Talanta 82 (2010) 9–24

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Review

Occurrence and chemical speciation analysis of organotin compounds in the environment: A review

Regina de Carvalho Oliveira, Ricardo Erthal Santelli*

Department of Geochemistry, Universidade Federal Fluminense, Outeiro de São João Batista s/n, – Centro – Niterói – RJ, CEP 24020-141, Brazil

ARTICLE INFO

Article history:
Received 13 January 2010
Received in revised form 18 April 2010
Accepted 19 April 2010
Available online 24 April 2010

Keywords:
Organotin
Chemical speciation
Environmental contamination

ABSTRACT

Environmental concerns regarding organotin compounds have increased remarkably in the past 20 years, due in large part to the use of these compounds as active components in antifouling paints [mainly tributyltin (TBT)] and pesticide formulations [mainly triphenyltin (TPhT)]. Their direct introduction into the environment, their bio-accumulation and the high toxicity of these compounds towards "non-target" organisms (for example: oysters and mussels) causes environmental and economic damage around the world. As a consequence, the presence and absence of organotin compounds is currently monitored in a range of environmental matrices (e.g., water, sediment and shellfish) to examine the utility of controls meant to regulate the level of contamination as required in some EC Directives and the Water Framework Directive 2000/60/EC. To evaluate the environmental distribution and fate of these compounds and to determine the effectives of legal provisions adopted by a number of countries, a variety of analytical methods have been developed for organotin determination in the environment. Most of these methods include different steps such as extraction, derivatisation and clean up. The aim of the present review is to evaluate the environmental distribution, fate and chemical speciation of organotin compounds in the environment.

Contents

1. Introduction

Over the years, the environment has received a large load of toxic compounds from both natural sources and human activities. Depending on the intensity, duration of impact, the resilience of the system and whether the presence of these substances in small

* Corresponding author at: Department of Analytical Chemistry, Universidade Federal do Rio de Janeiro, Brazil. Tel.: +55 21 2629 2192.
E-mail address: resantelli@globo.com (R.E. Santelli).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.04.046

quantities is considered critical, the consequences could be catastrophic. Organotins are one type of pollutant (e.g., Butyltin-BT and Phenyltin-PhT) that is used in applications including antifouling paints, PVC stabilisers, timber treatment, and others.

There is evidence that a direct relationship exists between the broadly different transport, bioavailability, toxicity and physicochemical properties of organotin compounds as a function of chemical form. As a result, the determination of species across which a chemical element is distributed is essential because it helps define their potential for action [1,2].

Studies on the occurrence and effects of organometallic compounds (mainly Sn linked to several alkyl groups) have been developed in several countries such as Spain, France, England and Japan, and have shown adverse effects like mutations and poisoning of microbiota. As a result, more and more species are approaching extinction [2].

Qualitative and quantitative monitoring of organometallic compounds in ecosystems is one of the most important instruments for environmental management. This monitoring is, basically, the identification and quantification of different species, forms or geochemical phases in which the tin occurs in a given matrix. Together, these species comprise the total concentration of this element in the sample. Therefore, the development of methods able to speciate organotin compounds in environmental matrices is an area of increasingly active research and concern because it provides a systematic and integrated measure of toxicological and environmental risk assessment [3]. This article aims to gather information about the chemistry, detection and speciation of organotin compounds in the biosphere.

2. Chemistry of organotin compounds

Organotin compounds (OTs) are characterised by the presence of one or more covalent bonds between atoms of carbon and tin (Sn-C) that have the general formula R_nSnX_{4-n}, where R is an alkyl or aryl group, X is an anionic species (for example, chloride, oxide, hydroxide or some other functional group), and with $n = 1,\ldots,4$ [4,5,6]. In general, organotin compounds with Sn (IV) occur predominantly on the Sn(II) forms [7]. The hydrophobicity depends on the degree of alkylation/arylation at the central tin atom (number of groups and length of alkyl chain).

The first organotin compound produced in a laboratory was diethyltin diiodide, obtained by Frankland in 1849 from his work with etilzinc compounds. However, for about 100 years, the OTs remained as a laboratory curiosity without any known practical application. More than a century after the original discovery, research intensified with the development of industrial applications for organotin in the United States in the late 1940s and in Europe in the 1950s. In large part, this increased interest came about when the plastics industry began its expansion and the importance of polyvinyl chloride (PVC) became evident. Since then, organotin compounds have been used as additives for thermal and light stabilisation in the plastic industry and as catalysts for polyurethane foams and silicones [8]. Other applications of organotin compounds have been developed since 1960, especially use in antifouling paints on ships and off-shore installations [8–10]. Other less significant applications include use in disinfectants and algicide treatments on construction materials. Some organotin compounds are also used as pesticides [11].

Use of organotins in some of these applications is currently being rethought because, although these compounds achieve their intended goals quite effectively, they have also shown considerable toxicity toward living organisms, high environmental persistence and the ability to transfer along the trophic chains [12,13]. Several studies have shown that tributyltin (TBT) and triphenyltin (TPhT) can cause changes in the endocrine system in marine organisms at concentrations as low as $1\,ng\,L^{-1}$ [14]. These changes include is the development of male sexual characteristics in female gastropods, known as imposex, which can lead to sterilisation and death of the affected organisms [15]. Chiavarini et al. [16] found high correlation between TBT concentrations and the appearance of male sexual organs in female gastropods when assessing the occurrence of imposex in gastropods on the coast of Sicily, Italy. Sousa et al. [17] also noted the occurrence of imposex in gastropods (*Nassarius reticulatus*) along the Portuguese coast. Other responses by marine organisms when exposed to organotin compounds usually involve reduced growth rates and photosynthesis, as well as cell death depending on the type and quantity of the organotin compound. For example, when examining the response of branchlets of adult corals (*A. formosa)* exposed to sediments with high concentrations of organotin compounds (tributyltin—TBT: $160\,mg\,kg^{-1}$), Smith et al. [18] observed that the organisms underwent significant mortality (38%).

Organotin compounds can also enter the food chain by accumulation in different marine species and plants destined for human consumption, such as oysters, farmed salmon, mussels, clams, snails and seaweed. This is especially true in poorly flushed water masses where the exchange rate with the open sea and tidal mixing are limited, as well as areas with high boating activity. While assessing the levels of organotin in sea foods (fishes, crustaceans, and molluscs) collected in the Portuguese markets, Santos et al. [19] found several organotin compounds (tributyltin—TBT, dibutyltin—DBT, monobutyltin—MBT, triphenyltin—TPhT). TBT was the predominant species in all analysed samples. Mussels showed the highest levels of OTs, with an average level of $170\,ng\,g^{-1}$. The other groups contained smaller quantities, with average values of 12.5, 11.2 and $5.5\,ng\,g^{-1}$ for cephalopods, fish and crustaceans, respectively. These findings warn of the potential environmental risk related to the biotransfer of these compounds in the food chain and provide a clear demonstration of how they can reach humans.

The biological activity of organotin compounds is mainly determined by the number and nature of organic groups linked to the central tin atom; the activity decreases in the following order: (tri) R_3SnX > (di) R_2SnX_2 > (mono) $RSnX_3$ [20,21,22,23]. In the trisubstituted group of organotin compounds (R_3SnX), trimethyltin species show a higher toxicity against fungi and insects, triethyltin compounds are the most toxic for mammals, and tripropyl and tributyltin species have a greater toxicity for fungi, molluscs, fish, bacteria and plants. In the case of butyltin compounds, the difference between their effect on insects, fungi, fish, molluscs, and mammals explains why they have been used so extensively as fungicides, wood preservatives and in antifouling paints. The biological activity of triorganotin compounds is thought to be due to their ability to bind to certain proteins. However, the sites where this binding occurs are not well known. In general, the effects of triorganotin compounds both in humans and in animals have been found to be reversible [24,25]. Tetraalkyltin compounds exhibit low toxicity to mammals. Ethyltins are the most toxic. Longer alkyl chains reduce toxicity. The danger regarding these compounds is their volatility and absence of odour, which makes them potentially hazardous [24]. Diorganotin compounds appear to have a different mode of action than triorganotins. Some of the compounds with a short organic chain in the R group of the formulation (R_2SnX_2) can inhibit the oxidation of α-ceto acids due to their combination with coenzymes with vicinal dithiol groups. In this case, the nature of the X group can affect the toxicity. As an example, dimethyltin dichloride is moderately toxic, while dimethyltin diisooctylthioglycolate [$(CH_3)_2Sn(SCH_2CO_2\text{-i-Oct})_2$] is relatively non-toxic since it has two Sn-S bonds in the molecule [24]. Both mono- and tetraorganotins have some mammalian biological activity. There is a potential

Table 1
Main features and applications of organotin compounds [20–25].

Organotin compounds	Features and Applications
R_4Sn R: butyl, octyl, phenyl .. R: butyl .. R: phenyl ..	Very stable, similar to paraffins, has no biocidal activity, relatively non-toxic. Materials from Co- catalysts Ziegler-Natta Stabilizers oil
R_3SnX R: butyl .. R: phenyl ..	Some compounds are fungicides and powerful bactericides, depending on the nature of group R. Industrial biocides (anti paintings, wood preservatives, disinfectants, acaricide) Agricultural fungicides, antifouling paints.
R_2SnX_2 R: methyl, butyl, CH_2CH_2COOR'	No antifungal activity, low toxic activity, except for derivatives of diphenyl. Stabilizers in PVC, polyurethane training. Can be used as water-proofing agents for cellulosic materials such as cotton textiles, paper and wood, and as a flame retardant for fabrics of wool.
$RSnX_3$ R: metyl, butyl, octyl, CH_2CH_2COOR'	Without biocidal activity, very low toxicity to mammals. Stabilizers in PVC

danger of toxicity with tetraorganotins due to their potential for degradation into more toxic species, especially trisubstituted ones. The tin metal and most inorganic tin compounds are relatively non-toxic, and their main use is in coatings for food cans. At physiological pH, the metal does not react and its oxides are insoluble [24].

Table 1 summarises the main characteristics and applications of organotin compounds.

In the face of these problems, the first regulatory actions and legislative management of tributyltin were adopted in France in 1982. The UK followed suit in 1985 [26]. These actions were based on an assessment of the impacts of TBT on commercially grown oysters (*Crassostrea gigas*), where there was a significant decrease in the abundance of oysters in the Bay of Arcachon on the Atlantic coast of France in the late 1970s. Additionally, 80–100% of shells were malformed. The British observed similar impacts on the populations of oysters living in areas of intense boating activity, and in 1985 introduced regulations to prevent the retail sale of TBT paints that released the biocide at higher rates. The regulations prohibited the sale of paints containing TBT to no more than 7.5% tin copolymers in total or 2.5% of total tin and tin free, or with a release rate greater than 4 ng cm^{-2} day^{-1}. The British legislation also limited the organotin concentration in water to 20 ng L^{-1}, with the goal of protecting the country's marine resources [27,28]. Several European countries also controlled the use of TBT-based antifouling paints (WFD, EC, 2000 Directive/60/EC) [29], and IMO (International Maritime Organization) has already banned application of organotin based anti-fouling paints on ship hulls since September 2008 by AFS Convention (International Convention on the Control of Harmful Anti-fouling Systems on Ships) [30,31].

However, there are still doubts regarding the effectiveness of available alternatives to TBT and the enormous costs to industry due to it ban because it is estimated that the use of anti-fouling paints based on TBT reduces spending in the marine industries by up to six billion dollars per year [30,32]. Furthermore, replacement of TBT compounds by other paints is more expensive [33,34]. Therefore, due to a lack of consensus, few countries regulate waste generated from the cleaning of hulls of ships. Thus, 0.8 billion litres of contaminated waste water, 2.3 million tonnes of waste paint and 1.8 million cans of paint are waiting for a solution [35]. Brazil has already adopted standards regulating the maximum organotin content of water [36].

3. Occurrence and distribution of organotin compounds in the environment

The biogeochemical behaviour of organotin compounds are a function of the prevailing species of Sn and depend mainly on their intrinsic properties, chemical structure and functional aspects of the molecule. Other factors such as the concentration of organotin compounds, physicochemical environmental factors and biological activity have similar importance.

3.1. Degradation of organotin compounds by biotic and abiotic factors

There is ample evidence that organotin species found in environmental samples are related by environmental degradation pathways. A large number of studies have been conducted on degradation of organotins in soil and water, demonstrating that the process usually involves the sequential removal of alkyl or aryl groups (stepwise dealkylation or dearylation) from the tin atom to form inorganic tin [37]. This reduces toxicity in the sequence [38,39]:

$$R_4Sn \rightarrow R_3Sn^+ \rightarrow R_2Sn^{2+} \rightarrow RSn^{3+} \rightarrow Sn(IV).$$

Rates of degradation for organotin compounds (OTs) may be influenced by several biotic and abiotic factors (such as the nature and density of microbial populations, photolysis and chemical degradation). Ultraviolet breakdown is one of the most significant modes of degradation in the environment [38–40]. Certain fungi and bacteria are able to break down organotins (particularly tributyltin and triphenyltin compounds) and biomethylate inorganic tin [40].

Bioalkylation or redistribution of inorganic Sn compounds to organic forms is also possible and has been observed in the environment and in stored samples. There is evidence for environmental methylation of inorganic tin (IV) and tin (II) in sediments [41–45].

