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DETERMINATION OF TIN SPECIES
IN ENVIRONMENTAL SAMPLES

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Determination of tin species in environmental samples (Technical Report)

INTRODUCTION

'Organometallic species (i.e. compounds, complexes or ions) may be found in the natural environment either because they are formed there or because they are introduced there' [1]. The occurrence of major toxicological impacts of some organometallic compounds, e.g. methylmercury on man in Minamata (Japan) or tributyltin on marine life has led to the necessary development of analytical techniques for the determination of a wide variety of compounds in different environmental matrices. In addition to the necessity of monitoring of these compounds, their identification allows a better understanding of the bio- and geochemical pathways of metals in the environment.

Organotin compounds may be represented by the general formula $R_pSnX_{(4-p)}$ where R is an alkyl or aryl group (e.g. methyl-, butyl-, ethyl-, phenyl-) and X is an anionic group (e.g. Cl⁻, Br⁻ or OAc). Organotins entering the environment are introduced deliberately as man-made products (e.g. biocides or stabilizers) or are formed after entry as inorganic species, then becoming components of global biogeochemical cycles. Owing to the high toxicity of some organotin species (mainly trisubstituted species), extensive studies have been focused on these compounds in the last decade. Their origin and fate has been widely described in the literature [1–4].

The best-known anthropogenic compounds include, e.g., tributyltin (TBT) species (used in antifouling paint formulations) which are responsible for deleterious effects on bivalves [5,6]; these compounds are usually detected along with their less toxic degradation products mono- and dibutyltin (MBT and DBT) which may, however, be released from leaching of PVC pipes [7].

Triphenyltin is used as a fungicide in agriculture and is also present in antifouling paints [8]. Recently, trisubstituted phenylneopentyltin compounds have been added to the list of tin- containing agricultural biocides [9]. Tetrabutyltin compounds are also introduced into the environment [10].

Naturally-occurring organotin compounds (mainly methylated forms) are mostly products of the methylation of inorganic tin; these compounds were observed in estuarine [11] or sewage waters [12], sediment [13,14] and biological tissues [15]. Moreover, volatile tin species have been observed in laboratory experiments [16,17] and in natural samples [12]. Mixed butyl-methyl compounds have also been identified [18] or suspected [19,20] and these species were attributed to the methylation of butyltin species because such compounds are not produced by industry.

Additional details will be found in the literature [21]. The purpose of this paper is to review and discuss the major techniques used for the determination of organotins. It presents the advantages and pitfalls at each step of an analytical procedure including the sample collection.

SAMPLING AND STORAGE

The strategies used for the monitoring of organotins differ strongly from one author to another, which leads to difficulties in the comparison of contamination levels and the evaluation of long- term trends. Precautions have to be undertaken at each step prior to analysis to ensure reliability of data, particularly the collection, pre-treatment and storage of samples. It is obvious that the representativeness of the analysis of environmental samples depends closely upon these different steps for which several sources of error are discussed in this report. Most references deal with butyltin analyses in aquatic environments where most recent analytical studies have been made.

Sample collection

The sources of error due to sample collection are numerous and are more critical when dealing with the low organotin concentrations usually found in the environment (ng/L or µg/kg).

The risks of organotin contamination from metallic sampling devices are unlikely, but plastic materials are nevertheless recommended. Polyvinyl chloride (PVC) has to be avoided as it may contain dibutyltin which can be leached and released into water along with monobutyltin [7]. Polytetrafluoroethylene (PTFE) and polyethylene have been used successfully either for water samplers and sieves for sediment treatment [22]. Glass bottles were also shown to be adequate; i.e. no strong adsorption of, for example, butyltins was observed during collection [22]. For larger volumes of water, PTFE pumping systems have been found to be suitable for organotin surveys [23].

It is obvious that materials used for sample collection and treatment have to be cleaned carefully prior to use; rinsing of devices with samples is recommended to limit possible adsorption phenomena.

Nalgene sterile filtration units were used for the filtration of water samples and no adsorption or contamination of samples was observed after centrifugation [23]. PTFE spatula for sediment collection may be used to scrape the two cm sediment surface layers without any contamination.

