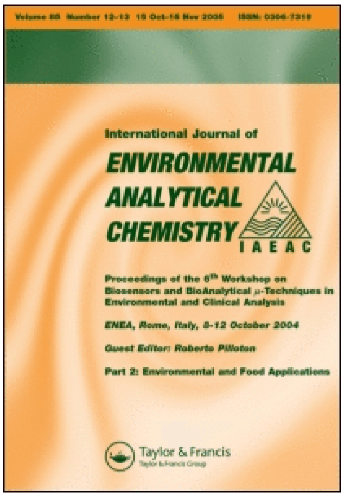

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Analytical methods and problems related to the determination of organotin compounds in marine sediments

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**To cite this Article** Staniszewska, Marta , Radke, Barbara , Namieśnik, Jacek and Bolałek, Jerzy(2008) 'Analytical methods and problems related to the determination of organotin compounds in marine sediments', International Journal of Environmental Analytical Chemistry, 88: 11, 747 — 774

**To link to this Article: DOI:** 10.1080/03067310802082310

**URL:** http://dx.doi.org/10.1080/03067310802082310

*Intern. J. Environ. Anal. Chem.*
Vol. 88, No. 11, 15 September 2008, 747–774

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# Analytical methods and problems related to the determination of organotin compounds in marine sediments

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(*Received 12 July 2007; final version received 26 March 2008*)

The determination of organotin compounds in bottom sediments is a complex process that requires a number of analytical steps, i.e. sample collection, transport and storage; extraction of analytes from sediment; derivatization; extract purification; enrichment; and the final chromatographic measurement. The whole process is time and labour consuming, and subject to securing sample representativeness. In this review the most frequently encountered problems and the examples of possible analytical solutions are presented, which encompass the specific steps of speciation analysis of these toxic compounds.

**Keywords:** organotin compounds; marine sediments; speciation analysis

## 1. Introduction

Organotin compounds are a group of organometallics that have a structure described by the following molecular formula: $R_nSnX_{(4\text{-}n)}$, where Sn is the tin atom, R is an alkyl group, such as methyl (Me,$CH_3$-), butyl (Bu,$C_4H_9$–), octyl (Oc, $C_8H_{17}$–) or phenyl, e.g. (Ph, $C_6H_5$–) and X corresponds to $O^-$, $OH^-$, $Cl^-$, $F^-$, $SH^-$ etc., and *n* ranges from 1 to 4.

At present, there are over 800 organotin compounds that are man-made and/or occur in the environment [1]. The butyl species (butyltins, BTs) of organotin derivatives, such as tributyltin (TBT) and its degradation products (i.e. dibutyltin, DBT and monobutyltin, MBT), and the phenyl species (phenyltins, PhTs) such as, triphenyltin (TPhT) and its degradation products (i.e. monophenyltin, MPhT and diphenyltin, DPhT) are quite broadly spread in the marine environment. Considering the wide distribution and strongly toxic effect of these compounds on marine organisms, their monitoring and pathway analysis in the environment are critical [1].

Many years of using organotin-based antifouling paints, in particular TBT for preventing the growth of marine organisms on ships' hulls, and triphenyltin-based pesticides have resulted in the penetration and accumulation of significant amounts of

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802082310
http://www.informaworld.com

these compounds in the bottom sediments of water bodies. River mouth areas in the coastal marine zone, and harbour and shipyard basins were particularly affected.

Recently, there has been a significant decrease in new loads of organotin compounds into the marine environment as a result of to the recommendations of the International Convention on the Control of Harmful Anti-Fouling Systems on Ships [2], formulated under the auspices of the International Marine Organisation (IMO), coming into force. Since 1 January 2003, the use of organotin-based anti-fouling paints on newly built or painted ships (shorter than 25 metres) has been forbidden [2]. Nevertheless, shipyards and harbours are still considered the areas vulnerable to these pollutants because of intensive ship traffic and activities such as removal of old paint from hulls and ship scrapping. The total ban on TBT-based paints will start in 2008, and it will also include older vessels, i.e., those produced before 2003.

Bottom sediments are a reservoir of toxic pollutants including organotin compounds; they constitute a potential ecotoxicological risk for live organisms long after the anthropogenic compounds have entered the environment. Organotin compounds adsorb onto very small sediment fractions (particle size $<0.063\,\mathrm{mm}$). These fractions are easily available to benthic organisms, in particular detritus feeders [3]. Due to the changing physicochemical conditions in water and sediment, for example, salinity, temperature, and quantitative and qualitative composition of organic matter, the release of specific forms of organotins from the sediment may take place [4]. After being released, they become bioavailable and therefore harmful to the marine organisms inhabiting the water column as well.

The deepening of channels and basins in harbours and shipyards, and storing the dredged spoils at sea, creates specific conditions for possible input of new organotin loads into the marine sediments. However, organotin compounds are dumped in smaller amounts at sea during dredging operations. In some countries the new loads of TBT-containing spoils from harbour channel dredging are being limited because the TBT content has been included in the quality criteria for the dredged spoils. For example, spoils containing more than 500 and $300\,\mathrm{ngSn\,g^{-1}}$ are considered contaminated in Great Britain and Germany, respectively [5], and cannot be dumped at sea. However, the international regulations dealing with this issue are still under preparation [5].

The occurrence of different organotin species in environmental samples, which are characterised by complex matrix composition (bottom sediment and animal tissues) and very low analyte concentrations, causes different problems during analysis. In this respect, the determination of organotin compounds requires the use of expensive equipment, and time- and labour-consuming analytical procedures in order to separate the analytes from the complex organic matrix, and enrich their content to the level permitting measurement by means of highly selective and sensitive chromatographic techniques.

In this review, the analytical techniques and problems related to the determination of the six most common toxic organotin compounds in the marine environment, i.e. butyltin and phenyltin derivatives, are described.

## 2. Characteristics of sediment composition

Bottom sediments differ in reference to chemical composition, particle size, origin, sedimentation rate and geographical distribution [6].

The content of many anthropogenic substances in bottom sediments depends on their physical (i.e., size of particles, sediment surface proper, density and magnetic properties) and chemical properties (i.e., ion exchange capacity, adsorptive properties, organic matter content and content of inorganic compounds, e.g. carbonates, oxides) as well as on the environmental conditions (i.e., pH, salinity and water temperature) [4,6,7].

Information about physico-chemical properties that determine organotins content in sediments have been collated in Table 1.

Terrestrial sediments, especially from ports and river mouths, usually contain considerable amounts of organic matter or mineral clays [4]. In ports and river mouths other environmental conditions conducive to the accumulation of organic compounds including organotins occur, for example, low salinity. Moreover, such locations are particularly exposed to the input of new portions of contaminants. The forming sediments become a kind of trap or sink for hydrophobic contaminants. However, under certain environmental conditions they may also turn into a source of renewed contamination.

The sediment's composition strongly influences desorption during the analytical step which, at the end, affects the level of recovery of a given compound from sediment. For example, Ceulemans and Adams [11] observed recoveries ranging up to 15% for DBT and TBT, and ranging up to 66% for MTB. They found a correlation between MBT recovery and total organic carbon content (TOC), i.e. for high TOC contents (36.2%) the recovery was 27%, while for low TOC contents (0.41%) the recovery was 94%.

## 3. Speciation of organotin compounds

Organotin compounds occur in the marine environment in various chemical forms which may affect live organisms in different ways, for example, toxicity, persistence or bioavailability effect. In such cases, it is therefore more critical to determine the content of a specific species (e.g., the most toxic one) than to measure the total content of all physicochemical forms present in a given environmental compartment [12]. Such an approach allows better assessment of the environmental risk posed by the studied compounds.