3.2. Organotins in water, sediment and biota

Organtotin compounds are released through several routes into the environment. The major input of triorganotin compounds into aquatic systems derives from their use in anti-fouling paints. TBT is used mostly in so-called self-polishing copolymers that release TBT continuously. Harbor areas are specially affected by TBT contamination. In harbor sediments, flakes of anti-fouling paints from the removal of old coatings may be present and may serve as reservoirs that cause locally high concentrations of TBT. For other compounds such as triphenyltin, the imput via their use as pesticides in agriculture is more important. Waters may be contaminated with organotin compouds by effluents from industrial plants. Further imputs to the environment result from the large-scale use of polyvnyl chloride (PVC), which contains mono- and diorganotin compounds as stabilizers. Leachate from landfills where organotin-containing wastes are dumped may contain organotin residues, as welll as municipal wastewater and sewage sludge [9].

Environmental studies conducted in different localities have shown that tributyltin (TBT) is present in surface water, the water

column and sediment [46]. The distribution of its species (e.g., neutral TBT-OH and cationic TBT^+) is influenced by factors such as the species and population density of aquatic organisms, dissolved and suspended organic material, pH, salinity, temperature, and solubility in water [47,48]. The cationic form (TBT^+) is stable at pH values below the acid constant (pK_a) of the organotin compound. Other compounds such as DBT, MBT, TPhT, DPhT and MPhT are also found in the aquatic environment [49,50].

In the aquatic environment, recent studies report that according to the species present (ionic compounds: TBT_n^+, DBT_n^{+2}, MBT_n^{+3}; and neutral compounds: TBTOH, DBTOH, MBTOH, $TBTNO_3$, TBTCl, etc.), may be retained by cation exchange and Coulomb forces. At pH between 4 and 7, DBT adsorbs to sediment more effectively than TBT. At pH < 7, the cationic organotin compounds are the dominant species in aqueous solution, and there is electrostatic attraction between the positively charged organotin molecule and the negatively charged surface of clay minerals. At pH 8, the affinity for these compounds in the sediment is inverted to TBT > DBT, corresponding to the hydrophobicity of the compounds [51,52].

Several authors have measured concentrations of organotin compounds in sediment. Arambarri et al. [53] detected MBT in the range from 0.86 to 2.87 mg kg^{-1}; BDT 0.15 to 0.71 mg kg^{-1} and TBT from 0.05 to 5.48 mg kg^{-1} in the sediments from five rivers in Spain. In coastal and estuarine areas several works can be found in the literature. Santos and co-workers studied Paranagua estuary in south Brazil [54], Carvalho et al. showed the distribution of TBT, DBT and MBT in surficial sediments coleted in Portugal coast [55], Choi et al. reported levels of TBT and DBT in harbour sediments in Korea in a period of five years [56], Garg et al. analysed surface sediments for TBT, DBT and MBT in six areas located in the Gulf or Cadiz, Spain [57] and Pletsch et al. [58] investigated TBT, DBT and MBT concentrations in coastal sediments from Todos os Santos Bay, Brazil.

The half-life of organotin compounds varies in the aquatic environment. For example, the time half-life of TBT in sea water is usually 6 h because TBT can degrade to form less substituted dibutyltin and monobutyltin, finally degrading to Sn (IV). In addition, the lipophilic character of the molecule plays a role in its environmental persistence [51,59]. However, the half-life of TBT in sediment and soil is several years [60]. In anoxic sediments, decomposition seems to occur slowly, with an estimated half-life of up to 8 years. Thus, TBT can accumulate in these sediments, leading to a persistent ecotoxicological risk [60].

Marine sediments, therefore, present problems for the long term because they remain a source of TBT for the water column and biota even after the source of contamination has been removed. This danger is particularly true in the context of ingestion of particles by bivalves [52]. The ability of marine sediments to accumulate these compounds varies geographically and geologically, according to the physicochemical characteristics of the sediment (e.g., particle size and organic carbon content) [14,55].

Marine organisms are good accumulators of persistent toxic substances in coastal waters and can be used as valuable biomonitors because they reflect the level of aquatic pollution. For example, mussels (filtrating organisms) can accumulate concentrations of tributyltin (TBT) above 5 μg g^{-1}. Fish and shellfish accumulate less because they possess mechanisms for enzymatic degradation of TBT. Nemanič et al. [61] observed organotin compounds in all samples analysed when assessing the concentration of TBT, DBT and MBT in mussels collected from 2000 to 2006 in the Northern Adriatic Sea. The concentrations ranged from 36 to 6434; 15 to 2660 and <11 to 1335 ng Sn g^{-1} for TBT, DBT and MBT, respectively. The level of BTs in the organisms showed temporal variation, and depended on the sampling site, salinity, concentration of metals in the water, the nutritional state of the individual, and its reproductive cycle [62].

Programs for monitoring organotin pollution, such as the International Mussel Watch, have been implemented worldwide. Many of these programs use bivalves and rock shells as bioindicators to monitor organotin pollution in the marine environment because of their geographic distribution, sessile lifestyle, resistance to stress, and ease of sampling. Organotin accumulation in organisms involves several processes, including uptake, distribution, metabolism and elimination, as well as multiple environmental factors [63]. Tang and Wang [64] studied the bioaccumulation of tributyltin and triphenyltin in oysters and rock shells; they found a negative correlation between the ratio of tributyltin/total butyltin and tributyltin content. These results suggested that the metabolic rate of tributyltin is burden-dependent in these organisms and that bioaccumulation factors are reduced by a high tributyltin burden. This in turn indicated that persistent accumulation of triphenyltin can cause food chain magnification.

Several others recent papers can be found in the literature dealing with bioaccumulation of organotin compounds in biota such as the studies in coastal waters from northern Spain conducted by Rodrigues et al. [65] and by Zanon et al. [66] in Venice lagoon.

3.3. Organotins in soil

The average concentration of tin in the earth's crust is 2.2 mg kg^{-1}. In mafic rocks, the concentration is 1.5 mg kg^{-1}, while granitic rocks have a concentration of 3.5 mg kg^{-1}. Cassiterite (SnO_2) is the main ore of Sn, but it can be found in other minerals such as stannite (Cu_2SnFeS_4) and montesita ($PbSn_4S_5$) [67].

Its origin in soils can be classified as pedogenic (tin released from rocks by weathering processes and cycles through the various compartments by biotic and abiotic processes, which depend on the type of rock on which the land is developed) or anthropogenic (tin added by anthropogenic sources such as sewage sludge, pesticides, insecticides, biocides, timber treatment, industrial waste and mining). The primary forms are Sn(II) and Sn(IV) [68–70].

Total content of tin in most uncontaminated soils is generally about 1.1 mg kg^{-1} and some authors have reported concentrations as high as 800 mg kg^{-1} at many polluted sites [69] The different forms organotin have to be found in soils. The presence of butyl and phenyltins up to 20–100 μg (Sn) kg^{-1} has been mentioned [70].

In a soil environment, Sn mobility can be affected by its sorption onto the soil solid phase and rate of degradation of organotin compounds in soil depend on its physical and chemical properties, such as polarity and chemical composition. Some compounds such as tributyltin (TBT) may be more stable than others such as triphenyltin (TPhT) when subjected to the same conditions. A study to assess the kinetics of degradation of butyl- and phenyltin in sandy soil collected in INRA (Pierroton Experimental Unit, near Bordeaux, France) noted that the order of persistence in the soil was as follows: TPhT < DPhT < TBT < MPhT < DBT < MBT. The authors related this to the stability of persistent organotin compounds, which was inversely proportional to the degree of substitution and the nature of the organic group present in the OTs, ranging from 24 (TPhT) to 220 (MBT) days. Monosubstituted compounds were the most persistent [71,72].

Soil characteristics such as pH, organic matter content, mineralogical composition, redox potential and the presence of microorganisms also have a huge influence on the destination of organotin compounds in soil. Sterckeman et al. [73] reported that Sn tend towards to associate with the <2 mm soil fraction and had affinities with soil organic matter, even though soil constituents which are relevant to Sn sorption are still unclear. Nakamaru and Uchida [74] studing the sorption behavior of tin in Japanese agricultural soils observed the relationships between Kd–Sn values and soil properties (constituents such as metal-(hydr)oxides or humus complexes). The authors also found high Kd values

indicating that Sn mobility was very low in the soils. Significant correlations were observed for Kd-Sn with active-Al contents. For paddy soils, active-Fe contents correlated with Kd–Sn. Active-Al/Fe contents indicate the amount of Al/Fe- (hydr)oxides such as non-crystalline or short-range-ordered Al/Fe-minerals or Al/Fe-humus complexes. Additionally, the authors observed that the low pH condition enhanced the Sn sorption in soils. Thus, it is possible that the low pH condition decreased the solubility of Sn due to coprecipitation of Sn (hydr)oxides onto soil constituents.

Although it is known that many factors influence the degradation and transport of organotin compounds in soils, only few results are reported concerning organotins in soils. Once incorporated into soil, organotin compounds may undergo a series of degradation processes (for abiotic and biotic factors) or be transported to other locations, causing a major environmental concern.

3.4. Relationship among organotins and organic matter

Organic matter is an important constituent of the environmental compartments since it has chemical groups that are considered as Lewis bases (e.g. carboxyl and phenol groups) which can form chemical bonds with metals and also have high surface area. Recent studies have shown that organic matter could alter the metal bioavailability and its phytorremediation efficiencies. In spite of that, scarce data has been reported in the literature on the association of organotin compounds with natural organic matter, mainly to the humic substances [75]. Giacalone et al. [76] studied the association of trimethyltin (TMT) cation with fulvic and alginic acids (FA and AA, respectively), which are important components of living (AA is one of the main components of brown algae) and nonliving natural organic matter in aquatic ecosystems. It is well known that fulvic acids represent the most soluble fraction of humic substances and are very rich in carboxylic groups. These binding sites allow fulvic acid to interact with metal ions, playing a key role in metal removal and/or transport in soils and aquatic ecosystems. Results show the following trend of stability for the species TMT(L) in the systems investigated: TMT–fulvate ≈ TMT–polyacrylate > TMT–alginate. This behaviour can be easily explained by remembering that fulvic acids contain more carboxylic groups than alginic acid. As a consequence, the stability follows the trend FA > AA and, in turn, alginate is not able to bind a second carboxylate group. Moreover, at pH > 7.5, where TMT hydrolysis species formation is quite high, alginate can not bind TMT in the hydrolysed form to give TMT(AA)(OH) species. These differences in complex species formation greatly influence the quantitative sequestration capacity of alginic and fulvic ligands towards triorganotin cations.

Pinochet et al. presented a very good study about the occurrence of TBT, DBT and MBT in sediments and its relationship with the organic matter content [77]. The mobility, bioavailability and degradation of TBT in coastal marine ecosystems are strongly influenced by organic matter. Adsorption mechanism of TBT onto suspended particular matter take place in its removal processes from water [77]. It depends on the complexation of TBT cation by carboxylic and phenolic ligands present in the humic substances [78,79]. Pinochet group also demonstrated that sedimentary matter has a significant influence on the distribution of these three compounds in sediments [77].

4. Chemical speciation analysis

A variety of analytical techniques have been developed for the chemical speciation of organotin compounds. However, several challenges still remain for the analytical determination of these compounds in different matrices. Among these challenges are the improvement of detection limits; the simultaneous determination of several organotin compounds using the same analytical procedure; and the selectivity of extraction procedures to avoid interferences from the matrix, degradation, and/or processing of organotin compounds [80,81].

As shown in Fig. 1, several critical steps are involved in the analytical procedure used for the chemical speciation of organotin compounds in sediment, water, soil, or biota. These steps include: sampling, sample storage, extraction of organotin compounds (transfer of the analytes of interest from a complex matrix to a simpler solution), preconcentration, “clean-up” (removal of impurities co-extracted together with the compound(s) of interest that may interfere with the quality of results), derivatisation (transformation of the analytes into a measurable species such as a more volatile compound), use of an appropriate analytical technique for the identification and quantification and interpretation of the results. All these aspects will be discussed step by step below.

4.1. Sampling

Sampling is the first step of a chemical analysis. The goal is to isolate a small quantity of sample that is representative of the whole sample. For the chemical speciation of tin compounds, extreme caution is necessary in this step since the environmental concentrations of organotin compounds are generally very low (on the order of ng L^{-1} in water samples and ng g^{-1} in sediment and biological samples), and there is great spatial and temporal variability of these concentrations. Therefore, the choice of sample locations and sampling period should be taken into account in both biotic and abiotic samples [82,83].

Seasonal variations in the concentrations of organotin compounds between hot and cold seasons often occur due to the increase of anthropogenic sources during the summer (for example, tourism and use of boats increases during spring and summer) and degradation of organotin compounds [84–87]. When studying surface sea waters from the Dona Paula Bay (west coast of India) collected at weekly intervals during March 2007 to April 2008, Meena et al. [88] noted the occurrence of butyltin-BT compounds [such as tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT)]. In the study, the authors found that the concentrations of DBT and MBT were higher from October to March of 2008, while the concentration of TBT decreased in the same period. This difference between the concentrations of organotin compounds (BT, TBT, DBT and MBT) were attributed to recreation activities that were reduced due to expansion of the pier. This reduced the input of TBT compounds to the water, and allowed degradation of TBT to its by-products DBT and MBT.