Sample conditioning

The sample pre-treatment is another source of possible errors. For water samples, many authors monitor organotins in filtered waters because the toxic impacts are assessed usually with dissolved concentrations. However, some compounds are adsorbed mostly on particulates, as for example TBT [23]. Consequently, the assessment of the contamination may be biased if filtered waters are analysed only. As an example, analyses of bulk water samples with low amounts of suspended matter (collected in the Rhine Estuary, The Netherlands) did not reveal high organotin contents (less than 2 ng/L as Sn) whereas concentrations of up to 200 µg/kg (as Sn) were detected for TBT in suspended particles collected by centrifugation [23]. This stresses the problem of reliability of data with regard to sample conditioning if an accurate estimation of contamination is required.

For sediment samples, sieving is very often used both to limit the heterogeneity of the samples and provide a common basis on which comparisons can be made, e.g. concentrations from the < 60 µm fraction. It has been recommended to wet-sieve the samples with overlying water from the sediment sampler to avoid eventual desorption of organotins during sieving [23]. Finally, the presence of light detrital fragments (mostly algal and leaf debris) was shown to result in overestimation of organotin concentrations in sands, as such detrital materials are an important sink for these compounds [24]. These fragments should therefore be considered separately for accurate measurements (viz washing of sands and collection of fragments by flotation).

Storage of samples

Storage of water and sediment samples may be an additional cause for unacceptable losses or contamination. Natural waters are systems consisting of suspended particles and biological and chemical species in equilibrium; equilibrium shifts and reactions may take place as soon as contact with oxygen or container walls, or physical changes (temperature, pressure) occur [25]. Sediments may also be subject to physico-chemical alterations when in contact with air (e.g. oxidation, flocculation). Furthermore, microbial activities may change analyte concentration and composition (e.g. methylation both of inorganic tin [26] and butyltin species [18], and volatilization of tin as stannane [17]).

The choice of adequate containers for the storage of water samples is of paramount importance. It was shown that no considerable adsorption of TBT took place in non-acidified water stored at 4 °C in Pyrex glass bottles over 5 months [27,28]. Some TBT adsorption on to Pyrex glass has been observed from synthetic solutions stored at pH = 5.3, but such adsorption could be reduced by using pre-equilibrated bottles. Pre-waxing or silanisation was less effective [29].

Acidification is thought to be a suitable means to achieve good stability of butyltins in solution. Synthetic solutions (butyltins in HCl) used in round-robin exercises were shown to remain stable over some months [30]. Moreover, the storage of natural (less than 0.45 mm) filtered water samples acidified to pH = 2 with HCl in the dark over 4 months was demonstrated to be suitable for achieving a good stability of TBT and MBT both at 4 °C and at ambient temperature whereas the stability of DBT was more doubtful [31]. However, the stability of butyltins appeared to be less easily achieved in samples rich in suspended matter due to possible interactions with particulates and/or microbial communities [31].

Systematic studies have shown that several different treatments for the storage (freezing, wet storage at 4 °C) and drying (air-, freeze and oven-drying) of sediment samples were all suitable for preserving the stability of TBT over at least 4 months. However, the degradation products MBT and DBT were often subject to variations (mostly losses) in most of the experiments. Freezing followed by oven-drying (at 50 °C) was shown to be the most suitable treatment to avoid changes in concentrations for the three species but this should be recommended for short term storage only as microbial activity may not be completely stopped at 50 °C. Wherever a long storage period is needed, freeze-drying would be a better compromise [31]. A long-term stability study to investigate the suitability of a sediment as a candidate certified reference material for certification of butyltin compounds has shown that an oven-drying treatment (60 °C for 48 h and 120 °C for 2 h) was adequate for stabilizing both DBT and TBT [32]. The two species were demonstrated to be stable at +20 °C in the dark for a period of 12 months; at +40 °C both compounds were found to be stable over a period of one month but a strong degradation was observed after this period. Recent findings, however, have shown that a certified sediment reference material (CRM 462) was not stable anymore after 36 months which justified the material to be withdrawn from the market and re-certified [33]. A mussel reference material (CRM 477) has also been tested over a long term period (44 months) and, while the butyltins were found to be stable at –20 °C, instability was demonstrated at +20 °C and +40 °C; in the case of phenyltins, the material was not stable even at –20 °C [34]. These studies illustrated the great care to be taken to minimize instability problems upon storage.

ANALYTICAL METHODS

Several reviews [3,8,35–36] have described the major analytical methods used for the determination of organotin species. A recent monography summarizes various techniques which were successfully used in interlaboratory studies and certification campaigns for environmental analysis related to speciation [37], one chapter of which is dealing with techniques for butyl- and phenyl-tin determinations.