Organotin toxicity in marine organisms increases with an increasing length of alkyl chain and the number of alkyl groups per molecule [13]. The highest toxicity has been observed in the case of organotin derivatives substituted with three butyl (TBT) or phenyl (TPhT) groups [1]. Exposure to TBT even at the very low concentrations between 1 and $10\,\mathrm{ng\,L^{-1}}$, which are typical for marine waters, is very harmful to molluscs, the most sensitive groups of invertebrates [14]. Generally, TBT doses smaller than $2\,\mathrm{ng\,L^{-1}}$ cause imposex and those higher than $2\,\mathrm{ng\,L^{-1}}$ cause intersex for molluscs [15]. A dose of 1 to $2\,\mathrm{ng\,L^{-1}}$ causes chronic and acute toxicity effects in algae, zooplankton and larval fish, too [1,16]. The imposex (the most sensitive test for smaller concentrations of TBT in the marine environment) and intersex caused by organotins in marine gastropods is well accepted as a ‘‘biomarker’’ for these compounds [15,17].

In order to characterise a given sample with regard to the content of specific species of chemical compounds, and to determine the content of those forms which are or may be most toxic in the *in situ* location, it is necessary to perform the so-called speciation analysis [12,18]. According to the IUPAC, speciation is a process of identifying and measuring the quantities of various chemical and physical forms of the same chemical species (element or chemical compound) present in the analysed sample [12,18].

Table 1. Basic information about physico-chemical parameters of sediment that influence the content of organotin contaminants in bottom sediments.

| Physico-chemical parameter | Comments |
|---|---|
| Sediment particle sizes | The finest size fractions ($<0.063$ mm) display particularly good sorptive properties, i.e. silty-clays [4,6,8]. This is due to physical (large surface proper) and chemical factors (high content of clay minerals) [6]. |
| Surface proper of sediment particles | Silty-clay sediments are characterised by the surface proper with high sorptive properties at the level of number of metres squared per gram, while for gravels, it does not exceed centimetres squared per gram [6]. |
| Percentage of expandable clay minerals in sediments | • Clay minerals show a high sorption capacity to organic contaminations of cationic or polar character [8]. It depends on their surface area and reactivity (negatively charged surface).<br>• Sorption coefficient ($K_d$) for TBT (at $pH = 6$) and surface proper values for the mineral particles can be arranged in the following sequence: montmorillonite ($Kd = 89\,L\,kg^{-1}$; surface area ca $32\,m^2\,g^{-1}$) > kaolinite ($Kd = 51\,L\,kg^{-1}$; surface area $= 10\,m^2\,g^{-1}$) > quartz ($Kd = 25\,L\,kg^{-1}$; surface area $= 0.31\,m^2\,g^{-1}$) [4].<br>• Particularly strong sorption of TBT in pure montmorillonite is caused by its big surface area. Hoch and Schwesig [4] observed the increase in $K_d$ value from 25 to $67\,L\,kg^{-1}$ for pure quartz sand after adding 10% of montmoryllonite, and to $K_d = 94\,L\,kg^{-1}$ after adding 20% of montmorillonite.<br>• When adding organic matter, higher sorption of TBT can be expected onto kaolinite because different minerals adsorb organic matter with varying strength. The sequence in which organic matter adsorbs onto minerals is as follows: kaolinite > montmorillonite ≈ quartz [4]. |
| Organic matter content in sediments | • Organic matter is the most significant factor that controls the content of organotins in sediment [7].<br>• Sediment-water partition coefficient ($K_d$) for organotins assumes very low values in the case of pure and low organic content minerals, e.g. $K_d$ for pure kaolinite is $51\,L\,kg^{-1}$, while the addition of 5% of organic matter results in the abrupt $K_d$ increase up to $2700\,L\,kg^{-1}$ [4,8]. |
| pH, salinity, temperature of water | • Adsorption onto clay minerals and organic matter increases with the decreasing pH (up to $pH \cong 4$), temperature and salinity [7].<br>• In the case of clay minerals, the adsorption of, for example, tributyltin is the most effective at $pH = 6$ for montmoryllonite, and at $pH = 7$ for kaolinite. At such pH values the concentration of organotin cations is the highest. This happens when the pH is closed to pKa (the acidy constant) – for TBT $pKa = 6.3$ and for TPhT $pKa = 5.2$ [9,10]. Cation forms can be easily adsorbed onto negatively charged surface of minerals [4], while the resulting bonds have electrostatic character.<br>• Adsorption onto sediments rich in organic matter is the most effective at $pH \approx 6$–7, when a cation is the dominant TBT form. Then the complex bonds between $TBT+$ and depronated organic matter ligands are formed [4]. |

Highly developed separation techniques by means of complicated and expensive equipment are particularly useful in speciation analysis of organotin compounds in samples of complex environmental matrices, such as marine sediments. In order to determine specific species of organotins at very low concentration levels (i.e. $\mathrm{ng\,L^{-1}}$ in water and $\mathrm{ng\,g^{-1}}$ in sediment and live tissues), gas (GC) and liquid chromatography (LC) techniques in combination with very sensitive and selective detectors are employed [19–21].

However, the complete separation and final chromatographic determination of BTs and PhTs in samples of marine bottom sediments requires multistep analytical operations. Classical speciation analysis of organotin compounds consists, in most cases, of the following steps: sample collection, transport and storage; isolation (extraction) of analytes from sediment; derivatization; extract purification; enrichment; and the final chromatographic determination [18–23]. Moreover, the complexity of the whole procedure creates an additional problem with securing the sample representativeness because a multistep analysis is more likely to result in the loss of analytes and sample contamination.

A flow chart presenting analytical solutions that encompass the specific analytical steps of speciation analysis of organotin compounds in marine sediment samples is shown in Figure 1.

## 4. Sampling, storage and preliminary preparation of bottom sediment samples prior to analysis

Sampling, storage and preliminary preparation of sediment samples prior to analysis may cause unacceptable contamination, losses by volatilization, adsorption, degradation and finally decomposition of real sample.

Sampling of sediments for the determination of specific organotin forms – as well as trace elements – should preserve the representativeness of a given object [22]. In order to achieve this goal, a low-disturbance sampler is most often used which allows the collection of the undisturbed layers of sediments [27]. For sampling small particle size sediments, a Niemistö gravity corer is most frequently used [28], while vibratory and Reinecke box corers are necessary in the case of coarse, gravel or stony sediments [29]. Sampling with such samplers additionally allows obtaining stratified sediments divided into specific geological layers.

The collected bottom sediments are sampled and usually stored in glass containers, however, containers made of polyethylene, Teflon, aluminium, and polycarbonate are also used. Polyvinyl chloride (PVC) has to be avoided as it may contain organotins [20,22,27,30–32].

Wet sediment should be stored at low temperature (−20°C), in the dark, without contact with air in order to avoid microbial activities and physico-chemical alterations – for example, oxidation, degradation of organotin compounds. Thus stored, sediment can retain the unaltered composition with regard to the derivatives of BT (for over one year) and PhT (for about seven months) [19,31,32].

The sediment can be safely dried – without the risk of analyte loss – in the drying oven, air-dried or lyophilized. Excessive temperature in the oven (above 50°C) may lead to decomposition of TPhT derivatives [20,30,32]. However, a drying oven temperature of 50°C may not completely stop the sediment's microbial activity. Therefore, for long sample storing, freeze-drying would be a better solution [30]. Both BTs and PhTs species were stable in lyophilized sediments stored at −20°C for over 18 months [21].