For sediments, only undisturbed, surficial layers must be sampled [89]. Higher concentrations of organotin compounds can be found in the water-sediment interface. The primary product of degradation of TBT in sediments appears to be DBT [87,89] which rapidly enters the water column due to its hydrophilicity. Resuspension of sediments can lead to resolubilisation of sorbed organotin compounds. Sediment collected from locations 10 m apart may show significant differences in organotin concentrations in locations with many maritime activities (shipyards and wharves near small and medium sized ships) [90].

Special care is also required for biotic and soil samples. When studying temporal fluctuations of tributyltin in the bivalve (*Venerupis decussata*) during spring, summer and winter in southwest Spain, Gómez-Ariza et al. [91] found that concentrations of TBT generally increased rapidly between spring and summer and returned to a minimum in winter. This may have been related to the high bioavailability of TBT for *Venerupis decussata* during spring and summer. Tang and Wang [64] found that the bioaccumulation of tributyltin and triphenyltin in oysters and rock shells was less

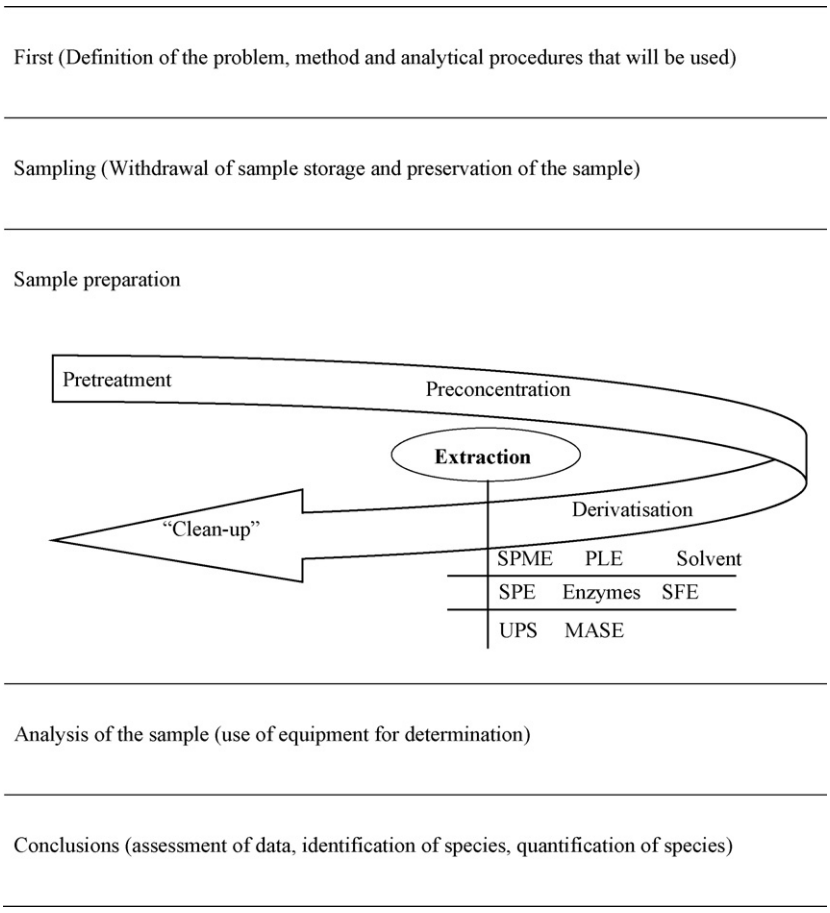

Fig. 1. Stages of a general analytical procedure used in the analysis of chemical speciation of organotin compounds. SPE: Solid Phase Extraction; SPME: Solid Phase Microextraction; UPS: Ultrasound Probe Sonication; PLE: Pressurized Liquid Extraction; MASE: Microwave Assisted Solvent Extraction; SPE: Supercritical Fluid Extraction.

efficient during the winter. For soil, the organotin content may vary with the depth and may be related to mobility of these compounds, especially for di- and tri-substituted organotin compounds [92].

Another aspect to be considered after sampling is the manner in which samples are stored, especially for biological samples and sediments because of the risk of physical and chemical changes that may affect the concentration of these compounds [92–95]. It was observed that TBT may remain intact for four months in samples of sea water filtered and acidified to pH 2 and stored in the dark at +4 and +20 °C, but DBT and MBT are stable only at +4 °C. No significant variation in concentrations of TBT and DBT was observed in samples of sediments stored at +4 and +20 °C, but MBT degraded significantly [92]. The storage of samples at lower temperatures (−20 °C) and in the dark ensures the long-term stability of organotin compounds [83] and maintains the balance between the chemical forms of tin. Therefore, the samples should be analysed as soon as possible [86].

4.2. Sample preparation for analysis

Sample preparation prior to analysis is one of the most critical steps of any analytical procedures and is often known as the "Achilles heel" of a chemical analysis. Initially, the sample must undergo a series of physical and chemical processes by such that the elements or compounds can be identified and/or adequately quantified. Because this stage involves direct sample handling (e.g., crushing, extraction, filtration, dilution, concentration, etc.), contamination can easily occur. Therefore, care should be taken to avoid loss or alteration of analytes via thermal processes during handling. Common approaches to assess recoveries include analysis of certified reference materials, isotope dilution, use of several spikes and use of "surrogates" (patterns used to correct for recovery losses during the mishandling of the sample, inefficiency of the extraction, incomplete conversion during the derivitisation, losses through volatilisation, etc.) to help in obtaining more accurate results [80]. Spiking is the most commonly applied, especially in the case of compounds for which certified reference materials are not available. The steps of a spiking experiment include the addition of known amounts of analytes in a proper solvent, an equilibration time to allow incorporation of the spike into the matrix and, finally, the removal of the solvent. Subsequently, the spiked material is analysed. The main risk is that the behaviour of the added analytes may be not the same as that of the native ones. Consequently the recovery value obtained in this way may be an overestimation. Spiking is generally carried out in each portion of sample to be analysed, and occasionally an aliquot of a previously spiked sample is stored and analysed. In the case of biological materials, spiking is usually performed on wet samples in their original form or after rewetting them. Dry biological material is seldom spiked. In contrast, spiking of sediment is usually performed on dried samples. To stimulate natural adsorption and to avoid the spiked compounds being adsorbed only on the surface of the sample, the original form of the matrix should be restored [72,96].

4.2.1. Extraction of organotin compounds

Organotin compounds are associated with a variety of counterions (carbonates, chlorides, sulphates, sulphides, hydroxides and biopolymers) in the environment, and they can interact with their matrices (biotic or abiotic) in different ways (ion–dipole, dipole–dipole, dipole–dipole induced, Van der Waals forces, and

hydrogen bridges). The analytical procedures for the chemical speciation of organotin compounds generally attempts to preserve only the organic component during extraction, paying little attention to the counterion and other ligands. There are several methods used for extraction of organotin compounds in different matrices [80,90]. The choice of the solvent to be used is the first step of extraction. Thus, the choice of suitable solvent is based on its ability in extract the various organotin compounds in the matrix (which mainly depends on the nature of intermolecular forces, the geometric arrangement and the balance between the polar and the non-polar characteristics of the compounds to be extracted), and the danger of generating interferences during the separation and determination steps.

The combination of an organic solvent of low to medium polarity with an acid (such as acetic acid and hydrochloric acid) accounts for more than 50% of the biotic and abiotic extraction procedures [80,90]. However, some authors suggest that high acid concentrations can lead to degradation of OTs, with this effect being more important in the case of phenyltin species [97,98]. Solvents such as hexane, toluene and dichloromethane (DCM) are commonly employed. A complexing agent is often added to the organic solvent to improve recovery of inorganic tin and organotin compounds with fewer and shorter alkyl chains attached to the tin atom. Like monobutyltins, these compounds have increased solubility in aqueous solutions. Tropolone and carbamates [diethyldithiocarbamate (DDTC), ammonium pirrolidindithiocarbamate (APDC) and sodium diethyldithiocarbamate (NaDDC)] are frequently used as complexing agents. Tropolone has been widely used in a variety of apolar solvents (dichloromethane, benzene, diethyl ether, toluene and hexane), and is stable in organic solvents. However, the use of tropolone during extraction of organotin compounds from biotic and abiotic matrices in liquid solvents also increases the solubility of co-extracted compounds, which makes purification of the extract necessary before chromatographic separation. Although less used, the carbamates also have good performance. Their primary disadvantage is associated with preparation prior to use [80,90]. Solvents with high polarity are sometimes needed to facilitate the extraction of more polar organotin compounds such as mono- and di-substituted alkylated tin compounds [59,90]. Gómez-Ariza et al. [93] reported the use of various types of non-polar solvents such as benzene, hexane, toluene, pentane and dichloromethane for the extraction of low-polarity organotins (TeBT, TBT). More polar species (MBT, DBT) could be extracted using solvents with medium polarity, suitable complexing agents and acids.

Extraction of organotin compounds with TMAH [97,99], KOH [100,101] and enzymes [97,102,103] to decompose the biological matrix can be an alternative to acid leaching. However, quantitative recoveries can only be achieved for butyltin species when using enzymatic hydrolysis [104].

Leal et al. [105] studied three extraction procedures for marine biological materials: Method A (adapted from the method proposed by Gómez-Ariza et al. [106] using methanol and sonication); Method B (adapted from the method proposed by Tsuda et al. [107] using ethyl acetate and hydrochloric acid, i.e., a non-water-miscible solvent plus acid); and Method C (described by Ceulemans et al. [97], and using an enzymatic procedure based on the hydrolysis of biological tissues by lipase and protease, with the subsequent release of the OTs into the solution). The authors concluded that extraction methods A and B can be used to obtain similar results for TBT in mussels, whereas method B yielded a higher TPhT concentration than method A. When methods A and B were applied to a fish reference material (NIES-11), neither TBT nor TPhT were detected in the extract. To ascertain whether the extraction or the determination step was responsible for the result, the analytes were added to NIES-11 extracts and, in this case, recoveries of about 100% were obtained for both compounds. This problem could be attributed to differences in the composition of the matrix between the mussel and the fish tissue. In particular, lipid content likely played a role. The enzymatic hydrolysis method (Method C) resulted in poorer results than methods A and B when applied to NIES-11, and was unable to identify either TPhT or TBT. The authors attributed these results to the high concentration of citrate in the extract, which interfered with fluorimetric detection of the analytes.

Different extraction techniques have been used to isolate and concentrate the analytes from the matrix. Among these the most used techniques are liquid–liquid extraction (LLE) [88,108], Soxhlet extraction [81], solid-phase extraction (SPE) [95], supercritical fluid extraction (SFE) [109], solid-phase microextraction (SPME) [110,111,112], stir bar sorptive extraction (SBSE) [113,114,115] and liquid-phase microextraction (LPME) [116].

Although the use of liquid–liquid extraction (LLE) and solid-phase extraction (SPE) is very widespread, these techniques have some disadvantages. LLE, for example, is slow and has relatively high economic and environmental costs due to the use of large volumes of organic solvents. SPE also has some limitations. One of these is the use of toxic solvents during analyte desorption from the SPE cartridge. The solvents volume is lower less than the amounts used in LLE and Soxhlet extraction but is still considerable. At the same time, SPE is quite convenient, has increased sensitivity relative to some other approaches, and is easy to use during field sampling. Organotin SPE cartridges are available in a variety of form factors such as disks and cartridges, and can be supplied with a variety of solid phases such as Carbopack, C18 (octadecyl), C8 (octyl), and C2 (ethyl).

Supercritical fluid extraction is an attractive approach for sample preparation due to the common effort to reduce the consumption, disposal and long term exposure to organic solvents. Intrinsic characteristics of supercritical fluids include viscosity and diffusion coefficients much lower than those of liquids, which contributes to a rapid mass transfer of solutes and faster extractions than those in the liquid phase. Alzaga and Bayona in 1993 [110] showed that the supercritical CO_2 extraction of di- and tributyltin compounds from aqueous matrices reduced the analysis time and the solvent volume by 50 and 90%, respectively, when compared to traditional methods involving liquid–liquid extraction in the presence of a complexing agent.

SPME is a very simple, efficient, solventless sample preparation method which was first developed by Arthur and Pawliszyn [111]. It integrates sampling, extraction, concentration and sample introduction into one step and one device, considerably simplifying the sample preparation procedure. Nevertheless, it requires a specialised apparatus, such as a SPME holder, and the fragile SPME fibres have a limited lifetime. The main methods of extraction in SPME are based on the characteristics of the analyte and the matrix, and the main experimental factors that affect the efficiency of extraction are the choice of fibre cladding (solid), the temperature and time of extraction, the pH, the stirring speed, the ionic strength of the medium, and the desorption time. SBSE uses the same basic principles as SPME, but applies a coating volume 50–250 times larger than SPME to significantly increase the preconcentration capacity [112]. Aguerre et al. [92] demonstrated that the quantification of organotin compounds combined with GC-FPD after the use of SPME can detect as little as 0.006–0.031 ng L^{-1} of Sn as butyltin and 0.2–0.6 ng L^{-1} Sn as phenyl ether compounds of tin.

Like SPME, SBSE also requires a special apparatus for desorption of the extracted analytes. The application of SBSE is restricted by the limited commercial available coatings, and carry-over effects cannot be ignored [113]. Although SBSE has been applied for a variety of organic compounds, only a few works can be found dealing with its application to extract organotin compounds [114,115].