Most techniques are based on separation by gas chromatography (GC) and detection with the classical types of detectors. Some of the first methods appeared in the 1970s. Meinema and co-workers [38] presented a method for butyltin determination by solvent extraction, derivatisation with a Grignard reagent prior to GC separation and detection by mass spectrometry. Simultaneously, methods for determination of phenyltin moieties in water by hydridisation with $LiAlH_4$ were published [39], using GC and electron capture detector (ECD) or a flame ionisation detector (FID). Later, Chau and co-workers [40] showed that atomic absorption using an electrothermal quartz furnace could be used efficiently for the determination of methylated tin in waters.

Since then, a wide variety of techniques focused on the application of GC have been published. They have concerned wide classes of organotin species such as methyl, butyl, ethyl, propyl, phenyl and cyclohexyltin compounds in matrices such as natural waters, sediments and, recently biological tissues. In general, early papers were concerned only with the highly-toxic trialkylated forms. The demand for understanding biogeochemical pathways and degradation patterns has required refinements of analytical schemes to allow simultaneous determination of other less substituted alkyltins. The best examples in this respect are the papers published by Müller. His first report [41] dealt with the determination of tributyltin in environmental samples. Three years later, his analytical method [42] was extended to the simultaneous determination of 19 organotin species by capillary GC and flame photometric detection (FPD).

Quantitative methods for their determination by GC all include at least 4 major steps: (1) extraction/concentration; (2) derivatisation (hydridisation or alkylation); (3) separation; and (4) detection.

The multiplicity of operations in the analytical schemes enhances the chances of errors leading to a poorer accuracy and precision.

Pre-treatment and extraction

A wide variety of acid extraction procedures has been used for sediment analyses. These involve leaching with different acids such as: 0.1 mol/L HCl [15] for methyltin, HCl-CH$_3$OH [43] and CaCl$_2$-HCl [44] for both methyl and butyltin compounds. Glacial acetic acid has been shown recently to extract TBT more efficiently than the above extractants [45] when using atomic absorption spectrometry (AAS) as final detection; this was also demonstrated for biological samples. Other leaching procedures have been used for biological samples (algae and invertebrates) and vegetable tissues particularly with: dilute acetic acid [46], HCl [15], a mixture of sorbitol, tris and acetate buffer [47] or NaOH [48]. Other tests have been conducted [19] which demonstrated a higher extraction efficiency for acids in comparison with other solvents.

Prior to derivatisation by a Grignard reagent, and after acid digestion of the sample, organotins are extracted into an organic solvent. Solvents commonly used are benzene, pentane, hexane and dichloromethane. Acidification of the sample is usually performed with HCl. The addition of HBr has been shown to enhance the recovery of organotin species [38,40,49,50] probably by preventing adsorption on the walls of the container. Simple extraction with a solvent is generally sufficient most of the time for trisubstituted alkyltin, but highly polar mono- and dimethyl or butyltin compounds of Sn(IV) require complexation with tropolone for efficient extraction of these species by the solvent [40,41,49]. These conditions are not directly applicable to methylated tin species. More drastic acidic conditions using a combination of hydrobromic, hydrochloric, acetic and sulfuric acids in a high ionic strength medium are required [40]. Differential evaporation during the preconcentration steps could lead to errors in quantification [51]. The use of tropolone should be performed in the dark since dismutation of trimethyltin to tetramethytltin in the presence of light has been reported [52].

Extraction for HPLC/AAS: Extractions are made for water, sediment and biological samples with dichloromethane [53], dichloromethane/chloroform [54], chloroform [55], toluene [56,57], hexane/isobutyl acetate [58], often with addition of tropolone, halogenated acids or halide salts. The greatest recoveries were obtained with toluene [59,60] or hexane [61]. The extraction of butyltins from water on a tropolone-loaded reverse phase column has also been shown to be efficient [62]. Solvents such as chloroform or hexane [63] are compatible with strong cation exchange HPLC but tropolone has to be avoided because of its high complexing power [62,64]. The quantitative extraction of all butyltin species is thus not always possible. Other organic compounds present in the sample are simultaneously extracted and they are injected directly in the HPLC column; this leads to a rapid degradation of the column. In other procedures the solvent is evaporated and replaced by a more polar one, leaving an organic residue. This may protect the column but some losses of organotins in this residue may occur.

