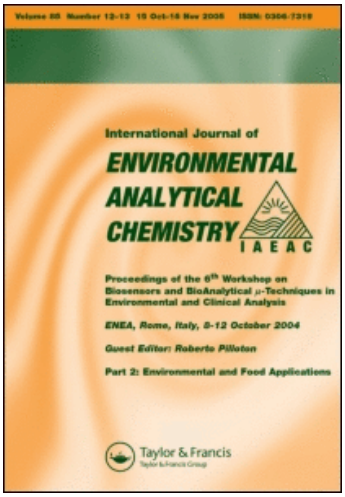

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ANALYTICAL METHODS FOR THE DETERMINATION OF ORGANOTINS IN THE MARINE ENVIRONMENT

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Analytical procedures for the determination of organotin compounds in sea water, sediments and mussels have been adopted in our laboratory, intercomparison/certification exercises with other European laboratories giving satisfactory results. The characteristics of the different methodologies are discussed, the balance between practical and analytical aspects leading to the selection of the following procedures.

For water samples two alternative extraction techniques are used: liquid/liquid extraction (0.3% tropolone in methylene chloride) or liquid/solid extraction (C18- or Carbopack B-loaded extraction tubes). Solid-phase extraction ensures good results and is more suitable in the field, avoiding high volumes of organic solvents and transport of fragile glassware. Extraction tubes can be easily stored, and problems with the transfer of whole samples to the laboratory, and storage and conservation problems are prevented.

For sediments and mussels, sonication (0.05% tropolone in methanol) can be used as the extraction procedure.

Final detection is performed by GC (FPD or MS detection) after pentylation. GC-MS is generally necessary to confirm doubtful results in highly polluted sediments, particularly if high sulphur levels are present. AAS can be used as an alternative detection technique after selective elution from the solid-phase tubes without any derivatization.

The detection limits are in the low-ppt range for water samples and in the low-ppb range for sediments and mussel samples, with a precision generally better than 10% for water samples and better than 15% for sediments and mussels.

KEY WORDS: Organotins, solid-phase extraction, liquid/liquid extraction, GC-FPD and GC-MS, graphite furnace AAS, water, sediments, mussels.

INTRODUCTION

Contamination of the marine environment by organotins has been well documented starting from the seventies[1,2]. At that time these compounds replaced copper salts as the active components in antifouling paints, because of their higher toxicity against fouling organisms[3,4]. Tributyltin (TBT) is the most used organotin compound, followed by triphenyltin (TPhT). In water TBT can be stepwise decomposed to less substituted compounds down to inorganic tin[5,6], absorbed by lipophilic phases such as the lipid fractions of organisms[7,8] or

adsorbed onto particulate matter[9], sediments being the final sink. The concentration levels of TBT and its degradation products dibutyltin (DBT) and monobutyltin (MBT) usually are in the ppb-ppt range in sea water[9–11] (concentration levels of TPhT and of its degradation products DPhT and MPhT are generally lower than butyltins), thus there is a need for analytical techniques with very low detection limits. Higher concentrations are found in sediments and biological samples due to high bioconcentration factors[7–9, 12–14]; however, the complexity of the matrices requires pretreatment, clean-up and deeper investigations for compound identification. Finally, as the organotins are much more toxic than inorganic tin (with trisubstituted compounds showing the maximum activity[1,15,16]), analytical techniques should also permit to discriminate at least between inorganic and organic tin.

EXPERIMENTAL

Reagents and materials

- Organic solvents were 'RS - per determinazione pesticidi' from Carlo Erba (Milan, Italy).
- Tropolone (2-hydroxy-cycloheptatrienone) from Lancaster Synthesis (Morecambe, U.K.).
- n-Pentylmagnesium bromide from Aldrich (Steinheim, FRG).
- Nitric acid 'ARISTAR' from BDH (Poole, UK).
- Sulphuric acid 'SPECTROSOL' from BDH.
- Potassium dichromate 'ANALAR' from BDH.
- Silica gel Davison 923 from BDH, activated overnight at 180°C.
- Florisil 60–100 mesh 'zur Rückstandsanalyse' from Merck (Darmstadt, FRG) stored at 130°C and pretreated overnight at 180°C before use.
- Anhydrous sodium sulphate RPE-ACS from Carlo Erba, treated at 550°C for 6 h before use.
- Tributyltin chloride 'laboratory reagent' (TBT) from BDH.
- Dibutyltin chloride (DBT) 97%, monobutyltin chloride (MBT) 95%, diphenyltin chloride (DPhT) 96%, monophenyltin chloride (MPhT) 98% from Aldrich.
- Tripropyltin chloride (TPrT) 98% and Triphenyltin chloride (TPhT) 99% from Merck (Hohenbrunn, FRG).
- SPE LC18 extraction tubes from Supelco (Bellefonte, PA, USA).
- Carbopack B 80–120 mesh from Supelco.
- Sn(IV) 'Titrisol' standard solution from Merck.

The purity of the organotin compounds is based on tin only. They were used as received and were checked for the presence of degradation products with GC-FPD and GC-MS after Grignard derivatization.

The organotin stock solutions were prepared gravimetrically in methanol at about 1 mg mL^{-1} (as Sn) concentration and diluted 1000-fold to give the working standard solutions. When stored refrigerated in the dark, stock solutions are stable for at least 3 months and the working solutions at least for 1 month; the latter were renewed weekly.

Instrumentation

Gas chromatographic analyses were carried out on a Varian Vista 6000 chromatograph equipped with a flame photometric detector (FPD) operated without filter.