Liquid-Phase Microextraction (LPME) is a methodology that was developed by miniaturising Liquid–Liquid Extraction (LLE), greatly reducing the volume of solvent to just a few microlitres. Additionally, the solvents can be completely renewable with negligible cost [116]. LPME has three different extraction modes: single drop microextraction (SDME), in which the extractant phase is a drop of water-immiscible solvent suspended in an aqueous sample or in the headspace of the sample [117]; hollow fibre based LPME (HF-LPME), where the microextraction is performed using immiscible liquid films to separate the acceptor and donor phases [118]; and dispersive liquid–liquid microextraction (DLLME), which is based on a ternary component solvent system. LPME is almost solvent-free when compared to LLE and is much less expensive than SPME fibres or SBSE coatings [119]. Additionally, the carryover associated with SPME and SBSE can be avoided. It is simple, fast, inexpensive, effective, and environmentally friendly. Additionally, HS-SDME can extract volatile and semivolatile analytes faster than direct sampling from the headspace of a variety of matrices without interference, and the microdrop in HS-SDME is more stable than that in direct sampling. Colombini et al. [117] developed a headspace (HS)-SDME-GC-MS method for the quantification of tributyltin in CRM PACS-2 sediment, and Shioji et al. [118] have proposed a direct-SDME procedure for GC–MS determination of tributyltin and triphenyltin with 4-fluorophenyl and ethyl derivatisation. Recently, DLLME has been employed for the determination of butyl and phenyltin compounds in water samples after derivatisation with $NaBEt_4$. Derivitisation was followed by GC-FPD detection. Xiao et al. [108] also demonstrated the efficiency of microextraction (HS-SDME), obtaining limits of detection ranging from 10 to 500 ng L^{-1} for organotin compounds (TBT, DBT, and MBT) in certified sediment, seawater and shellfish.

Factors such as the method of agitation (mechanic or ultrasonic assisted), the agitation time, and the extraction temperature should also be optimised to achieve a better extraction efficiency for organotin compounds in biotic and abiotic matrices. Extraction procedures using ultrasonic radiation and microwaves are well represented in the literature. In 2007, Nemanič at al. [119,120] evaluated the use of different techniques when studying the influence of acid concentration, exposure time, the mode of agitation (ultrasonic—700 W, mechanical agitation—300 rpm and by microwave assisted extraction—1200 W with temperature ramp) in different matrices. They observed that sonication was the best technique for OTs extraction from abiotic samples. Moreover, this technique allows faster extraction using smaller volumes of solvent when compared to the other two techniques.

Table 2 provides a summary of recent literature for extraction techniques applied within a representative selection of detection techniques most commonly used for chemical speciation of organotin compounds in different matrices.

4.2.2. Extract concentration and "clean-up"

Preconcentration is often necessary due to the small total concentration of the analyte in many types of samples, an amount which is further subdivided into a number of different chemical species containing organotin. Here the sensitivity of available detection systems may be insufficient and method detection limits may have to be improved by increasing the amount of analyte in a given volume. Several methods have been developed for the concentration of organotin compounds extracted from environmental samples. Preconcentration steps (e.g., hot- or cold-trapping, amalgam formation, immobilisation with chelating agents, chelating sorbents or ion-exchange materials) are often combined with either the extraction or the derivatisation step. However, preconcentration of the extract also leads to a simultaneous concentration of interfering species [121].

Most samples consist of a multitude of compounds which can interfere during the identification and quantitative determination of organotin compounds, leading to errors in the final analysis. Organotin compounds are particularly sensitive to interferents, and purification of extracts is of concern. Clean-up commonly refers to the removal of matrix components such as lipids, fats, proteins, sulphur, high boiling point compounds, etc. from the sample because they may seriously affect derivatisation or extraction yields. Activities related to sample manipulation are filtration, drying organic phases, use of membranes, etc.

The solid-phase adsorbents used during extract purification are generally characterised by a large surface area and the presence of specific sites for adsorption. Adsorption can be physical (where the molecules are trapped in the surface of the solid simply by Van der Walls forces) or chemical (where the molecules are retained more strongly and specifically by reversibly binding to the surface of the adsorbent). The basic property that governs adsorption is polarity, and thus it is a limiting factor for desorption. If the molecules are eluted with solvent as is commonly done, they can be extracted from the surface of the adsorbent or displaced by solubilisation of sites through adsorption of a solvent which is adsorbed more strongly than the analyte of interest [122]. The most common adsorbents used during clean up are silica gel (Si-OH active sites), alumina (Al-OH active sites) and florisil (preferred for biotic matrices with high lipid content). Typically, they must be activated before use by heating to desorb water and/or other compounds adsorbed from the atmosphere [123]. Magi et al. [124] found that extract clean up using solid phase extraction cartridges with florisil leads to a significant improvement in the chromatographic behaviour of organotin species. Specifically, it drastically reduces the baseline (background) and the occurrence of unknown peaks, thereby increasing the sensitivity of the method.

4.2.3. Analytical methods for organotin species determination

As organic forms of tin are more toxic than inorganic ones, it is necessary to know the exact concentration of each species present in the sample to estimate the overall toxicity. The different forms of an element have to be separated prior to their detection (for example by atomic spectrometry) since such techniques yield only the total elemental concentration.

Therefore, most of the analytical methods developed to quantify organotin compounds require hyphenated techniques, which are the on-line combination of a separation technique with a detection technique with a specific detector suitable for identification and quantitation of a specific molecule or element. Alternatively, separations can be performed off-line, with the species being separated and determined independently. Although a variety of separation techniques are used for organotin species, chromatography is the most common.

4.2.3.1. Separation techniques used in organotin speciation studies. There have been some attempts to differentiate between "soluble" and "non-soluble" tin in a particular solvent after a leaching procedure, but the most common way of separating the analytes is through chromatographic separations. The main modes of chromatography are based on gas chromatography and high performance liquid chromatography.

4.2.3.1.1. The use of gas chromatography for the separation of organotin compounds. Gas chromatography is most used technique for separation due to its resolution, the greater variety of coupled detectors, and its ability to simultaneously separate many different organotin compounds (for example, butyls, phenyl, octyl and propyl) in a single analysis [80]. Unfortunately, tri-, di- and monoalkylorganotin compounds are not sufficiently volatile and/or thermally labile, and these compounds require a derivatisation step prior to separation with gas chromatography. These derivatisation

Table 2
Sample techniques of extraction applied within a representative selection of research and application papers dealing with tin speciation analysis in environmental and biological samples using several detectors.

Matrix	Species	Techniques of Extraction						Reference
		Liquid–Liquid (ELL)	Solid-Phase (SPE)	Supercritical Fluid (SFE)	Soxhlet	Liquid-Phase Microextraction	Solid-Phase Microextraction	
Snails, sediments	MBT, DBT, TBT		X					[16]
Coral and branchlets	TBT, DBT, MBT	X						[18]
Mussels, clams and cockles	TBT, DBT, MBT, TPhT, TeBT, TcHT, MOcT, DOcT		X					[19]
Human Urine	TBT, DBT, MBT, TeBT, TPhT, DPhT, MPhT	X						[45]
Standards	TBT, DBT, MBT						X	[52]
Water, sediment and bivalve mussels	TBT, DBT, MBT, TPhT, DPhT, MPhT, MocT, DOcT, TOcT					X		[61]
Waters, sediment and mussel	MBT, DBT, TBT	X						[84]
Sediment	BT, PhT	X						[90]
Environmental and biological samples	TBT, DBT, MBT					X		[112]
Biota	TBT, DBT, MBT, TPhT, DPhT, MPhT		X					[177]
Oyters, fish	TBT, DBT, MBT, TPhT, DPhT, MPhT		X					[178]
Seawater and sediment	TBT, DBT, MBT, TPhT, DPhT, MPhT, MOcT, DOcT, TOcT, Sn inorg	X	X					[179]
Human Urine	TBT, DBT, MBT, TeBT, DPhT, MPhT						X	[180]
Wastewater, seawater	TBT, DBT, MBT, TPhT, DPhT, MPhT,	X						[181]
Marine Sediment and biota	TBT, DBT, MBT, TPhT, DPhT, MPhT, Sn total				X			[182]
Seawater	MMT, DMT, TMT					X		[183]
Sediments	TBT, DBT, MBT, BT						X	[185]
Sediment and biota	TBT, DBT, MBT	X						[186]
Fish	TBT, DBT, MBT, TPhT, DPhT, MPhT	X						[187]
Environmental samples (sediment, river water, wastewater, sewage sludge, sand and oyster)	TBT, DBT, MBT, TPhT, DPhT, MPhT	X	X					[188]
Waters of rivers, sediments	TBT, DBT, MBT, TPhT, DPhT, MPhT, MOcT, DOcT, TOcT	X	X					[189]
Natural Quartz Sand	TBT	X						[190]
Sediments, mussel	MBT, DBT, TBT	X						[191]
Sediments	MBT, DBT, TBT		X					[194]
Shellfish, finfish, water and sediment	MBT, DBT, TBT, TOcT	X	X					[195]
Water, sediment	TBT, DBT, MBT	X	X					[196]
Soil, sediment	TMT, DMT, MMT, TBT, DBT, MBT, DOcT, MOcT		X					[197]
Oyster	TBT, DBT, MBT, TPhT, DPhT, MPhT		X					[198]
Oysters, fish	TBT, DBT, MBT, TPhT, DPhT, MPhT		X					[199]
Seawater, sediment	TBT, DBT, MBT, TPhT, DPhT, MPhT, TOcT, DOcT, MOcT	X	X					[200]
Water	MBT, DBT, TBT, MPhT, DPhT, TPhT						X	[201]
Sediments	MBT, DBT, TBT		X					[202]
Water, sludge	TBT, DBT, MBT, TPhT, DPhT, MPhT	X	X					[203]
Sediment	DBT, TBT		X					[204]
Soils	TPhT		X					[205]
Sediment	TBT, DBT, MBT, TPhT, DPhT, MPhT		X					[206]
Soil	TBT, DBT, MBT, TPhT, DPhT, MPhT, TOcT, DOcT, MOcT		X					[209]
Sediment	TBT, DBT, MBT, TPhT, DPhT, MPhT	X						[210]
Tin stock standard solution	TBT, DBT, MBT		X					[211]
Agricultural Soils	Fenbutatin oxide (FBTO): (bis[tris(2-methyl-2-phenylpropyl)tin]	X						[212]
Beans, algae	TBT, DBT, MBT, TPhT, DPhT, MPhT		X					[213]
Textile, plastic	TBT, TPhT, TET		X					[216]
Shellfish	TBT, DBT, MBT, TPhT, DPhT		X					[217]
Water	TBT, DBT, MBT, TPhT, DPhT, MPhT					X		[218]

steps are time-consuming, subject to interference, and involve considerable sample manipulation that can lead to analyte loss.

The methods of converting the ionic compounds into alkyltin volatile species (derivatisation) and therefore determinable by GC include: sodium tetrahydroborate ($NaBH_4$); sodium tetraethylborate ($NaBEt_4$), and Grignard reagents (bromide/chloride of methyl-, ethyl-, propyl-, pentyl- or hexylmagnesium) [80]. The most widely used means of derivitisation is through reaction with tetrasubstituted "Grignard" reagents (bromide or chloride, ethyl, butyl or pentylmagnesium), comprising 53% of the procedures available in the literature [125]. Grignard alkylation results in quantitative production of stable derivatives, allowing the determination of different species of organotin (methyltin, butyltin, and phenyltin) [124,126]. Chemical derivatisation by alkylation depends on the reaction of organotin compounds with a Grignard reagent (R′MX; R′: organic group, M: metal and X: anion) to convert the ionic mono-, di- and tri-organotins into their corresponding non-polar tetrasubstituted compounds:

$$RnSn^{(4-n)+} \xrightarrow[\text{Solvent}]{R'MgX} RnSnR'_{(4-n)}$$

n = 1,2,3; R, R′ = organic groups.

The usual procedure for trace determination of organotin compounds with alkylation involves five basic steps: (a) acidification of samples; (b) extraction with an organic solvent; (c) derivatisation; (d) clean-up and preconcentration; and (e) analysis. Extraction with an organic solvent is necessary because reaction with the Grignard reagent has to be carried out in aprotic solvents such as benzene, toluene, diethyl ether or hexane. Protic solvents such as dichloromethane or chloroform can still be used for extraction but should be evaporated and replaced prior to the derivatisation step because they react with the reagent. A number of Grignard reagents have been used to convert the ionic organotins in environmental samples into volatile tetrasubstituted alkyltin derivatives, including methyl [127], ethyl [128], propyl [129], butyl [130], pentyl [131,132] and hexyl [133] -magnesium chlorides/bromides. The choice of alkylating reagent depends on the analytes being determined. Ethylation and pentylation are usually employed as they allow the determination of methyl-, propyl-, butyl- and phenyltin species, all of which are of environmental concern.