Some derivatisation techniques such as hydride generation often require clean-up procedures. Extraction procedures for biological tissue may lead to high levels of lipids. Direct determination of organotins can be performed but the high lipid content may cause deterioration of the column, reduce reproducibility and prevent good preconcentration in the solvent leading to overall poor detection limits. The clean-up procedure removes more than 90% of the lipid content of the sample but does not eliminate pigments or other extracted material [54]. Analyte recoveries should be checked carefully, since in the case of Ph$_3$SnCl, 75.9% was obtained for a 10 mg/kg concentration whereas it was only 33% for a 0.1 mg/kg concentration [65]. Despite this problem the clean-up stage has been shown generally to increase the sensitivity of the analysis, and to improve the tailing of the chromatographic peaks by decreasing drastically the presence of interfering compounds. Several types of commercial silica gel cartridges have been used and all give satisfactory results. Best results are obtained with 5% water-deactivated cartridges. Controlled moisture silica gel or alumina eliminates the main part of organic matter extracted

from organic-rich sediment but also traps a non-negligible fraction of the organotins [59]. An alternative clean-up procedure relies on saponification of the sample prior to dichloromethane extraction; however the recovery of TBT in these conditions is low [66].

Extraction and preconcentration of TBT from estuarine waters has been achieved using bonded C18 solid-phase adsorbent [62] prior to hydride derivatisation. Simultaneous extraction into dichloromethane and hydridisation by $NaBH_4$ of butyl- and methylbutyltin species demonstrated excellent recoveries of these compounds for natural water samples [6,10]. This method can process large sample volumes (800 to 1000 mL), however, one potential source of error lies in the fact that the concentration/evaporation step is still required. Minimal losses for high boiling- point species are reported but up to 50 % losses for tributyltin have been detected.

Finally, a supercritical fluid extraction procedure has been developed recently for the determination of TBT in sediment and has been used successfully in a certification campaign [67]; this procedure offers good possibilities for the determination of MBT, DBT and phenyltin species.

Derivatisation

The major derivatisation procedures are: (1) derivatisation of organotins by a Grignard reagent; (2) conversion of organotins to their hydrides derivatives; and (3) conversion of alkyltins to their chloride salts.

Derivatisation by a Grignard reagent: Many authors use an analytical scheme which includes reaction with a Grignard reagent in a solvent medium to convert alkyltin ($R_pSnX_{(4-p)}$) into non- polar mixed tetraalkyltin followed by GC separation. This protocol has been applied successfully to various matrices such as waters, sediments and biological tissues.

Derivatisation has to be performed in an aprotic solvent and a drying stage is required prior to the reaction. Peralkylation with a selected R'-group (R' can be methyl [38,41], ethyl [52], butyl [39], pentyl or hexyl) Grignard reagent substitutes an alkyl group for the counterion to convert organotin cations into volatile tetra-alkylated derivatives in the solvent medium. The choice of the size of the alkyl group R' depends both on the volatility of the compounds to be determined and on the selected analytical tool. Grignard reagents with hexyl groups require a high efficiency capillary GC. Methylation or butylation have been abandoned by various authors because mixed methylbutyltin species have been claimed to occur in the environment. In addition, the low boiling point of the methyl derivatives may lead to losses during the concentration step. For these reasons ethylation [52] and pentylation [49,72] have been applied successfully to environmental samples. Hexylalkyltins are also more thermally stable and consequently hexylmagnesium bromide was used to improve the separation between butyltin species [58,73,74). Finally,this derivatisation technique has the advantage of limiting evaporative losses [75].

Hydride generation: The reaction of tin, alkyltin or phenyltin compounds with sodium tetrahydroborate ($NaBH_4$) to produce tin hydride species has long been known [76,77]. This method of derivatisation has been used successfully for methyl- and butyltin compounds [48,60]. The reaction requires a slight acidification of the water samples using acetic acid or nitric acid. Acetic acid (0.05 to 0.1 mol/L) has been shown to give a higher yield of hydrides than hydrochloric or nitric acid [78]. This technique requires purge of oxygen by a flow of inert gas (e.g. He). The $NaBH_4$ is injected directly into the stirred sample [61] or from a modified hydride system [79].