Gas flows were modified as following: air(1) and hydrogen(1) were exchanged with respect to the standard instrumental configuration and air(2) was exchanged with hydrogen. Air(1), 200 cm^3 min^{-1}; hydrogen(1), 120 cm^3 min^{-1}; hydrogen(2), 80 cm^3 min^{-1}. Other chromatographic conditions were: carrier gas flow, helium 9 cm^3 min^{-1}; column, megabore DB-1 (methylsilicone, 0.53 mm i.d., 1.5 μm film thickness, 30 m length; J&W Scientific); temperature programme, 80°C × 1 min, then at 10°C min^{-1} to 280°C; injector, hot on-column, 240°C; detector temperature, 240°C. Data were collected and integrated by a Hewlett-Packard HP 3396A.

GC-MS was performed on a Hewlett-Packard HP 5890 GC/ HP 5970B MSD system with the following conditions: electron impact ionization mode, 70 eV; carrier gas, helium, 65 kPa head pressure; column: HP-5 (methyl-5% phenylsilicone, 0.20 mm i.d., 0.11 μm film thickness, 25 m length; Hewlett-Packard); temperature programme: 80°C × 2 min, then 10°C min^{-1} to 280°C; injector: splitless, 240°C; transfer line temperature: 280°C; SIM (selected ion monitoring) operation with the following programme (dwell time, 100 ms for all ions):

Ion	*Start time (min)*	*m/z*
TPrT	10	277, 275, 273
TBT	12.5	305, 303, 301
DBT	14	319, 317, 305
MBT	15	319, 317, 315
Sn(IV)	15.7	333, 331, 329
MPhT	17	339, 337, 335
DPhT	19	345, 343, 341
TPhT	20.5	351, 349, 347

Peak identification was based on the matching of retention times and isotopic mass ratios. The relative response factors were controlled by injecting standard mixtures on a regular basis (one injection every 3–4 samples) to follow the tuning conditions of the MS system.

A Varian SpectrAA-40 atomic absorption spectrometer with model GTA 96 graphite tube atomizer and model PSD 96 autosampler was used for all absorption measurements. Absorption signals were obtained by wall atomization (pyrolytic graphite tubes) with the gas stopped flow method. A hollow-cathode lamp was employed at a current of 7 mA. The graphite furnace thermal programme is as follows: drying with a temperature ramp from 75 to 120 °C in 80 s, charring with a temperature ramp from 120 to 600 °C in 30 s, and atomization for 2 s at 2600 °C. Potassium dichromate/nitric acid (0.04%/0.5% w/v) as matrix modifier was used for signal enhancement.

The other operative conditions were the following:

wavelength	286.3 nm
gas flow (argon)	2 L min^{-1}
spectral bandpass	0.5 nm
integration time window	2 s
injected volume	20 μL (+ 2μL of matrix modifier)

Analytical procedures

The analytical procedures selected in our laboratory for organotin determination in the various environmental compartments are summarized in Figures 1–3.

Water samples

Liquid/liquid extraction (Figure 1). Because of the relatively strong binding of organotin compounds to the particulate phase[1,17], the sample is filtered with a 0.45 μm glass fibre or polycarbonate filter in order to calculate the dissolved organotin concentrations.

The sample pH is adjusted to 2 in order to improve the extraction efficiency of the monosubstituted species (MBT, MPhT)[18,19]; sulphuric acid was used because hydrochloric acid (BDH Aristar and Carlo Erba RPE) and acetic acid (BDH Spectrosol) used have been found to frequently contain MBT as a contaminant.

10–100 ng (depending on the expected contamination level) of the internal standard (TPrT in methanolic solution) are added and the solution is allowed to equilibrate for 10 min. After extraction and solvent exchange, derivatization is performed in a reaction vial (15 mL volume) for at least 15 min. The final solution is then concentrated down to 1 mL under a moderate flow of nitrogen. The excess reagent is destroyed by carefully adding 1 M sulphuric acid. The organic phase is collected and subjected to clean-up after removal of diethyl ether. After reconcentration of the sample, 2 μL are injected for GC-FPD and 1 μL for GC-MS, with the above mentioned conditions.

Pentylmagnesium bromide (and other common Grignard reagents) often contains TBT impurities[20], so a careful blank evaluation is required.

Solid phase extraction[21] *(Figure 2).* LC18 pre-packed tubes (500 mg) and Carbopack B (100 mg) were tested. Both tube types are pre-treated sequentially with 10 mL of methanol and 10 mL of distilled water, avoiding the sorbent bed to run dry. The sample volumes to be extracted were selected on the basis of acceptable sample flowrates (the recommended flowrate of 5–10 mL min^{-1} was found to be satisfactory for LC18; 10 mL min^{-1} was adopted for Carbopack B, even if higher flowrates can be used with this phase[22]).

The adsorbent bed must be vacuum-dried before solvent elution.

The total organic tin determination by AAS can be performed after elution with a 0.03% methanolic solution of tropolone.

GC determination following the above procedure can be performed after liquid/liquid partitioning (50 mL of distilled water and 10 mL of methylene chloride are added to the eluate in a separatory funnel) and solvent exchange.