The simultaneous formation of mono-alkylated disulfides when sulphur is present, the time to process the reactions, the need for anhydrous conditions and the necessity to use apolar solvents are disadvantages of the Grignard reaction. An effective method for quantitative removal of sulphur compounds is essential for the determination of organotin compounds. Basically, three procedures for desulphurisation have been adapted to extract sulphur-containing compounds during organotin analysis: (a) selective retention of compounds containing sulphur through a column filled with activated copper powder, (b) adsorption of sulphur compounds by an amalgam of mercury, and (c) precipitation of sulphur compounds as tetrabutylammonium sulphite [134].

The reaction of hydrides was originally utilised for generation of trace amounts of stannane (SnH_4) from aqueous solutions of tin and further determination by atomic absorption spectrometry [135]. The sample is usually mixed and allowed to react with an acidic solution of $NaBH_4$ in a reaction chamber, and then the generated hydrides are scrubbed from solution by an inert gas and trapped cryogenically using liquid nitrogen in a U-trap filled with an appropriate chromatographic packing material. Upon warming they are separated based on their boiling points and/or their chromatographic properties and detected on-line by a tin-selective detector. In general, the reduction is usually performed at a pH that is a few units below the pK_a of the species of interest [136].

$$RnSn_{aq}^{(4-n)+} \xrightarrow[H^+]{NaBH_4} RnSnH_{(4-n)} + H_2$$

n = 1,2,3; R: organic group.

This method has good sensitivity for aqueous samples, however, for complex samples (such as sediment and biota) this method has a number of disadvantages. Among these disadvantages are the limited number of compounds that can be determined by this method because the $NaBH_4$ does not form a volatile product with some species such as phenyltin. Additionally, the reagents are unstable and should be prepared immediate before use [80,125]. A solution to extend the determination of organotin compounds, determining not only the compounds of butyltin as well as phenyltin, would be the use of sodium tetraethylborate ($NaBEt_4$) for derivatisation [125,126,137,138]. These compounds can be analysed easily when compared to derivatisation with a Grignard reagent. Some care should also be taken. First, $NaBEt_4$ is extremely air-sensitive and must be handled with care to keep its chemical integrity. For optimal derivatisation efficiency, the solution of $NaBEt_4$ should be freshly prepared immediately before sample processing, or stored frozen (−20 °C) for no longer than two weeks. A 30 min reaction time at a pH between 4 and 5 is optimal for reaction with $NaBEt_4$. As an exemple, Xiao et al. [108] developed an analytical procedure for determining butyltin compounds (MBT, DBT and TBT) in environmental and biological samples, comparing derivatisation $NaBEt_4$ and $NaBH_4$. The results showed that both modes of derivatisation showed good linearity for all butyltin compounds, with limits of detection (LODs, 3σ), reaching 1–2 ng L^{-1} with $NaBEt_4$. The authors concluded that the method using derivatisation with $NaBEt_4$ was more sensitive and robust.

Other effects that have been observed during the gas chromatography analysis of OTs include baseline drift, the appearance of large bands and the disappearance of some peaks. Such problems are due to matrix effects, and thereby call into question the reliability and accuracy of the analysis.

4.2.3.1.2. The use of high performance liquid chromatography for the speciation of organotin compounds. Organotin separations by using HPLC do not require derivatisation, which eliminates a potential source of uncertainty in the final result and can reduce analysis time significantly. Stationary and mobile phases can be varied to obtain the best separation. However, interfacing of HPLC to detection systems can be problematic and the number of compounds that can be analysed in a single run is limited when compared to GC [140].

The separation modes for organotin compounds with HPLC system include ion exchange, reversed phase, normal phase, ion-pair, size exclusion, micelle and vesicle-mediated, and supercritical fluid approaches. Almost all of the available methodologies fall under two basic categories: ion exchange and reversed phase.

Ion-exchange chromatography is carried out on ionisable analytes using column packing materials that possess charge bearing functional groups. In the case of organotin compounds, the cations $[R_nSn]^{(4-n)+}$ from samples compete with the mobile phase counterions Y^+ for the ionic sites X^- of the cation exchanger. The stationary phase consists of a solid matrix bearing fixed negatively or positively charged functional groups, depending on whether it is designed for anion or cation exchange. The support material is usually either a styrene divinylbenzene resin or silica. The resin ion-exchangers suffer from swelling effects with aqueous mobile phases, which results in their compression at high pressure. This drawback can be overcome to some extent by cross-linking, but this in turn leads to an unfavourable decrease in mass transfer processes. Silica based ion exchangers overcome these problems to some degree because they are mechanically stable and thus allow for fast, high-pressure separations. However, silica bonded phase

columns are chemically unstable and can only be used in the pH range from 2 to 8. To reduce the possibility of tailing, the mobile phase must be buffered. This ensures that the proportions of the neutral and ionised forms of the solute do not change throughout the chromatographic separation. In all of the systems that use silica based columns, the mobile phase consists of a certain percentage of methanol (50–90%, v/v) and a salt, which is usually ammonium acetate or citrate (0.005–0.2 mol L^{-1}). The use of lower percentages of methanol (30%) necessitates the inclusion of a small amount of acetic acid to elute the strongly adsorbed monobutyltin species from the column. The separation mechanism suggested for the organotin species is based on the three main characteristics of the column: cation exchange due to the presence of sulphonate groups; reversed phase due to the bonded phase; and adsorption arising from exposed silanol sites. The scheme used to qualitatively describe the separation involves equilibrium reactions between an organotin cation, a singly charged anionic ligand and a substrate. A number of column parameters must be optimised prior to the analysis of organotin compounds ($R_nSn^{(4-n)+}$, differing in their degree of substitution (n) and functionality (R)). Also, the development of element specific detection should be investigated, to compensate for the absence of chromophores in most organotin compounds (the exception being the phenylsubstituted compounds) and the low detection limits associated with conventional HPLC detectors [140–143].

The reversed phase mode involves the use of a polar eluent with a non-polar stationary phase and is particularly useful for the chromatography of polar molecules. The bonded stationary phase usually consists of an alkyl moiety which is chemically bound to a silica support material. The eluent is usually water containing an organic modifier such as methanol. The eluting power or 'strength' of the mobile phase dramatically increases with the proportion of organic solvent present [144,145]. The first successful use of the reversed phase mode for the speciation of organotin compounds differing in both type (e.g., methyl, ethyl, butyl, etc.) and number (e.g., mono-, di-, tri-, etc.) of substituents was performed by Kadokami et al. [146]. They established that aqueous, methanol or tetrahydrofuran eluents were unsuitable because the peak shapes of the di- and tri-substituted compounds were not symmetrical, and that the mono-substituted compounds could not be eluted from the column. In an effort to overcome these problems they added tropolone (2-hydroxy-2,4,6-cycloheptatrienone) or oxine (8-hydroxyquinoline) to the mobile phase due to the use of these reagents as complexing ligands in liquid/liquid extractions and also because oxine had been previously used to overcome adsorption interactions in the reversed phase separation of other organotin compounds. The inclusion of 0.2% (m/v) tropolone with tetrahydrofuran (54%, v/v), water (38%, v/v) and acetic acid (8%, v/v) allowed resolution of eight organotin compounds, including TBT, DBT and MBT, within a 10 min analysis time. The detection limits using FAAS adapted with a long absorption tube were 5 ng as tin for all eight organotin compounds. The same authors went on to demonstrate the use of this technique for the analysis of TBT in seawater. This separation system was further investigated by Dauchy et al. [147], who used ICP-MS as the detection technique. They found that the use of THF in the mobile phase produced a decrease in plasma stability, which they overcame by using methanol (80%, v/v), water (14%, v/v) and acetic acid (6%, v/v) containing 0.1% (m/v) tropolone. The limit of detection was on the order of 0.15 ng (as tin) for tributyltin and 0.24 ng (as tin) for di- and monobutyltin. Recently, Yu et al. employed similar chromatographic system to perform the determination of five organotin compounds in seawater [148].

Normal phase separation mode involves the use of stationary phases that have a higher polarity than that of the eluent. The bonded phase columns used in this approach are made by covalent attachment of a polar organic moiety to the surface of the silica gel microparticulate support. Non-polar organic solvents are usually employed as eluents, although chloroform, ethanol or aqueous acetonitrile have been used in some instances. The stationary phases are classified according to the degree of polarity of the functional groups at the surface. For organotin speciation, the majority of columns have cyanopropyl bonded phases which are considered to be of medium polarity. Most studies that employ reversed or normal phase separation modes encounter problems associated with adsorption of the organotin compounds onto unreacted silanol groups. A number of methods are available to overcome this unwanted interaction, including the use of a chelating agent such as morin (2,3,4,5,7-pentahydroxyflavone) or tropolone, or the inclusion of acetic acid or other reagents to block interactions with the silanol groups [149–152]. Various different stationary phases have been evaluated for the liquid chromatography of organotin compounds by Praet et al. [152]. Most of the phases evaluated were not suitable because of low efficiency [poly(styrendivinylbenzene)], adsorption from residual silanol groups (octadecyl silica gel) or reaction with the stationary phase (aminopropyl silica gel). However, separation of some tetraalkyl and dialkyl organotin compounds was achieved by using a cyanopropyl column which had been treated with iodine chloride to mask its silanol activity. Astruc et al. [153] used 0.005% (m/v) tropolone in toluene with a 0–5% (v/v) gradient of methanol to separate monobutyltin, dibutyltin, tributyltin and tetrabutyltin. This method could not be used routinely because it slowly degraded the column. With isocratic conditions using tropolone in toluene as the eluent, TBT and TeBT co-eluted. DBT was resolved, but MBT strongly adsorbed to the column. The HPLC system was interfaced to a GF AAS system and the method was used to determine the DBT and TBT concentrations in river water and sediment (it was assumed that no TeBT was present in the samples).

Size-exclusion chromatography (SEC), a mode of separation which has also been referred to a gel-permeation chromatography, is used for resolution of molecules on the basis of their molecular size. More simply, molecules too large to enter into the pores of the stationary phase remain in the eluent, while the smaller molecules which can permeate the solid phase are retained. By using polymers of accurately known molecular weight as calibrants and with a well controlled flow rate, the molecular weight of an unknown solute can be estimated. Two types of packing material are commonly used: inorganic packings based on silica gel or glass, and cross linked polystyrene gels. The latter are compatible with a wide range of organic eluents, whereas the inorganic packings are suitable for both aqueous and organic mobile phases. The pore size of the packing material is important and, where a large range of solute molecular sizes exists, a number of SEC columns of different pore sizes will be arranged in series. The use of size-exclusion chromatography (SEC) for the separation of organotin species has generally focused on the tin containing polymers used in anti-fouling paint formulations. In every case, the columns were packed with cross-linked poly (styrene–divinylbenzene). Several styrene–divinylbenzene polymer columns of different pore sizes have been used to separate and purify the methylated tin halides [154,155].

Micelle- and vesicle-mediated chromatographies are separation modes that have been used for organotin speciation and involve the inclusion of a surfactant in the mobile phase. Surfactant-based organised media, such as micelles and vesicles, assist in dissolving solutes that are not easily solubilised in aqueous eluents. The efficiencies obtained with these types of mobile phases can be comparable to those of hydro-organic eluents. Surfactants have a non-polar tail and a polar head group. Upon reaching a critical concentration they form micelles, with the polar head groups in contact with the aqueous solution and the tails directed into a central, non-polar core. If the surfactant has two or more hydropho-

bic tails it can form into a bilayer, which upon sonication forms a doughnut-shaped vesicle. The important difference between these two configurations is the number of compartments that the solute molecule can occupy. With the micelle there are five possible positions and with the vesicle nine available sites. In principle, vesicles offer a greater variety of interactions with the solute molecule than do micelles. Three different surfactants were tested for the separation of organotin compounds in the micellar mode. The use of mobile phases containing vesicles has not been as successful for the separation of organotin compounds as for other species such as arsenic, mercury and selenium. This is primarily due to the high degree of hydrophobicity exhibited by compounds such as the butyltins. A reversed phase C-18 column and an eluent containing ammonium citrate (0.1 mol L^{-1}), acetic acid (5%, v/v) and vesicles of dihexadecyl phosphate (10^{-5} mol L^{-1}) at pH 4.5, with a methanol gradient of 50–90% (v/v), was used to separate mono-, di and tri-butyltin. To obtain an acceptable capacity factor and peak shape for TBT, at least 60% methanol was necessary. The retention time of all the butyltin species increased with surfactant concentration, which was considered to be typical of ion-pair surfactant chromatography where no micellar aggregates form [156,157].

Ion-pair mode is particularly useful for the separation of ionised or ionisable compounds and has been used for the separation of organotin compounds. The 'ion-pair' is formed between the solute ion and a counter ion of opposite charge, and the 'ion-pair' has a low net charge and polarity. Ion-pair separations can be carried out in both the normal phase and the reversed phase, but in the case of organotin compounds only the reversed phase mode has been used. The mechanism by which separation takes place in reversed phase ion-pair chromatography is not fully understood, but three models have been developed to explain it. These are the ion-pair, the dynamic ion-exchange, and the ion-interaction models. Only a few reports using the reversed-phase ion-pair approach for organotin speciation have appeared in the literature and these have focused on the determination of mono-, di- and tri-methyltin chloride and of the tri-substituted methyl-, phenyl- and butyl-tin. No work has been reported on the separation of the more environmentally significant butyltin chlorides using this approach [158].