Hydrides may be generated in the presence of organic solvent [10]. A few mL of dichloromethane may be added to a 100–200 mL water sample prior to $NaBH_4$ addition. After reaction and shaking, the extract is evaporated gently. During this step a loss of very volatile organotin hydrides may occur. This is certainly less important for heavy compounds such as TBTH than for methyltin hydrides but may still be significant [80].

Hydride generation has been found to be most suitable for the analysis of large volumes of water [58]; however, water samples rich in suspended matter require an extraction step, otherwise very low recoveries (9–17%) are obtained [31]. Inhibition due to hydrocarbons in water has been shown [10].

For sediment analysis, interferences from metals [48], organics or sulfides have been shown in detail [52,81,82]. The interfering effects occurring in hydride generation have been described extensively in the literature [83]. A study of the determination of butyltins in a very heavily- polluted sediment demonstrated that the inhibition of hydride generation could be lowered by the use of increasing $NaBH_4$ additions [45]. Hydrogen microbubbles produced by the decomposition of $NaBH_4$ are very efficient in purging hydrides from the solution but may also produce foam; consequently, addition of an antifoaming agent may be useful, e.g., for biota analyses and sediments extracted with methanol [84].

Another procedure involving hydride generation is based on liquid-liquid extraction of organotins from the sample but the derivatisation is performed by reaction with borohydride in aqueous medium or in a solvent [55,66,85–87]. Organotin hydrides are concentrated gently by slow evaporation of the solvent and injected into a GC. This procedure has been applied mainly for di- and trialkylated compounds such as butyl and phenyltins. It has been applied to water and sediment samples but most applications reported are developed for analyses of biological tissues. All techniques include an important clean-up step which is accomplished usually by passing compounds extracted in the solvent (preferably hexane to prevent water deactivation of the cartridge) over a silica microcolumn.

On-column hydride generation has been also used which allows the direct injection of a solution of butyltin chloride into the gas chromatograph [52,88]. Derivatisation of the extracts is performed directly on top of the chromatographic column [88] or via a packed reactor placed in the injection part of the GC [55].

Trapping and separation

Cryogenic trapping and gas chromatography (GC): Hydride species may be carried by an inert gas (helium or nitrogen) to a cryogenic trap and desorbed sequentially according to their respective boiling points [89], after removing the column from liquid nitrogen and heating it gradually from about −196 to 200 °C. The column is usually a short U-tube (20–40 cm) filled with chromatographic material but, in some cases, only glass wool is used [43]. Improvements in column design and temperature programme have eliminated use of a water trap [45,79,89,90]. The materials used were either PTFE, silanised glass or borosilicate glass. Hydrides may be separated by GC with a possible preconcentration step (Tenax-GC) [91,93,94].

HPLC separation: Many attempts to set up a HPLC/AAS method for tin speciation have been made. The HPLC modes were: ion exchange, ion pairing, micellar and normal. Normal HPLC performed directly on non-polar extracts in the presence of tropolone has demonstrated its efficiency for the analysis of butyltins in sediment [94]. Gradient elution by a mixture of tropolone in toluene and methanol enables a complete separation of the four butyltin species to be made and a more simple isocratic elution by tropolone in toluene is suitable for separating the di- and tributyltin species. However, a risk of butyltin degradation on reversed phase material has been shown [65].

HPLC with a cyanopropyl-bonded silica column gives satisfactory separation of alkyltins and phenyl species [95,96,97]. Ebdon et al. [98] proposed an interesting procedure, applied to sea water, consisting of a preconcentration step, a separation step of the tin species by HPLC and a final step during which the tin species-Morin complex is formed in an aqueous, micellar medium. Recently, a novel procedure involving HPLC, ID-ICP-MS (isotope dilution ICP-MS) has been used successfully for the determination of DBT and TBT in sediment [99] and mussel [34].

Detection

After gas chromatography (GC): Several types of detectors have been used after GC separation. A well-known technique involves the detection by quartz furnace AAS after hydride generation. The hydrides are carried to a quartz tube heated to 900–1000 °C, by an electric furnace or a classical AA burner, where they are atomised. The atomisation rate is enhanced by addition of hydrogen and oxygen in the quartz furnace. The optimal conditions of flow rate as well as the geometry of the quartz cell vary widely according to the literature, e.g. [48,60,89]. In addition, the positions of oxygen and hydrogen inlets seem

to be of paramount importance as variations by a factor of 20 in sensitivity among different cell designs are not uncommon. Several wavelengths are generally used in determination of tin by AAS, both with hollow cathode lamp and electrodeless discharge lamps (224.6, 235.5, 284.0 and 286.3 nm). The possibility of redistribution of alkyl groups during the analytical steps, either in the reactor or in the GC column, has been mentioned [4].