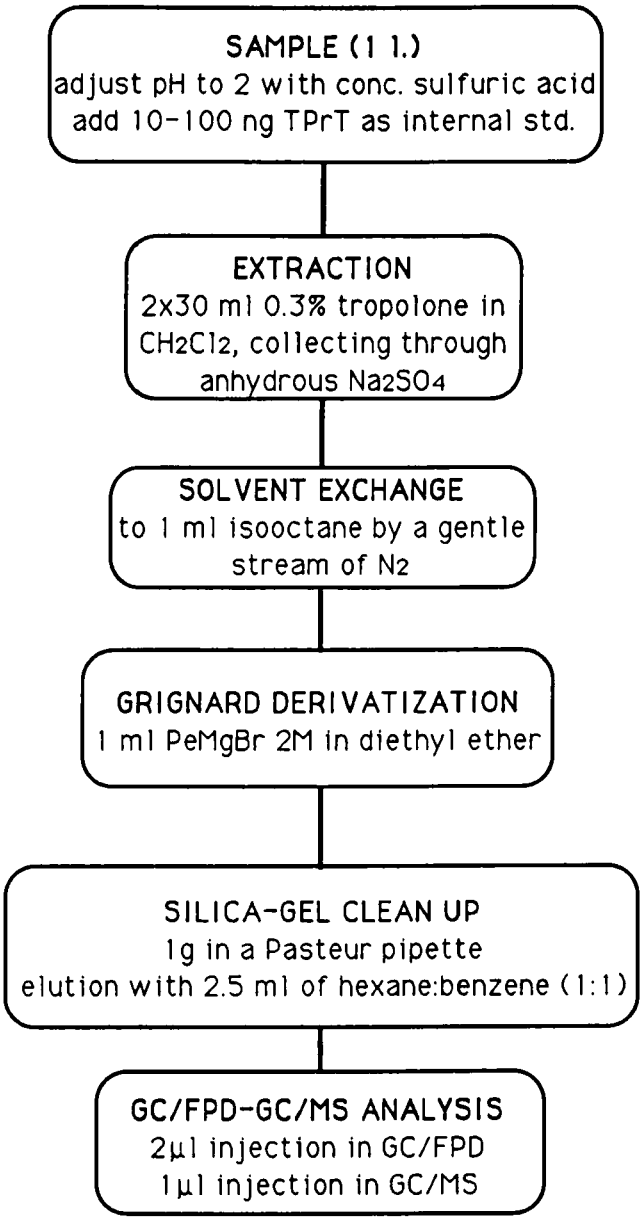

Figure 1 Scheme for analytical procedure for water samples – liquid/liquid extraction.

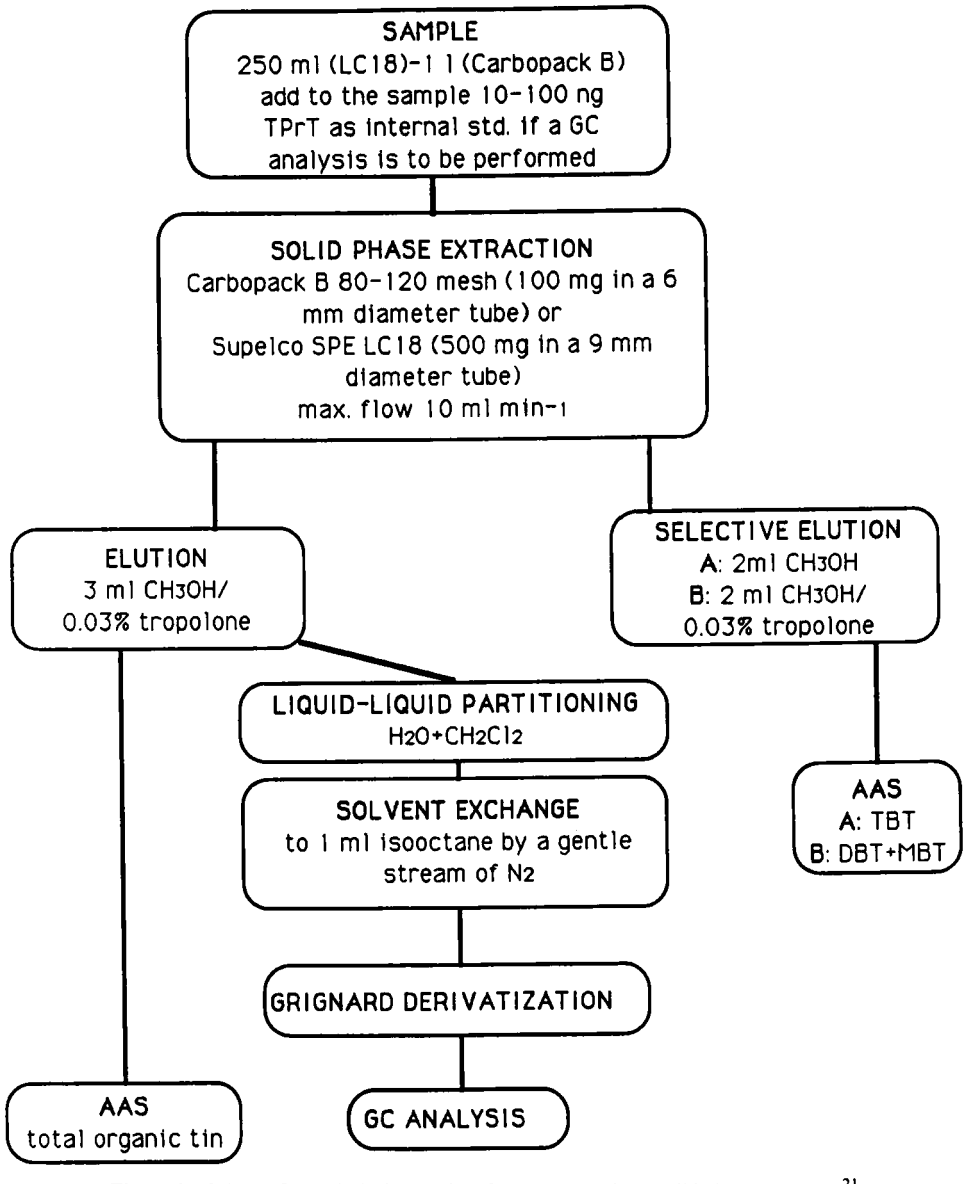

Figure 2 Scheme for analytical procedure for water samples – solid phase extraction[21].

A selective elution has to be performed in order to separately determine TBT and its degradation products DBT and MBT by AAS[23–25]. The efficiency of the selective elution is shown in Table 1. Interferences due to the possible presence of TPhT, DPhT and MPhT can be neglected in most cases, considering the production/usage ratio 9:1 between BTs and PhTs.