Supercritical fluid chromatography (SFC) can be used to separate thermally labile, non-volatile and high molecular weight compounds (especially suitable for the more substituted organotin compounds, such as tetra- and trisubstitutes), as well as having higher efficiency nebulisation into the detector, associated with gaseous samples. However, a number of operating parameters such as the interface temperature, the oven temperature, carbon dioxide pressure programme, mobile phase composition and column length must be evaluated to determine their effect on the separation and detection of these organotin compounds. Shen et al. [159] separated of TBT and TePhT using carbon dioxide as the eluent and a pressure programme consisting of 10.1 MPa held for 1 min followed by a pressure ramp of 8.1 MPa min^{-1} to a final pressure of 20.3 MPa. The detection limits for both compounds were very low, being in the range from 0.035–0.045 pg. However, they were unable to separate TBT, DBT or TeMT with any of the conditions that they have tried. It was concluded that the approach showed potential for simultaneously determining complex mixtures of organometallics containing arsenic, mercury, lead and tin.

4.2.3.1.3. The use of other techniques for the separation of organotin compounds. A relatively novel approach was the separation of organotin species with capillary electrophoresis and indirect fluorescence detection or indirect/direct ultraviolet absorbance detection. Pobozy et al. [160] have reported a separation of TMT, TET, TBT and TPhT using this technique. The four analytes were separated within 20 min; the detection limits, using indirect UV detection, reported were better than for HPLC approaches. Whang and Whang [161] also employed capillary electrophoresis and UV detection to separate TMT, TET, TPrT, TBT and TPhT. To separate di-organotins (DBT and DMT) from the tri-organotins (TMT, TET, TPhT and TBT), α-cyclodextrin (α-CD) was added as a modifier in the electrophoresis buffer. The authors report linearity of about two orders of magnitude with a relative standard deviation between 1.3 and 7.1%. The method was applied to the analysis of marine sediments.

4.2.3.2. Selective and specific detection techniques used in organotin speciation studies. For detection of organotin compounds, the system must be highly versatile and able to be coupled to a chromatographic system or some other separation device. Nevertheless, two problems appeared: (1) detection limits were sometimes not sufficient to detect real-world concentrations of analytes and (2) interferences are common in biota and environmental samples. The choice of the detector in speciation analysis depends on the chemical forms of the organotin compound to be determined, and also on the mode of separation used.

Tin has been determined at low concentrations by spectrophotometric methods using various reagents such as cacotheline, dithiol, haematoxylin, phenylfluorone, 3,5-dinitrocatechol with Nile blue, pyrocatechol violet, 2,6,7-trihydroxy-9-(3-pyridyl) fluorone, lumogallion and quercitin. Inorganic tin has also been determined spectrofluorimetrically using 3-hydroxyflavone as a complexing agent. Most of the reagents, however, lacked sensitivity and yielded detection limits in the range from 0.02 to 10 mg L^{-1}. Selectivity for direct analysis was poor, requiring elaborate extraction and separation procedures [162–167].

Detection limits can be lowered to μg L^{-1} levels by the use of fluorimetric and polarographic methods. Anodic stripping voltammetry has been utilised for determination of tributyltin oxide in water after steam distillation and thin-layer chromatography, and for triphenyltin determination after solvent extraction and thin-layer chromatography at 10 μg L^{-1} level [168]. Morin (2,3,4,5,7-pentahydroxyflavone) has been used as a fluorescence reagent for determination of sub-μg L^{-1} concentrations of organotin compounds, especially dialkyltin compounds, in aqueous and rat tissue samples after solvent extraction. Most of the methods do not offer adequate sensitivity for detection of organotin compounds in natural waters at the ng L^{-1} concentration level, and were limited in selectivity either to specific molecules or to a narrow range of compounds [150,169].

There are several different approaches to analyte detection in high performance liquid chromatography: ultra-violet absorption (UV) [150,170], fluorescence [169–173], electrochemistry [174], refractive index measurement [170], atomic absorption spectrometry (AAS) [171,173] and optical emission spectroscopy (OES) [172,173]. Fluorescence detection is facilitated by reaction of the organotin compounds with a suitable reagent such as morin during either pre-column or post-column derivatisation. Direct UV detection at 254 nm has been used to determine TPhT [175]. The lack of a suitable UV chromophore on the alkyl substituted organotin compounds has been overcome in a number of ways, including the use of a photometrically active counter-ion (benzyltrimethylammonium cation) in the mobile phase with indirect photometric detection of the organotin, and on-column complexation of mono- and di-butyltin with oxine (8-hydroxyquinoline) after conversion of TBT and TeBT to those species by photochemical decomposition and detection at 380 nm. Electrochemical detection methods [174] have not been widely reported for organotin speciation, probably because of their lack of selectivity. The use of refractive index detection has been reported, but for the methyl, ethyl and butyl-substituted organotin compounds it showed a marked lack of sensitivity [170].

Both atomic absorption spectrometry (AAS) and optical emission spectrometry (OES) have been used for specific detection of

metals. Both techniques eliminate many of the problems associated with conventional HPLC detectors. The general consensus is that the mode of atomisation (flame, furnace) or ionisation (plasma) must be able to handle large volumes of mobile phase, solvent flow rates in the range 0.1–2.0 ml min^{-1}, and eluents that may be non-aqueous in nature. Flame atomic absorption spectrometry normally does not provide detection limits able to determine organotin levels in environmental samples. Three approaches have been used to overcome this problem, including the use of the slotted tube atom trap, the quartz furnace or the generation of hydride. The first two approaches effectively increase the residence time of the analyte in the flame, whereas the hydride generation method overcomes the low nebulisation efficiency encountered with aspiration of liquid samples. For some species, the limit of detection can be lowered by a factor of 1000 by using hydride generation (HG-QT-AAS), and this approach also eliminates interferences from compounds that do not readily form hydride. Electrothermal atomisation offers higher sensitivity than the use of flames, but because the temperature cycle involves drying, ashing and atomisation steps, and analysis is usually off-line and discontinuous in nature. The interfaces used to couple HPLC to ET AAS are based upon those developed by Brinckman et al. [175] which comprised some form of fraction collector with autosampler for injection into the graphite cuvette. With organotin studies some form of modifier, such as palladium is usually added to reduce the formation of refractory tin carbide compounds.

Atomic emission spectrometry has the advantage of long linear calibration ranges and simultaneous on-line determination of a number of elements. For these reasons it comes closest to meeting the requirements of a universal HPLC detector for the determination of organometallic species. However, the low temperature of the flame used in atomic emission spectrometry does not offer detection limits low enough for environmental work and therefore has not been used for organotin speciation. The use of a plasma as the atomisation and excitation source in OES has been found to be more sensitive than the various flames used due to the greater atomisation/ionisation efficiency. The three principal plasma sources that have been used in analytical studies include inductively coupled argon plasma (ICP), a direct-current argon plasma jet (DCP) and microwave-induced helium plasma (MIP). However, only the first two (ICP and DCP) have been coupled to HPLC for organotin determinations. Both of these are able to accommodate large aqueous or organic flows, whereas MIP is unable to tolerate aerosol introduction without destabilisation or extinction of the plasma. For this reason MIP has been more widely used as a GC detector.

The high efficiency of singly charged positive ions production by an ICP means that it is a very effective ionisation source for mass spectrometry. Compared with ICP OES, the use of ICP-MS improves detection limits by two to three orders of magnitude (sub-picogramme levels) with the additional ability to perform isotopic analysis. For these reasons, as well as its ability to readily accept the eluent flow rates normally used in HPLC (0.2–1 mL min^{-1}), it is the most successful detection system for organometallic speciation studies [176]. The main problems normally found when coupling HPLC to ICP-MS result from the composition of the eluent. High buffer concentrations can block the sampling and skimmer cones of the mass spectrometer, which adversely affect the detection limits. The use of organic solvents in the eluent worsens the sensitivity due to plasma instability and carbon deposition on the sampling and skimmer cones. Both of these effects can be overcome by various methods including use of mixed gas plasmas, cooling the spray chamber, increasing the radio frequency power or using an acid wash between runs [173,177]. A significant drawback of the ICP-MS systems commonly in use is the inefficiency of the nebulisers. Conventional nebulisation is only 2–5% efficient, so very little of the sample reaches the plasma. As a result, the lowest detection limit is not realised. Methods used to overcome this problem involve the formation of hydrides and the use of other nebulisers, such as the direct injection nebuliser. The use of this kind of nebuliser minimises band broadening effects that are often apparent with larger volume nebulisers and thus allows for the use of microbore and capillary HPLC separation [178]. The use of plasma mass spectrometry for such research has increased over recent years.

Gas chromatography as separation method coupled with element-specific detection methods is the most widely used technique for the determination of OTs and allows the separation of many species with very good resolution. In the early years of organotin speciation, GC was coupled to AAS (GC-AAS) and AED (GC-AED) as element-specific detectors [19,45,52,86,88,93,118,123,179–185,187–193,195–204,206,208,209–213]. The use of hydride generation followed by flame atomic absorption spectrometry or plasma atomic emission spectrometry has lowered the detection limit approximately 1000-fold to the 0.05–25 μg L^{-1} range. The flame photometric detector (FPD) is also very well suited for the detection of OTs [206]. Although tin is difficult to thermally excite in flames, instrumental improvements and modifications have allowed the sensitive and selective detection of OTs based on the red molecular fluorescence of the Sn–H species at 609.5 nm. The recent introduction of the pulsed flame photometric detector (P-FPD) has further improved sensitivity and selectivity for OTs. OTs can also be detected with common gas chromatography–mass spectrometry (GC–MS) systems [61] with sensitivity comparable to gas chromatography–atomic emission detection (GC–AED). A sensitive flame photometric detector selective for tin has an absolute detection limit below 10^{-12} g (1 pg). The use of GC-ICP-MS is increasingly used for the analysis of OTs [52]. This technique has better sensitivity than the other common techniques. In addition, ICP-MS also allows quantitation based on isotope-dilution mass spectrometry (IDMS), which is a unique asset for both highly accurate and precise speciation measurements [112]. Furthermore, GC–ICP-MS in combination with isotopically labelled standards can be used to study the species-specific decomposition processes of OTs observed with various sample preparation techniques. Also, other hyphenated techniques such as HG–ICP-MS [214] and CE–ICP-MS [215] have been developed for organotin speciation analysis.

Other non-flame techniques have also been developed for determination of traces of tin, such X-ray fluorescence spectrometry and polarography.

5. Conclusion

It is widely accepted that the determination of the total concentration of an element in the environment reveals little about its toxicity, environmental occurrence, persistence and fate. It is for this reason that a great deal of research has been carried out to develop analytical techniques that are able to quantitatively determine the chemical form of trace elements in a wide variety of sample matrices. Organotins in particular have been shown to have a detrimental effect on the environment at reasonably low concentrations, and bioaccumulation can occur in real samples. As a result, it is necessary to monitor the environment for these compounds. The determination of the long-term cycling and toxicity of the organotin compounds present in the environment requires the combination of a separation technique with a sensitive detector. Generally speaking, such methods have to be sensitive to the ng g^{-1} level for solid matrices such as sediments and ng L^{-1} for waters and efluents. The combination of two analytical techniques (separation and detection) can provide useful

methods with enough sensitivity to quantify organotin species as well as supply important structural information, thus allowing comprehensive identification of unknown species. Of the separation techniques, gas chromatography enables the separation of most species in a single run with good resolution. Unfortunately as most organotins are not volatile, it is necessary to introduce a time consuming and potentially problematic derivatisation step. While liquid chromatographic approaches obviate the need for a derivatisation step, resolution is frequently poorer. Additionally, there is an interest in alternatives to traditional approaches such supercritical fluid chromatography and capillary electrophoresis. Inductively coupled plasma-mass spectrometry is increasingly being used as the detector of choice because its sensitivity enables measurements at the ng L^{-1} and ng g^{-1} level observed in real environmental samples. There is also the potential to use organotins labelled with stable tin isotopes to permit isotope dilution analysis, which improves the quality of results in difficult matrices.