The electron capture detector (ECD) is another classical technique which is sensitive to both trialkyltin and dialkyltin chlorides [100,101,102], triphenyltin [103] and up to tricyclohexyltin [104]. Several developments have been made to obtain quantitative data from biological material. However, detection limits obtained with the ECD are generally poor and the range of alkyltin determined in one sample is limited. One of the advantages of detection as chloride is the possible direct concentration of trialkylated compounds as their chloride salts 'in the field' using a solid phase adsorbent. In estuarine and marine environments where toxicity problems are more acute, the probability of occurrence of these compounds as chloride salts is high. Their direct extraction by adsorption/preconcentration on C-18 bonded adsorbents with GC separation and ECD detection suppresses many steps in the determination protocol [105]. The combined sample preconcentration may alleviate the storage problems mentioned earlier. Other detectors are being used and amongst them mass spectrometric detection was developed at a very early date [36] but it was not very sensitive. Considerable improvements have been made since, because cryogenic coupling techniques allow trapping and detection of picogram quantities of alkyltins in various matrices [106]. Although tin is difficult to excite thermally in flames, several important developments circumvent this difficulty, and flame photometric detection (FPD) is now the most popular detector for alkyltins [89,107,108,109]. Quantitation is based on the monitoring of the red fluorescence emission of the Sn-H species at 609.5 nm. This kind of detector yields excellent sensitivity [41,110]. Best overall sensitivity is obtained with a filterless FPD but then the detector lacks specificity [111]. To improve the selectivity, an additional scan can be performed in the broad and less sensitive 360–490 nm blue region (SnO band) [109]. Interferences in the detection have been mentioned. The most common interferences reported are sulfur compounds, hydrocarbons and germanium species [111–113].

Some references mentioned the use of a promising detector for the determination of organotin compounds : vapor phase organotin compounds have been found to quench ionisation in a hydrogen-atmosphere flame [114]. Organotin compounds produce negative peaks while hydrocarbon compounds produce a positive response that is 105 times less sensitive than that of the organotin. The sensitivity of this detector is equivalent to that of a classical flame ionization detector (FID) but its tremendous advantage is its selectivity against hydrocarbons [113].

Isotope dilution [99,115] has been used successfully for tin speciation and certainly represents a very promising analytical development. Other recent techniques which have gained importance in the past five years are microwave induced plasma atomic emission spectrometry and mass spectrometry coupled to capillary GC; both techniques have been successfully applied to the certification of butyltins in sediment and mussel reference materials [33,34] and are now considered in the group of the most reliable methods for tin speciation [36].

After HPLC separation: The detector may be flame, quartz furnace and electrothermal AAS. Classical flame AAS is now of very much reduced interest because of its insufficient sensitivity even with a 1-m long tube [116]. Extending atom residence time by a slotted-tube atom trap improved absolute detection limits down to 200 ng which is still too high for many applications [56]. The more sensitive electrothermal AAS has therefore been used frequently [88,117]. However, the design of the interface between the continuous flow of eluent out of the HPLC column and the discontinuous injection of sample into the graphite furnace often hampers a good determination [94]. Difficulties may occur with ion chromatography in which the high salt content of the eluent may lead to serious matrix effects for ETAAS determination and may produce very high background molecular absorption.

Detection has been performed by inductively coupled plasma atomic emission after HPLC [98,118,119]. Methods of nebulising the solution to be analyzed were developed in order to increase the residence time of the analyte in the plasma and therefore to lower the detection limits [120]. The advantages of this technique compared to AAS are the relatively easy coupling between HPLC and ICP and the continuous measurement of the tin concentration.

An improvement has been obtained by coupling HPLC with ICP-MS. In this technique, the detection is made after nebulising the HPLC eluate into an ICP which is itself coupled with a mass detector. On-line monitoring of the HPLC effluent is possible together with a multi-element detection [121]. As said before, isotope dilution ICP-MS has also been coupled successfully to HPLC for the determination of butyltins [99].