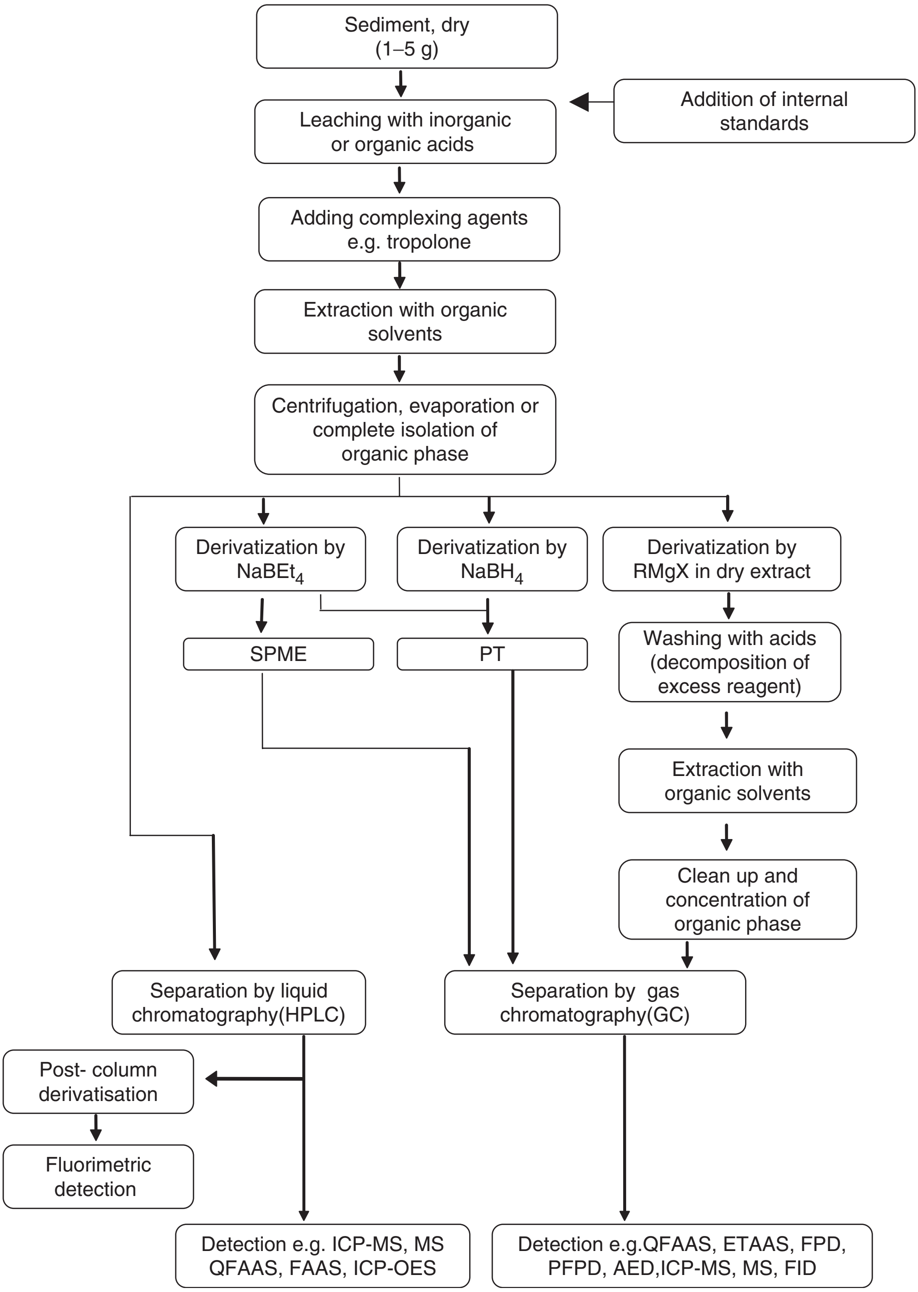

Figure 1. Examples of analytical steps necessary to perform of speciation analysis of organotin compounds in bottom sediments [20,22,24–26].

Notes: AED - Atomic Emission Detection; ETAAS - Electrothermal Atomic Absorption Spectrometry; FAAS - Flame Atomic Absorption Spectrometry; FID - Flame Ionization Detection; FPD - Flame Photometric Detection; GC - Gas Chromatography; HPLC - High Performance Liquid Chromatography; ICP-MS - Inductively-Coupled Plasma Mass Spectrometry; ICP-OES - Inductively-Coupled Plasma - Optical Emission Spectrometry; MS - Mass Spectrometry; $NaBEt_4$ - sodium tetraethylborate; $NaBH_4$ - sodium tetrahydroborate; PFPD - Pulsed Flame Photometric Detector; PT - Purge and Trap; QFAAS - Quartz Furnace Atomic Absorption Spectrometry; RMgX e.g. alkyl magnesium bromide; SPME - Solid Phase Microextraction.

Preliminary preparation of bottom sediment samples prior to analysis included homogenisation and sieving of sample. Homogeneity has to be achieve by intensive mixing techniques, for example ballmill [20]. For organotins analysis, sieving is very often used for determining analytes' concentrations in the $<0.063$ mm size fraction [27,30]. Wet-sieving with overlying water from the sample to avoid possible desorption of organotins has been recommended [30].

Organotins can be determined in wet or dry sediment. Analysis of wet samples reduces the cost and time of drying procedures, however dry sediment is more suitable for long-term storage. That is because samples of dry sediment are more homogenous and display better resistance to decomposition than the wet ones [20,30,31].

## 5. Controlling of accuracy and precision of speciation analysis

Before controlling every step in speciation, especially the liquid extraction of the analytes from a solid sample and the possibility of losses of organotin compounds, the sediment sample is spiked with internal standards. However, every methodology making use of spiked analytes is controversial because it is hard to be sure that the spiked analytes will be bound to the solid matrix in the same way as the original sample analytes. The spiking compounds are often bound to the matrix in a weaker way than the native compounds which makes it necessary to extend the equilibration time of solid sample and spiking standard (24 h or overnight is generally recommended). Unfortunately, it is possible that during this process a transformation of the analyte may take place [31]. Therefore, it is better to use certified references materials (CRMs) for validation procedures in speciation analysis.

In the case of quantitative validation, it is important that CRM matrix is as similar as possible to the analysed sample, and remains stable during long storage. Unfortunately, there are only a few available certified reference materials for limited species (especially not enough for phenyltins which are more unstable) and matrices. CRMs available for organotin speciation analysis in sediment samples are listed in Table 2.

In the past few years, the use of stable isotopes and Isotope Dilution Analysis (IDA) has proved very successful for improving the control of the accuracy and precision of measurements. IDA is an analytical technique based on the measurement of isotope ratios in samples by the addition of a known amount of an isotopically enriched element: a single-isotope element, e.g. $^{118}$Sn-enriched DBT or multiple spike and/or multi-isotope mix, e.g. $^{119}$Sn-enriched MBT, $^{118}$Sn-enriched DBT, $^{119}$Sn-enriched TBT [34–36].

IDA can control every single step of speciation analysis, and can be used to correct the systematic errors that often occur in speciation analysis such as, low derivatization yields, no quantitative separation procedure, signal drift and quantification of measurement errors. Especially, multi-isotope and multiple spike strategy allow detection and correction for organotin compounds' degradation from one species into another during the extraction process. Such an approach allows the determination of the correct species concentrations in samples of sediment by calculating degradation factors from one analyte into another. IDA is particularly useful when suitable CRMs are not available [34,35].

First, in order to secure the accuracy of results by the IDA method the effective equilibrium of the enriched spike and sample has to be achieved. For liquid samples, it is easy and it is possible by mixing the sample with the spike. Conversely, it is difficult for sediment and for achieving the equilibrium it is necessary a minimum of 24 h before the

Table 2. CRMs available for organotin speciation analysis in sediment samples.