Table 1 Selective elution of butyltins from Carbopack B and LC18 extraction tubes*

	Tropolone 0.03% in methanol		*Methanol*	
	Carbopack	*LC 18*	*Carbopack*	*LC 18*
TBT	105±7	94±7	105±4	96±8
elution volume	2 mL	2 mL	2 mL	4 mL
DBT	102±9	101±5	0	0
elution volume	2 mL	2 mL	10 mL	10 mL
MBT	107±5	89±4	0	0
elution volume	4 mL	2 mL	10 mL	10 mL

*Data are the average of five replicates. Tubes were loaded with 100 ng (as Sn) of each compound; data are expressed in ng (Sn) eluted.

Sediment and mussel samples (Figure 3)

The sample is freeze-dried and homogenized before extraction. 50–500 ng of TPrT are added to the sample as methanolic solution before extraction, allowing 30 mins for equilibration. Longer equilibration times, up to 16 h, do not affect the absolute recovery of TPrT.

The extraction is performed by sonication (twice, for 15 min) with 15 mL of 0.05% tropolone in methanol. Liquid-liquid partitioning is then performed in a separatory funnel after the addition of 150 mL of water and 30 mL of methylene chloride. The methylene chloride phase is collected through anhydrous sodium sulphate and the volume is reduced to approx. 5 mL in a rotary evaporator at 35°C under moderate vacuum, and finally to 1 mL under a moderate flow of nitrogen, effecting solvent exchange (methylene chloride to isooctane). Next, the procedure is essentially the same as previously described.

RESULTS AND DISCUSSION

Calibration curves in GC-FPD are linear (as peak heights) in the range 8 pg÷1 ng (as Sn) injected on column, corresponding, under the usual analytical conditions for water samples (1 L sample, 0.5 mL final volume and 2 μL injected), to a sample concentration in the range 2÷250 ng L^{-1}. The RSD for multiple injections (10 replicates) is 3%.

Calibration curves in GC-MS are linear (as peak areas) in the range 8 pg÷2 ng (as Sn) injected, corresponding to a sample concentration in the range 4÷1000 ng L^{-1}. The RSD for multiple injections (10 replicates) is 5%.

Relative response factors are to be calculated daily (by injecting standard mixtures) before starting the analytical runs, because relatively small variations occur in flame characteristics (FPD) and tuning (MS).

Recovery tests

Water. The recovery tests for water samples were performed on uncontaminated filtered sea water. Tripropyltin was used as internal standard for quantitative analysis, because it is

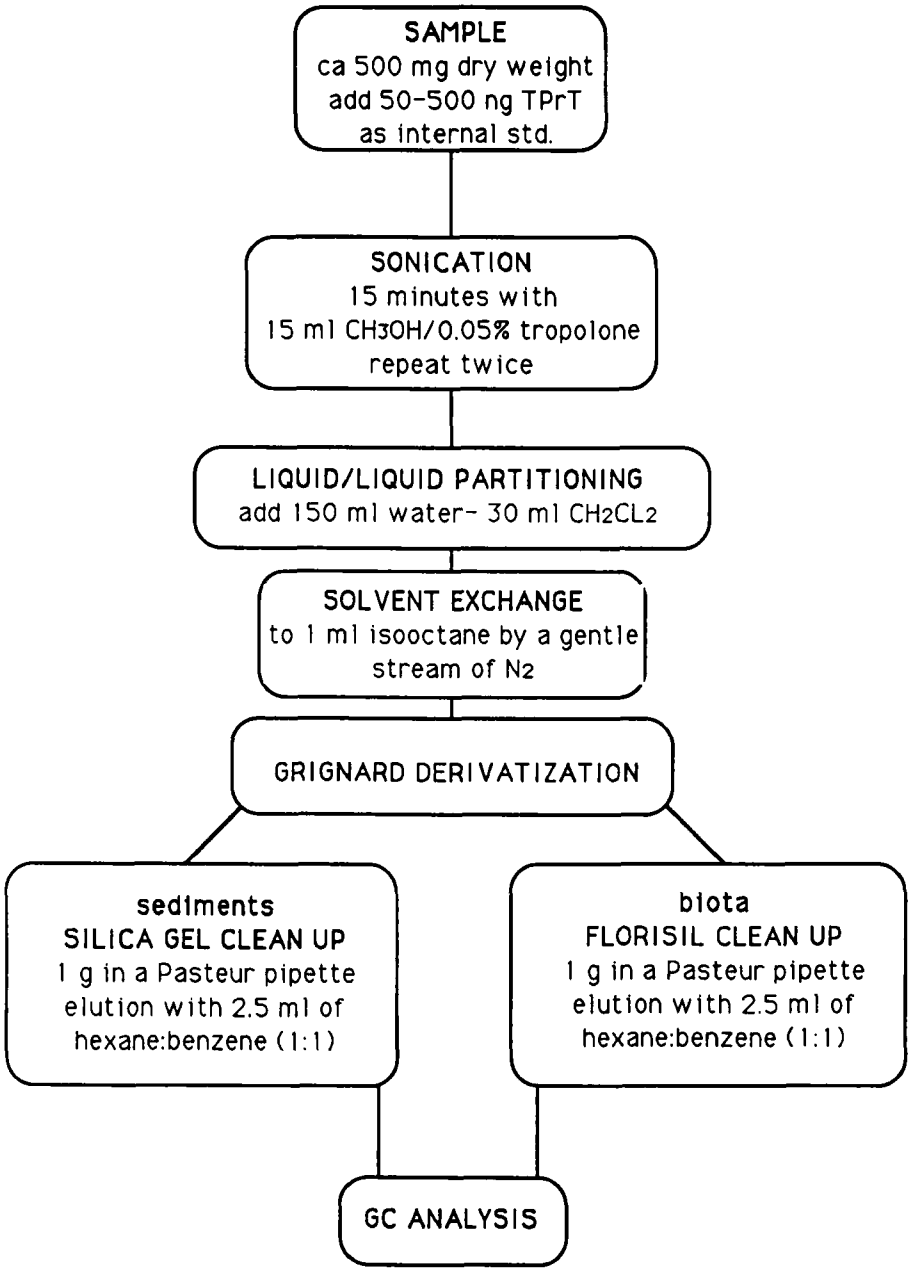

Figure 3 Scheme for analytical procedure for mussels and sediments.