High performance thin-layer chromatography (HPTLC) has been used to identify tin species in extracts of wood or environmental samples. This technique, although not very sensitive with colorimetric detection, may be useful prior to quantitation of tin species by more sophisticated techniques [122].

Other techniques: Electrochemistry has been applied to the determination of tin species. Differential pulse anodic stripping voltammetry (DPASV) was adopted for $DBTCl_2$ in natural waters [123,124], while differential pulse detection has been applied to tin species in a liquid chromatographic effluent [125]. The detection limits for the various species remain in the range of 10^{-4} to 10^{-6} mol/L.

Performance of the methods and quality control

A series of tests has demonstrated good agreement between detectors such as QFAAS and FPD [80]. A comparison of methodologies for butyltin determinations was carried out by the National Research Council of Canada [61]. The majority of measurement techniques were based on the selective detection of tin by techniques such as FPD, ICP-AES, ICP-MS, AAS etc. Separation was by gas or liquid chromatography or by selective extraction involving several organic solvents, sometimes in conjunction with acids and tropolone. For GC, butyltins were separated and eluted as hydrides, tetra-alkylated forms or halides after appropriate derivatisation. Ion exchange or ion pairing liquid chromatography was the second most popular means of separation, detection being by ICP-MS or ICP-AES, FAAS or ETAAS. Good agreement was obtained among the different techniques which enabled a certified reference material (CRM) to be produced (PACS-1) [126], see Table 1.

Intercomparisons were organized within the BCR programme (Community Bureau of Reference of the European Commission, Brussels) for improving the quality of tin speciation analyses [37]. This programme involved 15 laboratories from seven European countries. The first round-robin dealt with the analysis of solutions containing pure analytes (TBT and mixtures of MBT, DBT and triphenyltin). No systematic errors could be detected in the final determination techniques tested at this stage. A second exercise was undertaken in 1989 on the determination of TBT in a spiked sediment. The results of this interlaboratory trial did not reveal any systematic errors in the different analytical methods compared, which encouraged the BCR to organize a certification campaign on TBT in a sediment containing a representative level of TBT (i.e. around 100 µg/kg of TBT) [127].

Another exercise on TBT in harbor sediment (RM 424) was also organized. The very low TBT (around 20 µg kg^{-1}) levels and the presence of high organic matter contents created tremendous difficulties for analytical techniques using derivatisation [128]. The original results showed a very large scatter of data, ranging from less than 10 µg/kg of TBT to more than 150 µg/kg. Detailed discussions were necessary to explain the sources of discrepancies. Some laboratories reported 'not detected' values: three laboratories using hydride generation/GC/AAS reported 'not detected' values which corresponded to less than 15 µg/kg, 20 µg/kg and 146 µg/kg. Other laboratories using selective extraction/ETAAS and GC/MS reported values less than 49 µg/kg and 60 µg/kg. One laboratory using HG/GC/AAS submitted two results which were below their limit of determination: 15.6 µg/kg and 22.4 µg/kg. Later on, this laboratory could improve the sensitivity of its method and submitted five other replicates (mean of (12.0 ± 3.9) µg/kg) which confirmed the values found (values were above the limits of determination at this stage).

The laboratories reported their results of extraction recovery which were generally acceptable. A variety of extraction and clean-up procedures has been used in the exercise which was not able to detect any substantial systematic error due to, for example, incomplete extraction of TBT. It was suspected that the main problems were not due to extraction but to possible interferences in the derivatisation or detection steps. Laboratories using gas chromatographic separation and detection either by FPD or MS tended to agree, and this would confirm that these methods would be more suited for the determination of

TBT in this particular material. It was emphasized that such a complicated material should be reserved for the evaluation of techniques such as GC/FPD and GC/MS and recommended to very experienced laboratories only. Because of the potential risks of interferences, calibration by standard additions is a prerequisite.

Another (coastal) sediment reference (CRM 462) was certified for its TBT and DBT contents (Table 1). As mentioned above, instability of these compounds upon long term storage justified the material to be withdrawn from the market. The material has been re-processed and stored at −20 °C and its stability has been checked; a re-certification has been successfully performed for both TBT and DBT [33]. Another freshwater reference material (CRM 646) is being prepared by the BCR for the tentative certification of butyl- and phenyl-tin species (mono-, di- and tri-substituted compounds).

Biological materials have been certified for butyltins by the National Institute for Environmental Studies (NIES, Japan) and the BCR (see Table 1).