| Name of the CRM | Type of sediment matrix | Producer | Species | Certified value (unit) |
|---|---|---|---|---|
| BCR 646 [31] | Freshwater sediment | Institute for Reference Materials of the European Commission | TBT<br>DBT<br>MBT<br>TPhT<br>DPhT<br>MPhT | 480 ± 80 ($\mu g\,kg^{-1}$)<br>770 ± 90 ($\mu g\,kg^{-1}$)<br>610 ± 120 ($\mu g\,kg^{-1}$)<br>29 ± 11 ($\mu g\,kg^{-1}$)<br>36 ± 8 ($\mu g\,kg^{-1}$)<br>69 ± 18 ($\mu g\,kg^{-1}$) |
| RM-424 [19,31] | Industrial harbour sediment | Institute for Reference Materials of the European Commission | TBT<br>DBT<br>MBT | 20 ± 5 ($\mu g\,kg^{-1}$)<br>53 ± 19 ($\mu g\,kg^{-1}$)<br>257 ± 54 ($\mu g\,kg^{-1}$) |
| PACS-1 [19,31,31] | Harbour sediment | National Research Council of Canada (NRCC) | TBT<br>DBT<br>MBT | 1.27 ± 0.22 ($mg\,kg^{-1}$ as Sn)<br>1.16 ± 0.19 ($mg\,kg^{-1}$ as Sn)<br>0.28 ± 0.17 ($mg\,kg^{-1}$ as Sn) |
| PACS-2 [31,33] | Harbour sediment | National Research Council of Canada (NRCC) | TBT<br>DBT<br>MBT | 0.98 ± 0.13 ($mg\,kg^{-1}$ as Sn)<br>1.09 ± 0.15 ($mg\,kg^{-1}$ as Sn)<br>0.45 ± 0.05 ($mg\,kg^{-1}$ as Sn) |
| BCR 462R [31] | Coastal sediment | Institute for Reference Materials of the European Commission | TBT<br>DBT | 54 ± 15 ($\mu g\,kg^{-1}$)<br>68 ± 12 ($\mu g\,kg^{-1}$) |

next step of extraction is carried out [37] After achieving equilibrium between the added isotope-enriched standard and the sample, a possible loss of the isotope-diluted sample being determined and a recovery of the analyte lower than 100% do not influence the final result [36]. However, the loss of sample or spiking substances or the decomposition of compounds before complete isotope equilibration may cause important errors [36,38].

The next problem is the lack of commercially available isotopically-labelled species standards. In many cases, it is necessary to synthesise the relevant species from the isotopically enriched element (e.g. $^{118}$Sn or $^{119}$Sn enriched tin). Starting materials for synthesis are very expensive and the synthesis has to take place in small quantities ($<1$ g) which makes it a difficult and inconvenient process [37]. Then, the stability of the isotopically enriched species is difficult and critical to assure [36].

A single-isotope spike solution containing $^{119}$Sn-enriched butyltins mixture has recently become commercially available [39], but it is still too expensive and difficult to obtain for routine analyses. In general, the multi-isotope and multiple-spike BTs standards are not on the market; therefore, laboratories have to produce their own substitutes.

The determination and calculation of the true concentration of species and the procedure for isotope dilution involve several steps such as the correct determination of the analyte natural concentration and spiked analyte in the isotope-enriched stock solutions; the calculation of the isotope ratio e.g. $Sn^{120}/Sn^{118}$ or $Sn^{120}/Sn^{119}$ in the spiked stock solution, in real and spiked samples, and the amount of enrichment by the addition of the isotope standard [34,35,37,38]. A general scheme of the single-isotope IDA

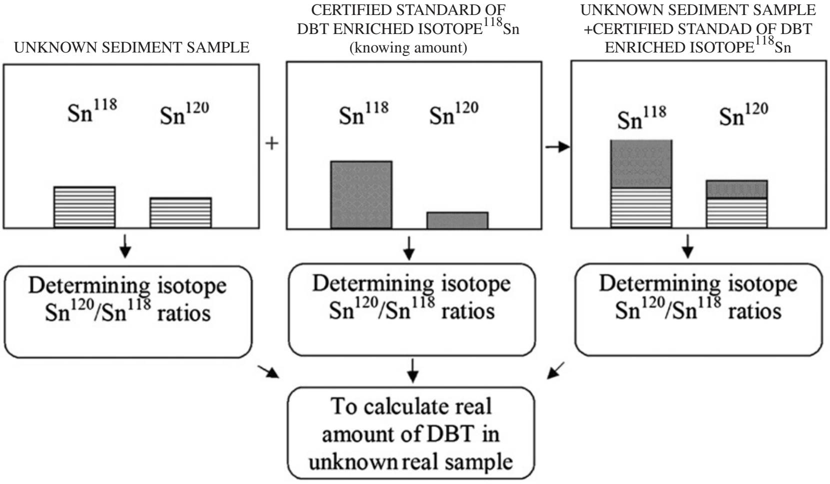

Figure 2. The example of basis steps for the single-isotope IDA analysis of determination of DBT in unknown sample of sediment [34–38].

procedure is shown in Figure 2. It is possible to calculate the real amount of organotins by determining only the isotope ratios in the sample and in the standard added to the sample. This solution requires calculating the response factor for a few solutions of isotope standard and the analyte [38].

The use of compounds enriched in stable isotopes is mainly associated with the use of plasma mass spectrometry (ICP-MS) [33–37,40,41] or rarely mass spectrometry (MS) [39,42]. These detectors, especially ICP-MS, have excellent sensitivity and selectivity but are rather expensive and not generally available.

In order to determine isotopic ratios in a sample correctly, the mass spectrometer must be free of spectral interferences within the desired measuring range, i.e. its operations cannot be disturbed – for example, by signals coming from other components present in the sample [37]. Frequently, it is necessary to use high resolution mass spectrometers to eliminate interferences and achieve the precise and accurate measurements. In recent years, multi-isotope-labelled IDA coupled with GC or LC and ICP-MS detection has created the possibilities to obtain the best results in speciation analysis of, among others, organotin compounds [36,38].

## 6. Techniques for isolating organotin compounds from marine sediments

Isolation of BT and PhT derivatives from the 'primary matrix' – sediments – and transfer them into a 'secondary matrix' for example, appropriate solvent is necessary because of the other analytical steps, such as derivatization and chromatographic analysis. Polar solvents, i.e. methanol and even methanol:water mixtures [43] as well as nonpolar ones, such as dichloromethane, pentane, hexane, benzene and toluene [30,31,44] can be successfully used for extracting organotin analytes.

Butyl and phenyl organotin derivatives strongly bind to the sediment surface via electrostatic and hydrophobic interactions. The strongest interactions occur at pH 6. At such pH, $BTs^+$ cations are dominant, and the maximum number of negatively charged adsorption centres appears on the surface of the sediment particles. Electrostatic interactions decrease at low pH values ($pH < 5$) when the number of negatively charged sites on the surface of minerals rapidly decreases as they become saturated with $H^+$ ions; however BT cations still remain a dominant form [4].

In order to secure the maximal desorption of BT and PhT analytes in the ionic form by an appropriate solvent, it is critical to weaken the binding forces between the analytes and sediment surface. To this end, strong inorganic acids, mainly HCl and HBr, or weak organic acids, i.e. acetic, are added to sediment.

Adding 1M HBr to the sediment results in an increase of octanol-water partition coefficient ($K_{o/w}$) for TBT, from $20^2$ to $10^6$ [20]. In order to completely purge MBT, whose ions have the highest electrical charge and form the strongest bonds with negatively charged centres in sediment, acids at the concentration of 1 to 6M should be used.

In the case of DBT and TBT and PhT such strong acidification of the sample is not necessary and rather unsuitable [20,45]. The application of excessively strong acids may result in the degradation of organotin compounds and decrease the number of alkyl or aryl functional groups bound to the Sn atom.

The derivatives substituted with aryl groups are particularly labile in the presence of strong acids. Carlier-Pinasseau *et al.* [45] reported a decrease in TPhT recovery ranging from 92 to 0% for 0.1 and $3\,mol\,L^{-1}$ HCl, respectively. Because of the significant degradation of phenyl derivatives, it is recommended to use hydrochloric acid at the concentration level of $0.1\,mol\,L^{-1}$. Moreover, the application of organic acids at lower concentration as compared to inorganic ones seems to be advantageous for the quantitative isolation (without degradation) of organotin compounds from sediment.

Carlier-Pinasseau *et al.* [45] obtained better recovery values for DBT, TBT and TPhT (range: 103 to 108%) using glacial acetic acid, while in the case of methanol extraction and acidification with HCl (at $0.1\,mol\,L^{-1}$) recovery values were lower (particularly for TPhT), ranging from 92 to 108%.

Sample acidification can be performed immediately before or during the sediment extraction of organotin analytes. The application of extraction and acidification in the same step decreases the loss of analytes.