Table 2 Recoveries of organotin compounds from spiked sea water (liquid/liquid extraction)*

Compounds	*Recovery (%) at*	
	20 ng L^{-1}	*200 ng L^{-1}*
TBT	102 ± 6	102 ± 4
DBT	104 ± 6	100 ± 4
MBT	97 ± 8	95 ± 10
TPhT	93 ± 9	91 ± 9
DPhT	94 ± 8	91 ± 8
MPhT	91 ± 10	92 ± 13

*Water samples were spiked at 20 ng L^{-1} and 200 ng L^{-1} (as Sn) concentration level for each compound. Analyses were performed by GC/FPD (n=6).

a compound that closely matches the environmentally most relevant compounds to be determined (TBT and TPhT) and because it was neither detected in natural samples nor its presence is expected, lacking a widespread use.

Recoveries obtained with liquid-liquid extraction are summarized in Table 2.

1 L samples can be extracted without losses using Carbopack B, whereas 100–250 mL is the useful range with LC18. Table 3 shows the results of recovery tests from spiked water samples. Differences between recoveries from artificial sea water and deionized water are not statistically significant. Volumes larger than 250 mL cannot be extracted by LC18 columns without significant losses (62% from distilled water and 78% from sea water are the measured recoveries from 500 mL samples at 200 ng L^{-1} TBT).

No significant differences are observed between the liquid/liquid and solid-phase extraction procedures so operational/practical aspects may be considered when selecting the most appropriate one. Liquid/liquid extraction followed by derivatization and GC-FPD or GC-MS can be carried out without problems in the laboratory and gives satisfactory results. Solid-phase extraction ensures good results as well and avoids high volumes of organic solvents and transport of fragile glassware; the extraction apparatus can be easily transported and automatically operated in the field. Extraction tubes can be easily stored, overcoming the transfer of 1 L samples to the laboratory and storage and conservation problems.

Table 3 Recoveries of organotin compounds from spiked distilled and sea water (solid phase extraction)*

Analyte		*Recovery (%) under stated conditions;*							
		250 mL Carbopack		*250 mL LC 18*		*500 mL Carbopack*		*1000 mL Carbopack*	
		40 ng/L	*200ng/L*	*40 ng/L*	*200 ng/L*	*20 ng/L*	*200 ng/L*	*20 ng/L*	*200 ng/L*
TBT	dw	92	97	94	92	91	94	88	93
	sw	95	103	96	96	97	98	99	102
DBT	dw	88	98	89	86	89	92	88	90
	sw	88	99	90	90	95	97	96	98
MBT	dw	84	91	85	84	87	92	80	88
	sw	87	94	88	90	90	94	90	94

*Recovered: n=2; dw= deionized water, and sw= artificial sea water.

Table 4 Recoveries of organotin compounds from spiked sediments*

Compound	*Spiked amount (ng Sn)*	*Recovery (%)*	*Spiked amount (ng Sn)*	*Recovery (%)*
TBT	80	91 ± 10	480	94 ± 7
DBT	83	89 ± 12	496	88 ± 11
MBT	75	80 ± 13	450	85 ± 11
TPhT	75	92 ± 11	451	90 ± 9
DPhT	79	87 ± 15	472	91 ± 12
MPhT	74	78 ± 16	442	81 ± 13

*Recoveries from 500 mg of spiked sediments (n=5)

Sediments. Recovery tests from sediments were carried out by spiking freeze-dried uncontaminated sediments collected in the open Adriatic sea. Organotins were added as solutions in methanol to the sediment wetted with the minimum amount of water. After the addition sediments were shaken for at least 30 min and allowed to equilibrate overnight. The sediments were then freeze-dried and analyzed. Results are shown in Table 4.

Tests on real samples at different organotin concentration levels demonstrated that the second extraction removes less than 10% of the amount extracted by the first extraction (with the exception of MBT: 14±3 %).

The extraction mixture (methanol/tropolone) was chosen after several tests on different extractants selected on the basis of a literature survey: methanol, glacial acetic acid, hydrochloric acid, hydrochloric acid/diethyl ether, methylene chloride. Tests on real samples showed that extremely acidic conditions (e.g. HCl > 6M) lead to excellent recoveries of butyltins, but at the same time phenyltins are not recovered at all. Therefore we preferred to accept a possibly less effective extraction of mono-substituted species than to risk uncontrollable losses of phenyltins, using strongly acidic conditions. The use of tropolone overcomes the necessity to operate at low pH for effective mono-substituted extraction. Probably, the best combination is to use tropolone/methanol solvent extraction under moderately acidic conditions; tests in this direction are being performed. The analytical procedure was checked on a sediment sample from Lake Maggiore (Varese, Italy), spiked with TBT by JRC of Ispra at a nominal level of 3.3 $\mu g\ g^{-1}$ (as TBT acetate) which was used for an intercomparison exercise held by BCR involving European laboratories[26]. We calculated a concentration of 2.7±0.3 $\mu g\ g^{-1}$ (five replicates), while the result of the intercomparison exercise as mean of mean values from 15 laboratories was 2.9 $\mu g\ g^{-1}$ (2.5 $\mu g\ g^{-1}$, considering only the laboratories which used GC-FPD or GC-MS). The recovery obtained using the described analytical procedure was 81.8% of the nominal level of the spike and 93.1% of the result of the intercomparison exercise.

These results support the reliability of the described analytical procedure, at least for TBT.