Table 1. Certified reference materials (CRMs) for the quality control of butyltin determinations in environmental and biological matrices

Matrices and RM reference	Butyltin compounds	Certified values	Certifying body
Harbor sediment PACS-1	TBT	1.27 ± 0.22 (g/kg)	NRCC [126]
	DBT	1.16 ± 0.18 (g/kg)	
	MBT	0.28 ± 0.17 (g/kg)	
Coastal sediment CRM 462 *	TBT	70 ± 14 (µg/kg)	BCR [127]
	DBT	128 ± 16 (µg/kg)	
Coastal sediment CRM 462R †	TBT	54 ± 15 (µg/kg)	BCR [33]
	DBT	68 ± 12 (µg/kg)	
Harbor sediment RM 424 ‡	TBT	20 ± 5 (µg/kg)	BCR [128]
Fish tissue NIES 11	TBT	1.3 ± 0.1 (g/kg)	NIES [129]
Mussel tissue CRM 477	TBT	2.20 ± 0.19 (mg/kg)	BCR [34]
	DBT	1.54 ± 0.12 (mg/kg)	
	MBT	1.50 ± 0.28 (mg/kg)	

* The CRM 462 has been withdrawn from the market in 1996 owing to instability problems

† The CRM 462R has been prepared by re-processing the CRM 462, storing it at −20 °C and re-certifying TBT and DBT.

‡ This material was not certified owing to the complexity of the matrix. This RM should be reserved for experienced laboratories and not used as a CRM for routine analysis.

NRCC: National Research Council Canada

BCR: Community Bureau of Reference (now Standards, Measurements and Testing Programme, European Commission)

NIES: National Institute for Environmental Studies (Japan)

Calibration

As underlined by many of these projects, calibration is one of the critical aspects of tin speciation analysis. Standard additions are used commonly to take into account the occurrence of matrix effects and a large variety of internal standards have been used; these are mostly trisubstituted compounds (mainly trialkyltin species are monitored) and the behaviour of alkyltins depends on the number of organic groups linked to tin. The most common internal standards are triethyltin, tripropyltin or dimethylbutyltin.

Several precautions should be taken for the calibrations. Usually, an internal standard is added at the beginning of the Grignard derivatisation to control the efficiency. One should use more than one internal standard (and standards with large differences in boiling point) if several alkyltin species are to be determined. It is emphasized that there is a strong lack of pure calibrants for verifying the yield of

derivatisation reactions (e.g. pentylated butyltin compounds) and that the production of such compounds would allow further improvements of derivatisation-based methods. Recent developments have enabled to systematically check the derivatisation yields in the frame of the certification of CRM 477 (mussel tissue); a series of derivatised organotin compounds have indeed been prepared and distributed to the participating laboratories for the purpose of verifying the reliability of the derivatisation procedures applied [34]. This evaluation represents a clear progress but efforts should be pursued for producing larger batches of derivatised calibrants for the purpose of routine quality control.

CONCLUSIONS

The two most popular methods for the determination of organotin species are Grignard derivatisation/FPD and hydride generation/AAS, which both involve a derivatisation step; GC coupled to MIP-AES or MS is also gaining popularity. As stressed in this report, the performance of techniques involving derivatisation procedures cannot be monitored fully in the absence of suitable calibrants to verify their yield. At this stage, the HG/GC/AAS is used frequently for the analysis of water but should be looked at critically for the analysis of solid matrices. Similarly, extraction and separation procedures should be investigated further; for separation, the transfer of technology from the well-validated separation procedures used in organic analysis should allow a better understanding of the procedures as applied to speciation and lead to easier and more rugged methods. Techniques existing for butyltin determinations are certainly very reliable but further investigations are necessary to validate them fully for use as routine analysis; in this view, interlaboratory studies on a wide variety of environmental and biological matrices, involving different categories of techniques, are still necessary as well as an increased production of relevant CRM's. It appears more important at this stage to identify clearly the respective advantages and limitations of the techniques rather that their optimum performances; this would allow us to rationalize our views with respect to the determination of butyltins in environmental and biological matrices.

Even when the techniques have been fully brought under control, huge efforts will still be necessary to evaluate the risks of errors at the sample collection and storage steps. The comparison of different techniques is again a means to optimize procedures which could possibly be standardized, e.g. for routine analyses to be performed in monitoring campaigns.

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