References

[1] J.W. Moore, S. Ramamoorthy, Heavy Metals in Naturals Waters, Applied Monitoring and Impact Assessment, Springer-Verlag, New York, 1984.
[2] E. Rosenberg, in: R. Cornelis, J. Caruso, H. Crews, K. Heumann (Eds.), Handbook of Elemental Speciation II, Species in the Environment, Food, Medicine and Occupational Health, Wiley, Chichester, 2005.
[3] IPCS (International Programme on Chemical Safety), Environmental Health Criteria 116. Tributyltin Compounds, 1990.
[4] S.J. Blunden, C.J. Evans, in: O. Hutzinger (Ed.), The Handbook of Environmental Chemistry, Springer–Verlag, Berlim, 1990, pp. 1–44.
[5] M. Hoch, Appl. Geochem. 16 (2001) 719.
[6] C.A.L. Filgueiras, Quim. Nova 21 (1998) 176.
[7] G.M. Lima, Quim. Nova 22 (1999) 178.
[8] K. Fent, in: M.A. Champ, P.F. Seligman (Eds.), Onganotin–Environmental Fate and Effects, Chapman and Hall, London, 1990, pp. 1–25.
[9] K. Fent, Sci. Total Environ. 185 (1996) 151.
[10] K. Fent, J. Humn, Environ. Toxicol. Chem. 14 (1995) 1123.
[11] S.A. Patin, Pollution and the Biological Resources of the Oceans, Butterworth Scientific, London, 1982.
[12] P.E. Gibbs, G.W. Bryan, in: M.A. Champ, P.F. Seligman (Eds.), Organotin: Environmental Fate and Effects, Chapman & Hall, London, 1996, pp. 259–280.
[13] M.A. Champ, Sci. Total Environ. 258 (2000) 21.
[14] P.S. Rainbow, Mar. Pollut. Bull. 31 (1995) 183.
[15] M.A. Fernandez, A.L.R. Wagener, A.M. Limaverde, A.L. Scofield, F.M. Pinheiro, E. Rodrigues, Mar. Environ. Res. 59 (2005) 435.
[16] S. Chiavarini, P. Massanisso, P. Nicolai, C. Nobili, R. Morabito, Chemosphere 50 (2003) 311.
[17] A. Sousa, S. Mendo, C. Barroso, Appl. Organomet. Chem. 19 (2005) 315.
[18] L.D. Smith, A.P. Negri, E. Philipp, N.S. Webster, A.J. Heyward, Mar. Biol. 143 (2003) 651.
[19] M.M. Santos, P. Enes, M.A. Reis-Henriques, J. Kuballa, L.F.C. Castro, M.N. Vieira, Chemosphere 75 (2009) 661.
[20] J.S. White, J.M. Tobin, J.J. Cooney, Can. J. Microbiol. 45 (1999) 541.
[21] P.T.S. Wong, Y.K. Chau, O. Kramar, G.A. Bengert, Can. J. Fish. Aquat. Sci. 39 (1982) 483.
[22] L. Pellerito, L. Nagy, Coord. Chem. Rev. 224 (2002) 111.
[23] M. Berg, C.G. Arnold, S. Muller, J. Muhlemann, R.P. Schwarzenbach, Environ. Sci. Technol. 35 (2001) 3151.
[24] L. Ebdon, S.J. Hill, C. Rivas, Trends Anal. Chem. 17 (1998) 277.
[25] P. D'Agati, C. Mansueto, V. Mansueto, C. Pellerito, M.V. Cangialosi, T. Fiore, M. Scopelliti, L. Pellerito, Appl. Organometal. Chem. 20 (2006) 357.
[26] A. Terlizzi, S. Fraschetti, P. Gianguzza, M. Faimali, F. Boero, Aquat. Conserv. 11 (2001) 311.
[27] S.M. Liu, M.P. Hsia, C.M. Huang, Sci. Total Environ. 355 (2006) 167.
[28] H. Harino, S.C.M. O'Hara, G.R. Burt, B.S. Chesman, W.J. Langston, Mar. Pollut. Bull. 50 (2005) 222.
[29] E.C., 2000/600 EC. Directive of the European Parliament and of the Council 2000/60/EC establishing a framework for comumunity action in the field of water policy. Official Journal of the EC C513, 23/10/2000.
[30] M.A. Champ, Mar. Pollut. Bull. 46 (2003) 935.
[31] S. Sonak, P. Pangam, A. Giriyan, K. Hawaldar, J. Environ. Manage. 90 (2009) S96.
[32] N.B. Bhosle, in: Distribution of tributyltin (TBT) in the Mandovi estuary, 2007, pp. 105–145.
[33] L.D. Chambers, K.R. Stokes, F.C. Walsh, Surf. Coat. Technol. 201 (2006) 3642.
[34] L. Gipperth, J. Environ. Manage. 90 (2009) S86.
[35] http://www.ortepa.org/pages/b5.htm.
[36] CONAMA (Environmental National Council of Brazil), 2008, Standards for domestic water supply, resolution number 397, CONAMA, Brasília, DF.
[37] R.J. Maguire, R.J. Tkacz, Y.K. Chau, G.A. Bengert, O.T.S. Wong, Chemosphere 15 (1986) 253.
[38] J.J. Cooney, Helgol. Mar. Res. 49 (1995) 663.
[39] J.J. Cooney, A.T. Kronick, G.J. Olson, W.R. Blair, F.E. Brinckman, Chemosphere 17 (1988) 1795.
[40] D. Barug, Chemosphere 10 (1981) 1145.
[41] D. Amouroux, E. Tessier, O.F.X. Donard, Environ. Sci. Technol. 34 (2000) 988.
[42] WHO, Tributyltin compounds, Environmental Health Criteria No. 116, Geneva, Switzerland, 1990.
[43] WHO, Mono- and disubstituted methyltin, butyltin, and octyltin compounds, Concise International Chemical Assessment Document No. 73, Geneva, Switzerland, 2006.
[44] D.N. Van, S.R.K. Muppala, W. Frech, S. Tesfalidet, Anal. Bioanal. Chem. 386 (2006) 1505.
[45] G.A. Zachariadis, E. Rosenberg, J. Chromatogr. B 877 (2009) 1140.
[46] E.A. Clark, R.M. Sterritt, J.N. Lester, Environ. Sci. Technol. 22 (1988) 600.
[47] M.A. Champ, F.L. Lowestein, Oceanus 30 (1987) 69.
[48] A. Weidenhaupt, C. Arnold, S.R. Muller, S.B. Haderlein, R.P. Schwarzenbach, Environ. Sci. Technol. 31 (1997) 2603.
[49] P.H. Dowson, J.M. Bubb, J.N. Lester, Appl. Organomet. Chem. 7 (1993) 623.
[50] G.M. Gadd, Sci. Total Environ. 258 (2000) 119.
[51] M. Hoch, J.A. Azcarateb, M. Lischick, Environ. Pollut. 123 (2003) 217.
[52] F. Bianchi, M. Careri, M. Maffini, A. Mangia, C. Mucchino, J. Anal. At. Spectrom. 21 (2006) 970.
[53] I. Arrambarri, R. Gracia, E. Millán, Chemosphere 51 (2003) 643.
[54] D.M. Santos, I.P. Araujo, E.C. Machado, M.A.S. Carvalho-Filho, M.A. Fernandez, M.R.R. Marchi, A.F.L. Godoi, Mar. Pollut. Bull. 58 (2009) 1922.
[55] P.N. Carvalho, P.N.R. Rodrigues, M.C.P. Basto, M.T.S.D. Vasconcelos, Environ. Monit. Assess. 159 (2009) 183.
[56] M. Choi, H.-B. Moon, J. Yu, J.-Y. Eon, H.-G. Choi, Arch. Environ. Contam. Toxicol. 58 (2010) 394.
[57] A. Garg, R. Anton-Martin, E. Garcia-Luque, I. Riba, T.A. del Valls, Ecotoxicology 18 (2009) 1029.
[58] A.L. Pletsch, M. Beretta, T.M. Tavares, Quim. Nova 33 (2010) 451.
[59] M. Ceulemans, F.C. Adams, Anal. Chim. Acta 317 (1995) 161.
[60] C.L. Alzieu, J. Sanjuan, J.P. Deltreil, M. Borel, Mar. Pollut. Bull. 17 (1986) 494.
[61] T.M. Nemanič, R. Milačič, J. Ščančar, Water Air Soil Pollut. 196 (2009) 211.
[62] R. Yang, D. Cao, Q. Zhou, Y. Wang, G. Jiang, Environ. Int. 34 (2008) 804.
[63] A. Sudaryanto, S. Takahashi, I. Monirith, A. Ismail, M. Muchtar, J. Zheng, B.J. Richardson, A. Subramanian, M. Prudente, N.D. Hue, S. Tanabe, Toxicol. Chem. 21 (2002) 2119.
[64] C.H. Tang, W.H. Wang, J. Environ. Monit. 11 (2009) 1601.
[65] J.G. Rodrigues, A. Borja, J. Franco, J.I.G. Alonso, J.M. Garmendia, I. Muxika, C. Sariego, V. Valencia, Sci. Total Environ. 407 (2009) 4333.
[66] F. Zanon, N. Rado, E. Centanni, N. Zharova, B. Pavoni, Environ. Monit. Assess. 152 (2009) 35.
[67] B.J. Alloway, Heavy Metals in Soils, John Wiley & Sons, New York, 1990.
[68] I. Héninger, M.P. Gautier, M. Astruc, L. Galvez, V. Vignier, Chem. Spec. Bioavailab. 10 (1998) 1.
[69] A.K. Pendias, H. Pendias, Trace Elements in Soils and Plants, third ed., CRC Press, Boca Raton, 2001.
[70] R. Götz, O.-H. Bauer, P. Friesel, T. Herrmann, E. Jantzen, M. Kutzke, R. Lauer, O. Paepke, K. Roch, U. Rohweder, R. Schwartz, S. Sievers, B. Stachel, Chemosphere 67 (2007) 592.
[71] J. Heroult, Y. Nia, L. Denaix, M. Bueno, G. Lespes, Chemosphere 72 (2008) 940.
[72] J.H. Huang, E. Matzner, J. Plant Nutr. Soil Sci. 167 (2004) 33.
[73] T. Sterckeman, F. Douay, D. Baize, H. Fourrier, N. Proix, C. Schvartz, Geoderma 136 (2006) 912.
[74] Y. Nakamaru, S. Uchida, J. Environ. Radioact. 99 (2008) 1003.
[75] D.L. Sparks, Environmental Soil Chemistry, Academic Press, San Diego, 1995.
[76] A. Giacalone, A. Gianguzza, A. Pettignano, S. Sammartano, Appl. Organometal. Chem. 20 (2006) 706.
[77] H. Pinochet, C. Tessini, M. Bravo, W. Quiroz, I.D. Gregory, Environ. Monit. Assess. 155 (2009) 341.
[78] C.G. Arnold, A. Ciani, S.R. Müller, A. Amirbahman, R.P. Schwarzenbach, Environ. Sci. Technol. 32 (1998) 2976.
[79] M. Bueno, A. Astruc, J. Lambert, M. Astruc, P. Behra, Environ. Sci. Technol. 35 (2001) 1411.
[80] M. Abalos, J.M. Bayona, R. Compañó, M. Granados, C. Leal, M.D. Prat, J. Chromatogr. A 788 (1997) 1.
[81] C. Dietz, J. Sanz, E. Sanz, R.M. Olivas, J. Chromatogr. A 1153 (2007) 114.
[82] P. Quevauviller, O.F.X. Donard, E.A. Maier, B. Griepink, Mikrochim. Acta 109 (1992) 169.
[83] J.J. Cleary, A.R.D. Stebbing, Mar. Pollut. Bull. 18 (1987) 238.
[84] S. Chiavarini, C. Cremisini, T. Ferri, R. Morabito, A. Perini, Sci. Total Environ. 101 (1991) 217.
[85] P.M. Stang, R.F. Lee, P. Seligman, Environ. Sci. Technol. 26 (1992) 1382.
[86] J.L. Gómez-Ariza, I. Giáldez, E. Morales, Environ. Pollut. 108 (2000) 279.
[87] P. Quevauviller, O.F.X. Donard, Fresenius J. Anal. Chem. 339 (1991) 6.
[88] R.M. Meena, A. Garg, S. Jadhav, Bull. Environ. Contam. Toxicol. 82 (2009) 586.
[89] M.I. Venkatesan, N. Chalaux, J.M. Bayona, E. Zeng, Environ. Pollut. 99 (1998) 263.
[90] M. Abalos, J.M. Bayona, P. Quevauviller, Appl. Organomet. Chem. 12 (1998) 541.