Adding acids allows the release of organotin analytes from the sediment surface. However, the quantitative extraction into the organic phase (i.e. solvent) is difficult because of the presence of ionic and additionally polar forms of butyl and phenyl species. Therefore, the extractions are combined with the use of complexing agents, i.e. tropolone (2-hydroxy-2,4,6-cycloheptatrienone) or sodium diethyldithiocarbamate (NaDDTC) [20]. Adding tropolone highly improves the extraction efficiency of organotin derivatives with one or two substitution groups [31]. However, it has to be underlined that the complexing capacity of tropolone or NaDDTC in reaction with BT ions decreases with increasing acidity of the medium because they both undergo protonation. Moreover, high sample acidity is undesired during the further analytical steps because it interferes with derivatization as well as having a negative effect on the columns and detectors used in gas and liquid chromatography.

Extraction can be performed by classical methods, e.g. by shaking the sediment sample placed in extractant, or it can be intensified by repeating it multiple times in a Soxhlet apparatus (Soxhlet Extraction, SE). The above mentioned methods are inexpensive, but time-consuming. In order to secure high recovery and process efficiency, the extraction of organotin compounds from bottom sediment samples can be conducted by using fast extraction techniques, as shown in Table 3.

Table 3. Characteristics of fast extraction techniques.

| Extraction technique | Advantages/Disadvantages |
|---|---|
| Supercritical Fluid Extraction (SFE) [44,46,47–49] | *Advantages*:<br>● Minimised consumption of toxic organic solvents.<br>● $CO_2$ is commonly used for extraction which is a non-toxic, non-flammable and relatively cheap gas that can be easily obtained.<br>● Short extraction time; supercritical fluid is the excellent extrahent with properties of a liquid and gas.<br>● It is necessary to use a small amount of sample.<br>● Extract obtained by SFE can be analysed without further evaporation (small volume of extract obtained) and without further clean-up (high extraction selectivity) [49].<br>● High recovery (under 90%) for TBT and DBT [48].<br>● High degree of automation of the procedure.<br>*Disadvantages*:<br>● Rather low recovery for mono-substituted organotin compounds [46] for example for MBT (below 63%) [48].<br>● Rather low recovery for TPhT (60%) [46].<br>● It is necessary to add complexing agent such as sodium diethyldithiocarbamate (NaDDC) for improving the extraction efficiency [44,47,48]. |
| Pressurised Liquid Extraction (PLE) Accelerated Solvent Extraction (ASE) [34,35,43,44,50,51] | *Advantages*:<br>● Less concentrated and less toxic reagents and acids can be used.<br>● Use of organic solvents at high temperature and pressure results in better extraction efficiency.<br>● The amount of extracted interfering substances is minimal.<br>● Possibility to exactly control extraction parameters such as, pressure, temperature and solvent composition.<br>● Possibility to process several samples in one run.<br>● Possibility to produce extracts without further evaporation and purification.<br>● Average extraction time of few minutes.<br>● Quantitative recovery for BT's and PhT's (except MBT) [43].<br>● No significant degradation of TPhT to DPhT may to occur [51].<br>● High degree of automation of the procedure.<br>*Disadvantages*:<br>● Possibility of degradation reactions (TBT to DBT and DBT to MBT) under high temperature, and recovery even up to 140% for MBT [34,35]. |

(*Continued*)

Table 3. Continued.

| Extraction technique | Advantages/Disadvantages |
|---|---|
| Microwave Assisted Extraction (MAE) [34,35,44,48,51] | *Advantages*:<br>● No significant degradation of TPht to DPhT may occur [51].<br>● Average extraction time of few minutes.<br>● Possibility to process several samples in one run.<br>*Disadvantages*:<br>● Additional enrichment and purification of extracts is necessary [44].<br>● Possibility of degradation of BTs [51]; Encinar *et al*. [34,35] noted that MAE yielded higher degradation factors of up to 7% (TBT to DBT) and up to 16% (DBT to MBT) than those obtained using ASE or ultrasonic extraction. |
| Ultrasonic Probe Extraction (UPE) [51–53] | *Advantages*:<br>● It is modification of classical ultrasound-assisted extraction [60].<br>● No significant degradation of TPht to DPhT snd DBT to MBT may to occur [51].<br>● Simple, fast and reliable method.<br>● Reduction of analysis time: sonication time 30 s, compare to classical ultrasound- assisted extraction where it take a few minutes [60].<br>● High recoveries up 90% for all derivatives [52] (only Campillo *et al*. [53] obtained smaller recovery for MBT and MPhT - 70%) the cheapest equipment among the fast extraction methods.<br>*Disadvantages*:<br>● Extract purification methods are needed. |

By increasing the extraction efficiency, the extraction time and solvent volume can be lowered; the latter eliminates the necessity for the additional analytical step of extract enrichment. The basic disadvantage of the techniques is the expensive extraction apparatus (Table 3).

## 7. Derivatization of organotin compounds

Organotin compounds in environmental samples occur in ionic form and are characterised by low volatility which precludes the use of gas chromatography for further analysis. Therefore, the derivatization of fully alkyl-substituted compounds becomes necessary [20]. A derivatization step is time- and labour-consuming. In the case of using the most popular Grignard reaction, there is an additional problem of having to work in an environment completely devoid of water traces.

At present, the application of sodium tetraethylborate ($NaBEt_4$) as derivatization agent is recommended [1,20,43,44,54]. $NaBEt_4$ has become the most popular derivatization agent used in the course of the organotin compounds analysis because it allows fast and simple derivatization in aqueous as well as non-aqueous samples, i.e. in the organic phase (e.g. hexane and isooctane [1]). The reagents used in the derivatization step are presented in Table 4.

In most cases, derivatization is combined with the extraction of analytes and their transfer into a solvent that is compatible with the final determination technique, for example, isooctane [19,43,45,56,57].

## 8. Post-derivatization extract purification and analyte enrichment prior to the final chromatographic determination

Extracts prior to the final separation and chromatographic determination by gas or liquid chromatography in most cases must be purified from interfering substances, and the analytes – due to their low concentrations – have to be enriched to the level required by a given method used for final determination. It is only in the case of applying post-derivatization, simultaneous isolation/enrichment techniques with direct injection into the chromatographic column, i.e. Purge and Trap or Solid Phase Microextraction, that the further extract purification and enrichment of analytes are not necessary [24,26].

### 8.1 *Extract purification*

Solvent extraction of organotin compounds from sediment results in the co-extraction of other compounds, e.g. sulphur and its derivatives, mineral oils and many other organic impurities. During derivatization many impurities also react with the reagent, e.g. boroxin, diethylsulfide and diethyltrisulfide are derivatized with $NaBEt_4$ [20]. The presence of large amounts of additional substances in the extract makes it difficult – or even impossible – to perform the final identification and measurement of organotin analytes by means of chromatography. Interfering components lower the separation capacity of the column; they cause the widening of chromatographic peaks, superimposition of impurity peaks on the analyte peaks, the appearance of ghost peaks, and contamination and shortening of the column's life span.

