of organotin compounds analysed in waters (ng $dm^{-3}$)

| Sample[b] | TBT | DBT | MBT | MPhT | DPhT | TPhT |
|---|---|---|---|---|---|---|
| Tap-water **1** | 38 ± 1 | 42 ± 2 | 36 ± 2 | 89 ± 3 | 95 ± 3 | 99 ± 2 |
| Tap-water **2** | 197 ± 3 | 193 ± 5 | 185 ± 10 | 450 ± 15 | 480 ± 10 | 493 ± 6 |
| Tap-water **3** | 1000 ± 5 | 975 ± 10 | 890 ± 20 | 1800 ± 15 | 1920 ± 10 | 1980 ± 10 |
| Seawater **1** | 41 ± 1 | 40 ± 3 | 37 ± 4 | 93 ± 3 | 94 ± 5 | 101 ± 2 |
| Seawater **2** | 200 ± 1 | 195 ± 5 | 179 ± 3 | 470 ± 7 | 483 ± 6 | 490 ± 5 |
| Seawater **3** | 995 ± 7 | 1002 ± 8 | 910 ± 15 | 1810 ± 13 | 1910 ± 15 | 2000 ± 12 |

[a] Mean ± standard deviation, $n = 3$.

[b] Composition of spiked waters:

Tap-water **1** and seawater **1**: TBT, DBT and MBT 40 ng $dm^{-3}$; MPhT, DPhT and MPhT 100 ng $dm^{-3}$.

Tap-water **2** and seawater **2**: TBT, DBT and MBT 200 ng $dm^{-3}$; MPhT, DPhT and MPhT 500 ng $dm^{-3}$.

Tap-water **3** and seawater **3**: TBT, DBT and MBT 1000 ng $dm^{-3}$; MPhT, DPhT and MPhT 2000 ng $dm^{-3}$.

Fluorisil has been applied, eluting with pentane which is then concentrated for injection in the gas chromatograph.

**Recoveries of spiked waters**

The usefulness of this speciation procedure has been checked in several spiked tap-water and seawater samples. the levels of the six organotin species (TBT, DBT, MBT, TPhT, DPhT and MPhT) are given in Table 8, which shows good recoveries especially for tri- and di-alkyltin species.

## CONCLUSIONS

The method proposed makes possible the simultaneous speciation of a broad range of organotin compounds, with detection limits for 1000-$cm^3$ samples in the range of 19–55 ng $dm^{-3}$, adequate for its application to the analysis of many environmental samples, especially waters. The method could also be useful in degradation studies in which dealkylation processes produce the simultaneous presence of several organotin species.

Although the method involves extraction and concentration steps which are tedious and time-consuming, the general procedure does not require extremes of skill, as may occur sometimes in other combined techniques (GC AA, HPLC AA, etc.). This makes the method useful in routine analysis, especially for pollution control of natural waters.

Finally, the method can be extended (Gomez-Ariza, J. L., Morales, E. and Ruiz-Benitez, M., private communication) to the determination of other samples of environmental interest such as sediments or tissues.

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