Mussels. Recovery tests on biological materials are difficult to be performed because uncontaminated samples are rarely collected and reference materials are still not available (except the NIES-Japan Environment Agency fish tissue).

Table 5 Recoveries of organotin compounds from non-spiked and spiked mussels*

Compound	*non-spiked (ng Sn)*	*spiked (ng Sn)*	*Found (ng Sn)*	*Average recovery (%)*
TBT	185 ± 24	160	314 ± 27	91
DBT	61 ± 10	165	201 ± 23	89
MBT	80 ± 13	150	195 ± 29	85
TPhT	n.d.	150	138 ± 13	92
DPhT	n.d.	157	133 ± 18	85
MPhT	n.d.	147	120 ± 20	82

*Data (n=5) give absolute amounts in 500 mg of sample in ng of Sn.

Extraction performance was assessed on mussels analyzed before and after spiking of organotin compounds. The results shown in Table 5 are rather satisfactory.

DISCUSSION

Grignard derivatization was preferred to hydride generation [11] because of the possibility to obtain accurate and reproducible results for MBT, DPhT and MPhT, which otherwise would suffer from poor recoveries and/or critical chromatographic conditions.

In the analytical procedure for sediment and biological samples, solvent exchange from methanol to non-polar isooctane was performed in two steps because of the easy handling of the methylene chloride/water system, complete recovery of the analytes (no significant influence of the evaporation step was observed) and removal of water-soluble co-extractants.

As previously said, pentylmagnesium bromide and similar Grignard reagents are often contaminated by TBT, so a careful blank evaluation is required. In our experience, TBT levels are in the range 2–8 ng mL^{-1}; this is of particular concern, when using this kind of derivatization for water samples containing less than 20 ng L^{-1} TBT and for sediment and biota samples containing less than 20 ng g^{-1} TBT. Finally, it is important to remember that organotin contamination from DBT, MBT or dioctyltin (which interferes with the TPhT determination by GC-FPD) can arise from common laboratory plastic (PVC) materials.

A typical GC-FPD chromatogram of organotin derivatives is shown in Figure 4. The peak at 16.42 mins is the Sn(IV) tetrapentyl derivative. The corresponding GC-MS chromatogram is shown in Figure 5. GC-MS chromatograms of a sediment sample and of a blank procedure are shown in Figs. 6a and 6b, respectively. Highly polluted sediments, particularly those in which high sulphur levels are present, often interfere with FPD detection. GC-MS is necessary to confirm doubtful results. The detection limit is 5 ng g^{-1} (as Sn) both for sediments and mussels.

The AAS determination of organotins in real matrices is very often hindered by interferences from other matrix components. Problems especially arise during the ashing and atomization steps due to the formation of volatile compounds and the interaction of tin with carbon furnace walls. Several approaches have been described in order to overcome these