Table 4. Reagents used for deriving organotin compounds [1,20,45,54,55].

| Derivatization agent | Application | Advantages and limitations of application |
|---|---|---|
| Grignard reagent (RMgX, e.g. alkylmagnesium bromide) | Derivatization to mainly pentyl and hexyl derivatives | *Advanatages*:<br>● Obtained derivatives are volatile enough to be analysed next by GC and, at the same time, have relatively high boiling point to avoid excessive analyte loss during further analytical steps.<br>*Limitations*:<br>● Multi-step, complicated and time consuming process which creates possibilities of analyte loss.<br>● Prior to derivatization organotin analytes have to be transferred into aprotic solvent (e.g. hydrocarbon, ether).<br>● In the case of chloroform or dichloromethane extraction, analytes have to be transferred into another – preferably nonpolar-solvent.<br>● Extract cannot contain even trace amounts of water; drying by e.g. sodium sulphate prior to derivatization is necessary.<br>● After opening the ampoule with Grignard reagent (diethyl ether solution), the solution has to be washed with an inert gas, e.g. nitrogen to prevent the absorption of moisture from the air by the reagent.<br>● Necessity of using complexing agents, i.e. tropolone.<br>● Long time duration of derivatization reaction, i.e. from 10 to 60 minutes.<br>● Post reaction elimination of derivatization agent is necessary; to this end, shaking in aqueous solution of sulphuric acid is most frequently used. |
| Sodium tetraethylborate ($NaBEt_4$) | Derivatization to ethyl derivatives | *Advantages*:<br>● Quick and easy process that can be conducted *in situ*.<br>● Possibility to conduct derivatization in aqueous or other polar solvent.<br>● Reagent is stored in aqueous or organic solvent, i.e. methanol, ethanol and tetrahydrofurane which makes it more stable. |

| | | |
|---|---|---|
| | | • Derivating volatile ethyl derivatives that are more volatile than pentyl and hexyl derivatives allows the use of purge and trap (PT) technique for direct injection of analytes into chromatographic column (without transferring the analytes into nonpolar solvent post derivatization) or the extraction of the obtained derivatives with other solvent (e.g. hexane or isooctane).<br>*Limitations*:<br>• $NaBEt_4$ is not recommended for deriving phenyl derivatives.<br>• Use of buffers is necessary; it is important that pH remains within 4–6. At $pH < 4$, $NaBH_4$ undergoes accelerated decomposition, while at $pH > 6$ BT compounds transform into nonionic forms. |
| Sodium tetra (*n*-propyl)borate ($NaBPr_4$) | Derivatization to propyl derivatives | Similar advantages and disadvantages as in the case of $NaBEt_4$ use. |
| Sodium tetrahydroborate ($NaBH_4$) | Derivatization to highly volatile hydrides | *Advantages*:<br>• Hydrogenated butyl derivatives are characterised by high volatility which allows the application of PT technique to inject the analytes into chromatographic column and elimination of the extract purification step.<br>• Highly efficient derivatization can be conducted within the wide pH range, i.e. 4–11.<br>*Limitations*:<br>• Possibility of analyte loss due to high volatility of the obtained derivatives.<br>• Not suitable for different matrices than water ones. |

Solid phase extraction in a glass column packed with deactivated $SiO_2$, $Al_2O_3$ or Florosil is the most commonly used technique of extracts purification. Analytes are desorbed with hexane, which easily elutes nonpolar organotin derivatives, and separates them from more polar compounds [20].

The above described methods of extract purification are however insufficient in the case of bottom sediments exhibiting high content of sulphur species. High contents of elemental sulphur and methylated derivatives (which are also formed during derivatization) make it difficult – or even impossible – to quantitatively determine butyltin derivatives, particularly DBT, and phenyl derivatives [43,56].

In order to eliminate sulphur compounds from the extract, a purification method that employs activated copper and which is also used for other organic compounds can be applied [58]. Another option is a recently employed purification method based on oxidation of sulphur compounds with dimethyldioxirane (DMD) and elimination of the reaction products by adsorption on $Al_2O_3$ [59].

The above mentioned solutions are in many cases insufficient for successful removal of sulphur compounds from the extract. Moreover, they are costly and labour consuming, and may result in additional loss of analyte. The elimination of sulphur compounds already performed during the extraction step seems more advantageous. Wasik *et al.* [43] optimised the extraction process by applying Pressurised Liquid Extraction (PLE). The optimal extraction conditions, i.e. temperature = 50°C, pressure = 13.8 MPa, time equal to a couple of minutes, and the use of an appropriate extraction mixture (75% MeOH and 25% water with admixture of tropolone) minimised the transfer of sulphur and its organic compounds into the extract. In addition, the isolation of sulphur compounds from the extract was performed by crystallisation at low temperature, i.e. 4°C, and centrifuging two times. This allowed the separation of sulphur compounds from organotins and, in turn, the quantitative determination of all BT and PhT derivatives, and a high recovery (>98%) for all analysed analytes [43].

### 8.2 *Enrichment of organotin analytes*

Enrichment is most often achieved by solvent evaporation, but the biggest problem is the possibility of releasing the more volatile derivatives. In the case of post-derivatization as pentyl and hexyl derivatives, it is not such a big problem [20]. In any case, it has to be remembered that a complete evaporation of solvent will lead to the total loss of analytes. This can be avoided by adding a small amount of isooctane into the extract prior to evaporation. Analytes after the evaporation step and prior to chromatographic analysis will be transferred into isooctane, a solvent used by the majority of analysts [19,20].

As regards to lowering the analyte loss, combining the isolation and enrichment into one analytical step is also advantageous. This can be done by applying gas phase isolation and enrichment techniques, as described in earlier, i.e. Purge and Trap (PT) or Solid Phase Microextraction (SPME), or liquid–liquid extraction conducted with a small portion of organic solvent such as, ASE, MAE and SFE.

## 9. Techniques for final determination of organotin compounds

Final determination of analytes is the last analytical step in a given procedure. To this end, chromatographic techniques such as, GC and LC combined with appropriate detectors are used [1,19,20]. Other techniques for final determination (despite high resolution) such as, Capillary Electrophoresis (CE) and Supercritical Fluid Chromatography (SFC) are rarely applied in the analysis of organotin compounds. The CE technique has to be coupled with very expensive and sensitive detectors, while SFC requires expensive equipment and, in addition, is characterised by low recovery of monosubstituted organotin derivatives [19,22,47].

### 9.1 *Gas chromatography techniques*

Gas chromatography is the most popular technique employed in the speciation analysis of organotin compounds. However, it has a limitation because it is necessary to derive volatile hydrides or alkyl derivatives of the analysed analytes (that have insufficient volatility) prior to chromatography, which extends and complicates the analysis. Among the post-derivatization compounds, it is the analysis of very volatile and thermolabile hydrides that causes most problems due to possible analyte loss.

Post-derivatization compounds are most often injected into the chromatographic system in a splitless mode [45,60], or in a temperature and pressure pre-programmed mode [57,61]. Techniques combined with gas chromatography that allow direct injection of the derivatized analytes (in particular highly volatile hydrides or ethyl derivatives) into the column can also be used, i.e. Purge and Trap, and Solid Phase Microextraction [24,26].

Nonpolar capillary columns, e.g. polydimethylsiloxane [45] or medium polar phases, e.g. 35% phenyl and 65% methylpolysiloxane [60], are most suitable for separating organotin compounds. A typical column which allows the separation of a broad spectrum of post-derivatization organotin analytes is 25 to 30 m long, with an inner diameter of 0.25 mm and film thickness of 0.1–0.3 μm [45,57,60,61]. In order to achieve optimal separation of analytes, it is necessary to use temperature programming.

After the separation of analytes in a chromatographic column, they are subjected to final detection by means of different detectors. Detectors, in general, allow detection of organotin compounds at the level ranging from below to tens of $\mathrm{ng\,g^{-1}}$. Flame Photometric Detector (FPD) and Pulsed Photometric Detector (PFPD) are the most often used because they are relativity inexpensive, user-friendly and commonly available in many laboratories. But the most selective and sensitive measurements are obtained by means of ICP-MS coupled with IDA. Unfortunately, it is a rather expensive and not commonly available technique.

Table 5 shows the advantages and disadvantages of detectors coupled with GC that have found the broadest application in the analysis of organotin compounds.

### 9.2 *Techniques for analyte isolation and enrichment in combination with gas chromatography*

Usually, the post-derivatization compounds are transferred into an organic solvent, and such extract is purified and enriched. In reference to time and labour consumption (i.e. no need to repeat the purification step) and a significant decrease in the risk of loosing volatile analytes, it is more advantageous to use the so-called solvent-free isolation and enrichment methods that allow simultaneous isolation and enrichment, and direct injection of analytes into the chromatographic column [24,26].

Table 5. Typical detectors coupled with GC used for determining organotins compounds in sediment samples.

| | Detection characteristic | | |
|---|---|---|---|
| Analytes | Detector | Advantages and limitations of application | Limit of detection |
| BTs PhTs | Flame Photometric Detector (FPD) | FPD is the most often used detection type for determining organotin compounds.<br>*Advantages*:<br>● Especially very high recovery for DBT, TBT [57].<br>● Detector's sensitivity at 610 nm is 100 times lower for sulphur compounds in comparison to organotin compounds [57], this creates a significant problem only in the case of compounds with high sulphur content [45,56,57,61].<br>● For low concentrations of sulphur compounds, it is possible to obtain good separation between organic compounds of sulphur and tin if an appropriate column and chromatographic parameters are chosen [57], in order to decrease interferences, a 610 nm filter is also necessary [22,57].<br>● Inexpensive, user-friendly and commonly available in many laboratories [62].<br>*Disadvantages*:<br>● The most interference-sensitive detector due to co-extracted sulphur and/or phosphorus compounds [45,56,57,61,63].<br>● For very complex samples, the special preparation and elimination of sulphur compounds, that cause low recovery of PhTs and prevent MBT identification, is necessary [45,62]. The correct choice of extraction parameters and the special sample preparation allowed the elimination of the | ng Sn $g^{-1}$ (pg as Sn).<br>Example:<br>0.5–1.5 ng Sn $g^{-1}$ [45].<br>3.3–9.9 pg as Sn [57,61].<br>4–10 pg as Sn [62]. |

| | | | |
|---|---|---|---|
| | | negative interference of sulphur compounds on the quantitative determination and separation of BTs derivatives [5] as well as all the derivatives of BTs and PhTs [43] in harbour sediments with high content of sulphur compounds. | |
| BTs<br>PhTs | Pulsed Flame Photometric Detector (PFPD) | *Advantages*:<br>● Higher sensitivity, specificity and lower detection limits by 25 to 50 times as compared to FPD [61], and only 2 to 10 times higher detection limits than ICP-MS [62].<br>● Reduced sensitivity to interferences; PFPD is less sensitive to the interfering presence of sulphur compounds in sample matrix [56,60,61,63].<br>● Inexpensive, user-friendly and commonly available in many laboratories [62]. | Below:<br>ng Sn $g^{-1}$ (pg as Sn).<br>Example:<br>$<1$ ng Sn $g^{-1}$. |
| | | *Disadvantages*:<br>● Narrow dynamic range [62,63].<br>● Lower selectivity than ICP-MS which could be remedied by using two different optical filters at 390 nm and 610 nm [62]. | 0.07–2 pg as Sn [57].<br>0.07–0.38 pg as Sn [62]. |
| BTs<br>PhTs | Atomic Emission Spectrometry (AES) | *Advantages*:<br>● Excellent selectivity and sensitivity [19,20].<br>● High recovery for TBT, TPhT (100–126%) [64] and MBT (85%) [65].<br>● Inexpensive, user-friendly and commonly available in many laboratories [62].<br>● Very low detection limits even in highly contaminated samples [19,20]. | Below:<br>ng Sn $g^{-1}$ (pg as Sn even) [20].<br>Example:<br>0.2–1.0 pg as Sn [62]. |
| | | *Disadvantages*:<br>● Occasional low recoveries for MBT and MPhT ($<10\%$) [64].<br>● Co-extracted compounds may cause chromatographic interferences [11].<br>● When coupled with ICP has very low detection limit [12]. | (MBT) 0.01 ng Sn $g^{-1}$ [11].<br>(MBT) 0.5 ng $g^{-1}$ [65]. |

(*Continued*)

Table 5. Continued.

| | Detection characteristic | | |
|---|---|---|---|
| Analytes | Detector | Advantages and limitations of application | Limit of detection |
| BTs | Atomic Absorption Spectrometry (AAS) quartz furnace (QF), graphite furnace (GF) and flame (F) | *Advantages*:<br>• Low cost detection system [19]. | Ng Sn $g^{-1}$ (pg as Sn even). |
| | | *Disadvantages*:<br>• Co-extracted compounds may cause chromatographic interferences [11].<br>• Occasionally, the method is not satisfactorily selective and/or sensitive for processing the environmental samples with solid matrices [12,30]. | Example:<br>(MBT) 2.5 ng Sn $g^{-1}$ [11]<br>5 ng $g^{-1}$ (QFAAS) [66]. |
| BTs<br>PhTs | Mass Spectrometry (MS); Inductively-Coupled Plasma-MS (ICP-MS) | *Advantages*:<br>• Particularly sensitive and selective; besides speciation analysis of organotin compounds, both techniques create additional possibilities to measure the tin and organotin contents [20].<br>• ICP-MS is the most sensitive detector for organotins [22].<br>• High recovery for all derivatives (98–105%) [67]. | pg Sn $g^{-1}$ (fg as Sn).<br>Example:<br>HR-MS<br>0.35–1.45 pg $g^{-1}$ [63]. |

| | | | |
|---|---|---|---|
| | | ● MS and ICP-MS techniques can be coupled with isotope dilution analysis (IDA) for improving the accuracy of organotins determinations (see sec. 4) [33–38,68,69].<br>*Disadvantages*:<br>● Especially ICP-MS is rather expensive and not generally available [19].<br>● More complicated servicing.<br>● High operating cost as compared to FPD and PFPD [19].<br>● Low resolution MS suffers from interferences in the regions where organotins ions appear, while high resolution MS is more selective and sensitive [63]. | ICP-MS.<br>0.05–0.08 pg as Sn [62]. |
| BTs | Flame Ionization Detection (FID) | Nowadays, this type of detection is rarely used for determining organotin compounds [19].<br>*Advantages*:<br>● Inexpensive, user-friendly and commonly available in many laboratories.<br>*Disadvantages*:<br>● Low selectivity and/or sensitivity [19,30]. | Higher than ng Sn g$^{-1}$ (pg as Sn) [24]. |
| DBT, TBT, TPhT | Electron-capture Detection (ECD) | Nowadays, this type of detection is rarely used for determining organotin compounds [19].<br>*Advantages*:<br>● Inexpensive, user-friendly and commonly available in many laboratories.<br>*Disadvantages*:<br>● Low selectivity and/or sensitivity, poor detection limits [19,30]. | Higher than ng Sn g$^{-1}$ (pg as Sn) [30]. |

### 9.2.1 *Purge and Trap*

The Purge and Trap (P&T) technique is used to analyse the organotin compounds that have been derivatized into highly volatile derivatives such as, hydrides and ethyl derivatives; it is the most advantageous method for determining ethyl derivatives of DBT and TBT [20]. The advantage of this method is the possibility to determine very low analyte concentrations because the whole amount of the compounds extracted into the gas phase can be injected into the chromatographic column as a result of thermal desorption.

This technique allows taking final measurements after the preliminary isolation and derivatization of organotin analytes from samples characterised by high content of inorganic compounds, i.e. water and marine sediment, and large molecules of organic compounds (humic substances) without the need for complicated purification procedure and extract preparation before the chromatographic analysis itself.

### 9.2.2 *Solid-Phase Microextraction (SPME)*

Similarly to P&T, SPME technique allows the analysis and determination of volatile derivatives, and it also consists of two steps, namely the adsorption onto the fibre and the injection. Also in this case less volatile compounds, which could potentially disturb the further analysis, are not adsorbed onto the fibre, but remain in the extract. On the other hand, the application of thermal desorption during the injection of analytes allows a significant lowering of the detection limit.

Fibres coated with polydimethylsiloxane (PDMS), PDMS-divinylbenzene (PDMS-DVB) and Carboxen-PDMS are the most widely used [24,26,70,71].