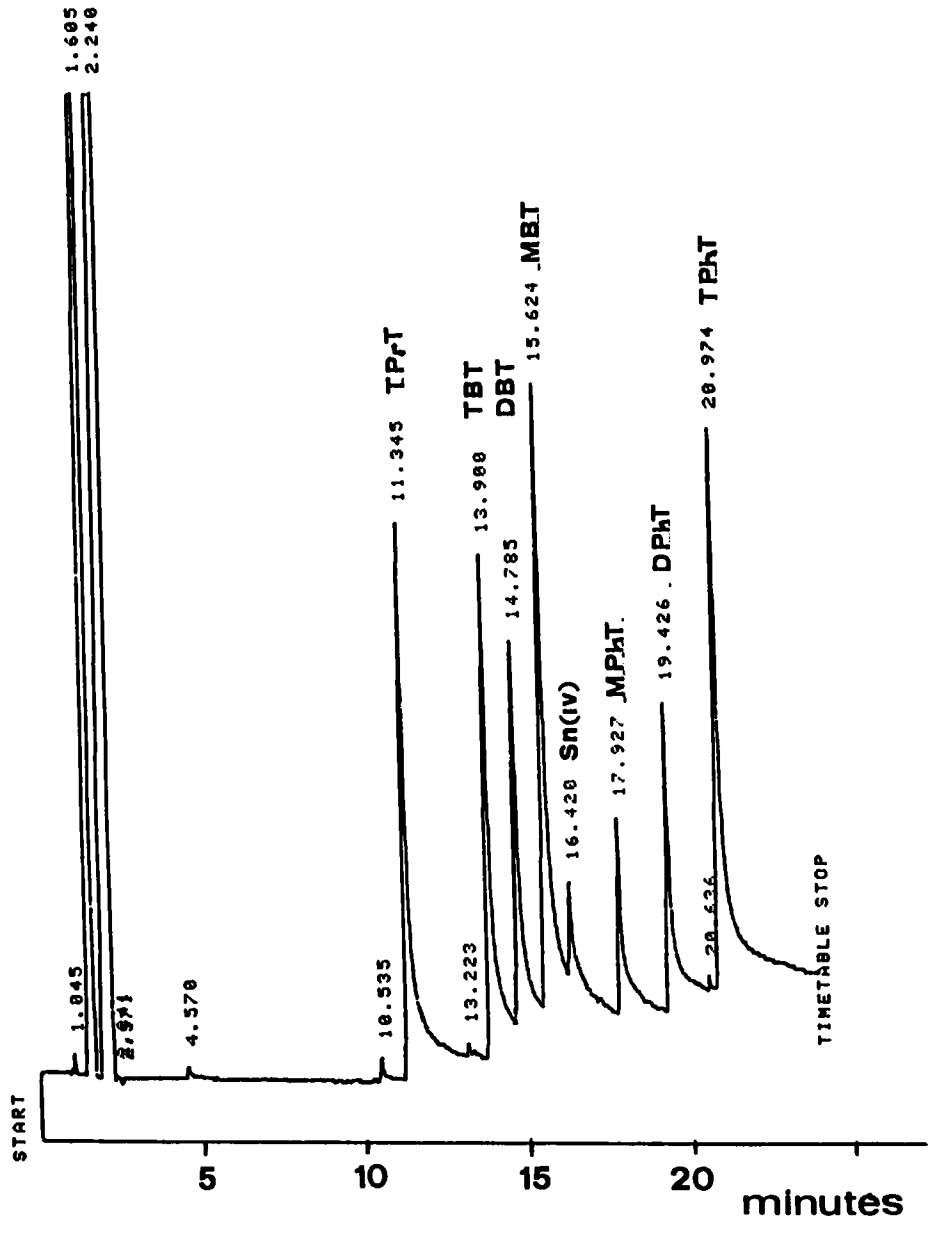

Figure 4 GC-FPD of pentylated organotin compounds standard mixture. Amounts injected on column TPrT, 0.40 ng; TBT, 0.34 ng; DBT, 0.24 ng; MBT, 0.40 ng; MPhT, 0.23 ng; DPhT, 0.22 ng; TPhT, 0.24 ng.

problems including the addition of a matrix modifier to the sample[27-30]. This should essentially prevent tin volatilization before the atomization and decrease interference problems, but it may often be employed simply to obtain a signal enhancement.

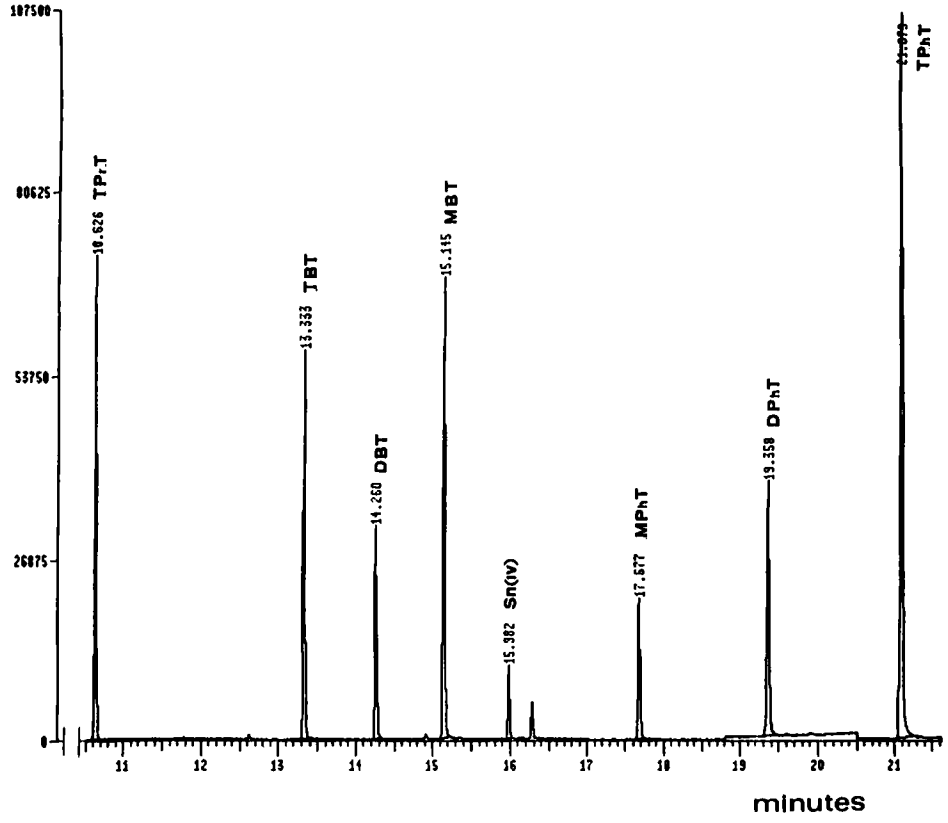

Figure 5 GC-MS of pentylated organotin compounds standard mixture. Amounts injected on column: TPrT, 0.20 ng; TBT, 0.17 ng; DBT, 0.12 ng; MBT, 0.20 ng; MPhT, 0.12 ng; DPhT, 0.11 ng; TPhT, 0.12 ng.

The optimization of some experimental parameters, including the choice of the matrix modifier, was carried out by varying wavelength, gas flow, drying time, ashing and atomization temperatures.

The modifier was automatically introduced, together with the sample, by the autosampler in a single 20 μL injection. The GFAAS enhanced signal followed Beer's law in the range 0.2÷2 ng of tin, with a detection limit of 0.2 ng (signal = 5 × noise level). The results of the parameter optimization are summarized in Table 6. The effect of signal enhancement on the determination of TBT by GFAAS is shown in Figure 7.

The solid phase extraction/selective elution/GFAAS combination provides a practical analytical procedure if GC instrumentation is not available. Obviously, if full speciation is needed, its performance is inadequate, allowing discrimination between TBT and its degradation products DBT and MBT only.