Millan and Pawliszyn [24] used SPME to determine BT in bottom sediments; a fibre coated with a 100 µm layer of PDMS was employed as sorbent. First, the organotin analytes were released from the sediment with a 20% hydrochloric acid-methanol (1:1) mix in an ultrasound bath and derivatized into tetraethyl derivatives by adding $NaBEt_4$ to 2 $cm^3$ of the obtained solution at pH 4.3 (sodium buffer solution). Next, the extraction was conducted from the near-surface gas phase at 40°C for 15 min. The analytes adsorbed onto the fibre were desorbed at 250°C for 1 min directly into the chromatographic column. The obtained recovery values were higher than 90% for DBT and TBT derivatives. But the measurement of MBT obtained with SPME gives higher final results (even up to 200%) caused by organic interferent coeluted with MTB [24,62].

SPME is solvent free, simple, fast for one analysis (extraction and isolation can be realised in only one step), easily automated and does not require any complicated apparatus. In order to perform SPME, very volatile organotin derivatives have to be formed prior to the extraction step, which may result in unintended analyte loss. Matrix components may cause decreases of sensitivity up to 70%, particularly for TPhT determinations (especially by SPME direct extraction of liquid phase method [62].

## 9.3 ***Liquid chromatography techniques***

Liquid chromatography allows determination of organotin compounds in ionic form without the need for deriving nonionic species and the use of derivatization reagents [25]. Only when a fluorimetric detector is used for final determination it is necessary to prepare fluorescent derivatives. However, in this case, the process is conducted during the final step of the chromatographic measurement by means of the appropriate post-column reaction and usually by deriving ionic analytes into flavone derivatives [72–74]. The basic limitation of liquid chromatography is mainly a higher limit of detection as compared to gas chromatography [20].

In the case of using liquid chromatography for determining the organotin compounds, prior to chromatographic analysis it is only necessary to extract the analytes from the sediment, e.g. with ethyl acetate dissolved in 0.6M HCl, to dry the extract (e.g. with anhydrous sodium sulfate), remove the solvent by evaporation and replace the solvent with the one that is more compatible with the final chromatographic determination (e.g. methanol) [73]. Due to the above mentioned reasons, a procedure employing LC in the final separation step seems faster and less labour consuming.

For the final determination of organotin compounds, normal- and reversed-phase chromatography [75–78] as well as ion-exchange chromatography can be employed [25,72–74,79]. The basic problem encountered during analyte separation by normal-phase chromatography is the excessively strong retention (adsorption) of organotin compounds by silane groups. In order to allow the quantitative desorption from the stationary phase, a complexing agent – most often tropolone or morin (2′,3,4′,5,7-pentahydroxyflavone) – is added into the mobile phase. However, in a normal-phase system even adding those reagents it is not enough to quantitatively remove the strongly adsorbed $MBT^+$ ions from silane groups, therefore normal-phase chromatography is rarely used [20].

Reversed-phase separation is more recommended for determining mono- and dibutyltins [74]; the most frequently used eluents are methanol, water, acetic acid and tropolone mixes (e.g. at 80:14:6:0.1 ratio) [20].

A very promising and the most often used solution that allows the determination of all BT derivatives is ion-exchange LC [25,79] and cation-exchange column. In this case, the most critical analytical step is also the strong binding between $MBT^+$ cations and the stationary phase. Therefore, in order to separate all BTs, the mobile phase with a complexing agent or a pH gradient column are used [25]. An example of the latter solution is the application of silica-based ion-exchange columns and water-methanol mix, acidified with ammonium acetate or citric buffer to $pH = 6$, as eluent; such eluent's pH is sufficient to wash out TBT and DBT from the column. During the elution, pH drops to about 4 which enable the elution of MBT and inorganic tin [20].

In comparison to GC, the application of LC to organotin analysis has a big limitation, i.e. poorer resolution and inefficient sensitivity of most of the used detectors. The efficient sensitivity, selectivity and a relatively low detection limit of the final measurement can be achieved by employing fluorimetric [72,73], MS [77,78] and ICP-MS [40,75–77,79,80] detectors.

Other detectors proposed for detection of organotins like Atomic Absorption Spectrometry (AAS) (in electrothermal, quartz furnace or flame modes), Inductively-Coupled Plasma – Optical Emission Spectrometry (ICP-OES) and a combination of LC and ICP-AES detection are not used for analysing sediment samples because of insufficient detection limits and lack of sensitivity [19,20,25,30].

Examples of the application of liquid chromatography to the identification and measurement of organotin compounds in sediments, including the characterisation of the more suitable detectors for organotins are shown in Table 6.

Table 6. Examples of the application of liquid chromatography to the identification and measurement of organotin compounds in sediments.

| | | Detection characteristic | | | |
|---|---|---|---|---|---|
| Analytes | Chromatographic mode | Detector | Advantages/disadvantages | Limit of detection | Reference |
| TBT, DBT | Ion-exchange | ICP-MS | *Advantages*: excellent sensitivity; wide linear dynamic range; high speed analysis; ability to perform isotopic analysis [25,36,37]. | 40, 20 (pg Sn) | [79] |
| DBT, TBT, DPhT, TPhT | Reversed-phase | ICP-MS | *Disadvantages*: clogging the nebulizer and cones by non-volatile components of mobile phase; plasma stability decreases with increasing percentage of organic solvents; isocratic mode is preferred over the gradient mode because gradient elution changes the solvent load and may cause plasma instability [25], poor compatibility with most mobile phases [19]. | 10 (pg Sn) | [77] |
| TMT, TET, TPrT, TPhT, TBT | Reversed-phase | ICP-MS | | 2.8–16 (pg Sn) | [75] |
| BT's | Ion-pair | ICP-MS | | 1.8, 2.5, 1.85 (pg Sn) | [80] |
| BTs, PhTs | Reversed-phase | ICP-MS | | 0.7–2 (ng Sn $g^{-1}$) | [76] |

| | | | | | |
|---|---|---|---|---|---|
| TBT, TPhT, DBT, DPhT | Reversed-phase | MS (SIM Mode) | *Advantages*: tolerates mobile phases with high percentage of organic solvents; gradient solvents are acceptable, preferably in RP chromatographic mode [25]. | 1.8, 0.8, 1.9, 0.9 (ng Sn) | [77] |
| TBT, TPhT, DBT, DPhT | Reversed-phase | MS (SIM Mode) | *Disadvantages*: not as sensitive as ICP-MS; salts cause ion suppression and/or contamination of the interface; eluent systems should contain low amounts of dissolved solids and have high volatility [25]. | 20–65 (pg Sn) | [78] |
| TBT, TPhT | Cation-exchange | Fluorimetric | *Advantages*: sensitive and selective; has been used in combination with normal-phase, ion-exchange, or reversed-phase chromatographic modes; lower cost than ICP and MS [74].<br>*Disadvantages*: OTs are non-fluorescent compounds therefore post-column derivatization of flavone derivatives is used to allow detection; limited sensitivity for TBT [74]. | 0.9, 0.03 (ng Sn in 200 µl of injected sample) | [72,73,74] |

## 10. Conclusions

The procedures developed and/or applied for the quantitative determination of organotin compounds in sediments are usually a compromise among costs, availability of proper equipment and the efficacy of separation, sensitivity and selectivity.

Extraction of organotins from solid matrices requires the use of different conditions to quantitative desorb various forms and species of organotins, which are being bonded to sediment with different strengths. A rather low recovery is usually found for MBT by its strong bonding to sediments. For DBT, TBT and PhT's degradation may also occur. The use of novel, fast and easy to automate extraction techniques like SFE, PLE, MAE, are advantageous but they are too expensive for many laboratories.

Nowadays, GC is preferred to LC because of its great resolution power and the availability of sensitive detectors. But there is a need for a derivatization step for increasing the volatility of the analytes.

ICP-MS is the most sensitive and selective detector for organotins. ICP-MS coupled with multi-isotope-labelled IDA is one of the most powerful tools for improving the accuracy and precision of speciation analysis. Unfortunately, ICP-MS and stable isotope enriched materials are rather expensive and not generally available. In many cases, FPD and PFPD detectors are the most often used because they are inexpensive, user-friendly and commonly available in many laboratories. When FPD is used it is necessary to eliminate the sulphur compounds that disturb the analysis.

From all the above, it is not possible to point out one analytical procedure which would allow the optimal solution to all the problems.

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