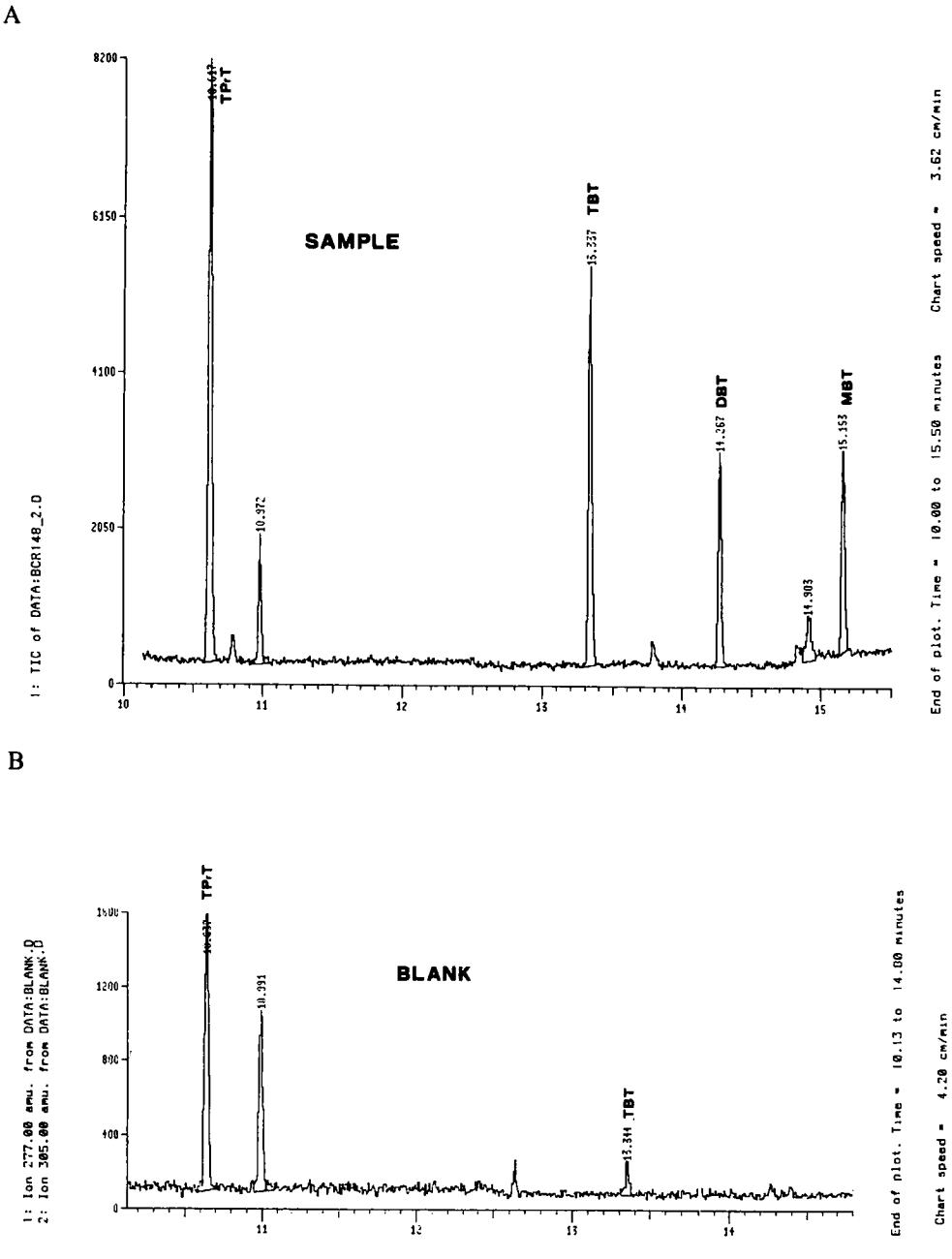

Figure 6 (a) GC-MS of a sediment sample: TPrT, 60 pg; TBT, 44 pg. (b) GC-MS of a procedure blank (TBT, 8 pg).

Table 6 Calibration data and detection limits of AAS determination

Analyte	*Linearity range (ng)*	*Sensitivity (abs/ppm)*	*Y intercept (abs × 10^2)*	*Correlation coefficient*	*Detection limit (ng)*
TBT	0.2 – 2	9.85	1.52	0.997	0.2
DBT	0.2 – 2	9.32	2.20	0.998	0.2
MBT	0.2 – 2	9.41	4.04	0.998	0.2
Sn (IV)	0.2 – 2	8.03	1.32	0.997	0.2

CONCLUSIONS

The analytical procedures adopted in our laboratory proved to be reliable and suitable for the environmental monitoring and organotin speciation studies. They have been successfully used in many research projects, such as the La Spezia Gulf water quality study[11,13,31], the determination of organotins in marine mussels from Italian coasts[12], and the monitoring of Italian harbours sediment pollution levels[32]. Other studies, especially on bioaccumulation phenomena, are in progress.

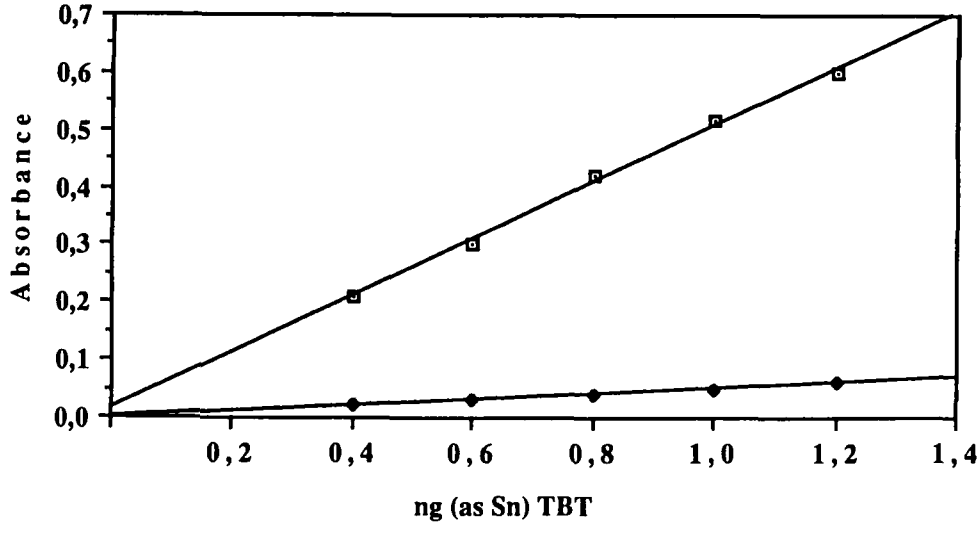

Figure 7 Signal enhancement in AAS determination: (a) without matrix modifier; (b) with matrix modifier.

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