[91] J.L. Gómez-Ariza, E. Morales, I. Giáldez, D.S. Rodas, A. Velasco, J. Chromatogr. A 938 (2001) 211.
[92] S. Aguerre, G. Lespes, V. Desauziers, M.P. Gautier, J. Anal. At. Spectrom. 16 (2001) 263.
[93] J.L. Gómez-Ariza, E. Morales, I. Giáldez, R. Beltran, J.A.P. Escobar, Fresenius J. Anal. Chem. 357 (1997) 1007.
[94] H. Serra, J.M.F. Nogueira, J. Chromatogr. A 1094 (2005) 130.
[95] J. Muñoz, J.R. Baena, M. Gallego, M. Valcárcel, J. Chromatogr. A 1023 (2004) 175.
[96] E. Graupera, C. Leal, M. Granados, M.D. Prat, R. Compañó, J. Chromatogr. A 846 (1999) 413.
[97] M. Ceulemans, C. Witte, R. Łobiński, F.C. Adams, Appl. Organomet. Chem. 8 (1994) 451.
[98] F. Pannier, A. Astruc, M. Astruc, Anal. Chim. Acta 287 (1994) 17.
[99] J. Kuballa, R.D. Wilken, E. Jantzen, K.K. Kwan, Y.K. Chau, Analyst 120 (1995) 667.
[100] M. Nagase, K. Hasebe, Anal. Sci. 9 (1993) 517.
[101] M. Nagase, H. Kondo, K. Hasebe, Analyst 120 (1995) 1923.
[102] D.S. Forsyth, C. Cleroux, Talanta 38 (1991) 951.
[103] F. Pannier, A. Astruc, M. Astruc, Anal. Chim. Acta 327 (1996) 287.
[104] C.C. Pinasseau, A. Astruc, G. Lespes, M. Astruc, J. Chromatogr. A 750 (1996) 317.
[105] C. Leal, M. Granados, R. Compañó, M.D. Prat, J. Chromatogr. A 809 (1998) 39.
[106] J.L. Gómez-Ariza, E. Morales, R. Beltran, I. Giraldez, M.R. Benitez, Analyst 120 (1995) 1171.
[107] T. Tsuda, H. Nakanishi, S. Aoki, J. Takebayashi, J. Chromatogr. A 387 (1987) 361.
[108] Q. Xiao, B. Hu, M. He, J. Chromatogr. A 1211 (2008) 135.
[109] N.P. Vela, J.A. Caruso, J. Anal. At. Spectrom. 11 (1996) 1129.
[110] R. Alzaga, J.M. Bayona, J. Chromatogr. A 655 (1993) 51.
[111] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[112] S. Aguerre, C. Pecheyran, G. Lespes, E. Krupp, J. Anal. At. Spectrom. 16 (2001) 1429.
[113] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcolumn Sep. 11 (1999) 737.
[114] J. Vercauteren, C. Pérès, C. Devos, P. Sandra, F. Vanhaecke, L. Moens, Anal. Chem. 73 (2001) 1509.
[115] A. Prieto, O. Zuloaga, A. Usobiaga, N. Etxebarria, L.A. Fernández, C. Marcic, A. de Diego, J. Chromatogr. A 1185 (2008) 130.
[116] H. Liu, P.K. Dasgupta, Anal. Chem. 68 (1996) 1817.
[117] V. Colombini, C.B. Montigny, L. Yang, P. Maxwell, R.E. Sturgeon, Z. Mester, Talanta 63 (2004) 555.
[118] H. Shioji, S. Tsunoi, H. Harino, M. Tanaka, J. Chromatogr. A 1048 (2004) 81.
[119] T.M. Nemanič, R. Milačič, J. Ščančar, Int. J. Environ. Anal. Chem. 87 (2007) 615.
[120] T.M. Nemanič, J. Ščančar, R. Milačič, L.K. Zupančičkralj, Acta Chim. Slov. 54 (2007) 40.
[121] W.M.R. Dirkx, R. Lobiński, F.C. Adams, Anal. Chim. Acta 286 (1994) 309.
[122] R. Anderson, Sample, Pretreatment and Separation, John Wiley & Sons, London, 1987.
[123] M. Takeuchi, K. Mizuishi, T. Hobo, Anal. Sci. 16 (2000) 349.
[124] E. Magi, C. Liscio, M. Di Carro, J. Chromatogr. A 1210 (2008) 99.
[125] R. Morabito, P. Massanisso, P. Quevauviller, Trends Anal. Chem. 19 (2000) 113.
[126] M.B.d.l.C. Guntiñas, R. Scerbo, S. Chiavarini, P. Quevauviller, R. Mobarito, Appl. Organomet. Chem. 11 (1997) 693.
[127] J.A. Stäb, U.A.Th. Brinkman, W.P. Confino, Appl. Organomet. Chem. 8 (1994) 577.
[128] J. Dachs, R. Alzaga, J.M. Bayona, P. Quevauvillier, Anal. Chim. Acta 286 (1994) 319.
[129] H. Harino, M. Fukushima, M. Tanaka, Anal. Chim. Acta 264 (1992) 91.
[130] Y.K. Chau, P.T.S. Wong, G.A. Bengert, Environ. Sci. Technol. 54 (1982) 246.
[131] R. Lobinski, W.M.R. Dirkx, M. Ceulemans, F.C. Adams, Anal. Chem. 64 (1992) 159.
[132] W.M.R. Dirkx, F.C. Adams, Mikrochim. Acta 109 (1992) 79.
[133] D.S. Page, Mar. Pollut. Bull. 20 (1989) 129.
[134] P. Schubert, I.F. Escobar, E. Rosenberg, J.M. Bayona, J. Chromatogr. A 810 (1998) 245.
[135] K.C. Thompson, D.R. Thomerson, Analyst 99 (1974) 595.
[136] K.M. Attar, A. Appl. Organomet. Chem. 10 (1996) 317.
[137] E. Beceiro-Gonzáles, A. Guimaraes, M.F. Alpendurada, J. Chromatogr. A 1216 (2009) 5563.
[138] L. Segovia-Martínez, A. Bouzas-Blanco, P. Campíns-Falcó, A. Seco-Torrecillas, Talanta 80 (2010) 1888.
[140] J.I.G. Alonso, A.S. Medel, L. Ebdon, Anal. Chim. Acta 283 (1993) 261.
[141] F. Pannier, X. Dauchy, M.P. Gautier, A. Astruc, M. Astruc, Appl. Organomet. Chem. 7 (1993) 213.
[142] G. Schulze, C. Lehmann, Anal. Chim. Acta 288 (1994) 215.
[143] R. Compañó, M. Granados, C. Leal, M.D. Prat, Anal. Chim. Acta 302 (1995) 185.
[144] C. Lattard, J.L. Rocca, Analysis 9 (1993) 457.
[145] W.G. Lakata, E.P. Lankmayr, K.F. Müller, Fresenius J. Anal. Chem. 319 (1984) 563.
[146] K. Kadokami, T. Uehiro, M. Morita, K. Fuwa, J. Anal. At. Spectrom. 3 (1988) 187.
[147] X. Dauchy, R. Cottier, A. Batel, R. Jeannot, M. Borsier, A. Astruc, M. Astruc, J. Chromatogr. Sci. 31 (1993) 416.
[148] Z.H. Yu, M. Jing, X.R. Wang, D.Y. Chen, Y.L. Huang, Spectrosc. Spect. Anal. 29 (2009) 2855.
[149] X. Dauchy, R. Cottier, A. Batel, M. Borsier, A. Astruc, M. Astruc, Environ. Technol. 15 (1994) 569.
[150] W. Langseth, Talanta 31 (1984) 975.
[151] E.G. Toledo, R. Compañó, M.D. Prat, M. Granados, J. Chromatogr. A 946 (2002) 1.
[152] A. Praet, C. Dewaele, L. Verdonck, G.P.v.d. Kelen, J. Chromatogr. A 507 (1990) 427.
[153] A. Astruc, M. Astruc, R. Pinel, M.P. Gautier, Appl. Organomet. Chem. 6 (1992) 39.
[154] D.W. Hausler, L.T. Taylor, Anal. Chem. 53 (1981) 1227.
[155] E.J. Parks, R.B. Johannesen, F.E. Brinckman, J. Chromatogr. A 255 (1983) 439.
[156] A.S. Medel, B. Aizpun, J.M. Marchante, E. Segovia, M.L. Fernandez, E. Blanco, J. Chromatogr. A 683 (1994) 233.
[157] J.G. Dorsey, M.T. DeEchegaray, J.S. Landy, Anal. Chem. 55 (1983) 924.
[158] U.T. Kumar, J.G. Dorsey, J.A. Caruso, E.H. Evans, J. Chromatogr. A 654 (1993) 261.
[159] W.L. Shen, N.P. Vela, B.S. Sheppard, J.A. Caruso, Anal. Chem. 63 (1991) 1491.
[160] E. Pobozy, B. Gloèd, J. Kaniewska, M. Trojanowicz, J. Chromatogr. A 718 (1995) 329.
[161] K.S. Whang, C.W. Whang, Electrophoresis 18 (1997) 241.
[162] M. Farnsworth, J. Pekola, Anal. Chem. 26 (1954) 735.
[163] R.E.D. Clark, Analyst 61 (1936) 242.
[164] H. Teicher, L. Gordon, Anal. Chem. 25 (1953) 1182.
[165] C.L. Luke, Anal. Chem. 28 (1956) 1276.
[166] A. Engberg, Analyst 98 (1973) 137.
[167] F. Vernon, Anal. Chim. Acta 71 (1974) 192.
[168] M.D. Booth, B. Fleet, Anal. Chem. 42 (1970) 825.
[169] W. Langseth, J. Chromatogr. A 315 (1984) 351.
[170] E.J. Parks, R.B. Johannesen, F.E. Brinckman, J. Chromatogr. A 255 (1983) 439.
[171] M.J.F. Leroy, P. Quevauviller, O.F.X. Donard, M. Astruc, Pure Appl. Chem. 70 (1998) 2051.
[172] S.G. Salgado, M.A.Q. Nieto, M.M.B. Simón, Talanta 68 (2006) 1522.
[173] W. Kleibohmer, K.F. Cammann, Freseius' Z. Anal. Chem. 335 (1989) 380.
[174] W.A. MacCrehan, Anal. Chem. 53 (1981) 74.
[175] F.E. Brinckman, W.R. Blair, K.L. Jewett, W.P. Iverson, J. Chromatogr. Sci. 15 (1977) 493.
[176] P. Rivaro, L. Zaratin, R. Frache, A. Mazzucotelli, Analyst 120 (1995) 1937.
[177] R.M. Harrison, S. Rapsomanikis, in: R.M. Harrison, S. Rapsomanikis, E. Horwood (Eds.), Ellis Horwood, Chichester, 1989, p. 299.
[178] S.C.K. Shum, R. Neddersent, R.S. Houk, Analyst 117 (1992) 577.
[179] V.F. Hodge, S.L. Seidel, E.D. Goldberg, Anal. Chem. 51 (1979) 1256.
[180] A.O. Valkirs, P.F. Seligman, G.J. Olson, F.E. Brinckman, C.L. Matthias, J.M. Bellama, Analyst 112 (1987) 17.
[181] J.L. Gómez-Ariza, R. Beltrán, E. Morales, I. Giraldez, M.R. Benitez, Appl. Organomet. Chem. 8 (1994) 553.
[182] G.A. Zachariadis, E. Rosenberg, Talanta 78 (2009) 570.
[183] N.S. Thomaidis, A.S. Stasinakis, G. Gatidou, R. Morabito, P. Massanisso, T.D. Lekkas, Water Air Soil Pollut. 181 (2007) 201.
[184] B. Antizar-Ladislao, J. Environ. Monit. 11 (2009) 85.
[185] R. Cassi, I. Tolosa, J. Bartocci, S.d. Mora, Appl. Organomet. Chem. 16 (2002) 355.
[186] G. Zhai, J. Liu, L. Li, L. Cui, B. He, Q. Zhou, G. Jiang, Talanta 77 (2009) 1273.
[187] P.N. Carvalho, L.F. Pinto, M.C.P. Basto, M.T.S.D. Vasconcelos, Microchem. J. 87 (2007) 147.
[188] M. Üveges, L. Abrankó, P. Fodor, Talanta 73 (2007) 490.
[189] C.H. Tang, W.H. Wang, Anal. Chim. Acta 581 (2007) 370.
[190] C.B. Montigny, G. Lespes, M.P. Gautier, J. Chromatogr. A 896 (2000) 149.
[191] C.B. Montigny, G. Lespes, M.P. Gautier, Water Res. 38 (2004) 933.
[192] P. Behra, É.L. Théobald, M. Bueno, J.J. Ehrhardt, J. Colloid Interface Sci. 263 (2003) 4.
[193] J.S. Burt, G.F. Bell, Mar. Pollut. Bull. 30 (1995) 723.
[194] L. Yang, J.W.H. Lam, J. Anal. At. Spectrom. 16 (2001) 724.
[195] K. Elgethun, C. Neumann, P. Blake, Chemosphere 41 (2000) 953.
[196] P.M. Sarradina, Y. Lapaquellerieb, A. Astruc, C. Latoucheb, M. Astruc, Sci. Total Environ. 170 (1995) 59.
[197] J.H. Huang, D. Schwesig, E. Matzner, Environ. Pollut. 130 (2004) 177.
[198] T.C. Hung, W.K. Hsu, P.J. Mang, A. Chuang, Environ. Pollut. 112 (2001) 145.
[199] T.C. Hung, T.Y. Lee, T.F. Liao, Environ. Pollut. 102 (1998) 197.
[200] R.B. Rajendran, H. Tao, A. Miyazaki, R. Rameshb, S. Ramachandranb, J. Environ. Monit. 3 (2001) 627.
[201] G. Lespes, V. Desauziers, C. Montigny, M. Potin-Gautier, J. Chromatogr. A 826 (1998) 67.
[202] S.K. Atirekalanp, S. Tanabe, J. Sanguansin, Mar. Pollut. Bull. 34 (1997) 894.
[203] A.S. Stasinakis, N.S. Thomaidis, A. Nikolaou, A. Kantifes, Environ. Pollut. 134 (2005) 431.
[204] N. Watanabe, H. S-i Sakai, Takatsuki, Chemosphere 31 (1995) 2809.
[205] J.H. Yen, C.C. Tsai, C.C. Su, Y.S. Wang, Ecotoxicol. Environ. Saf. 49 (2001) 164.
[206] C.C. Pinasseau, G. Lespes, M. Astruc, Talanta 44 (1997) 1163.
[208] J. Sanz, M. Pérez, M.T. Martínez, M. Plaza, Talanta 50 (1999) 149.
[209] J. Heroult, T. Zuliani, M. Bueno, L. Denaix, G. Lespes, Talanta 75 (2008) 486.
[210] M. Ceulemans, S. Slaets, F. Adams, Talanta 46 (1998) 395.
[211] P.B. Barrera, G.G. Campos, M.F. Novais, A.B. Barrera, Talanta 46 (1998) 1479.
[212] P. Canosa, R. Montes, J.P. Lamas, M. García-López, I. Orriols, I. Rodríguez, Talanta 79 (2009) 598.
[213] S. Simon, M. Bueno, G. Lespes, M. Mench, M. Potin-Gautier, Talanta 57 (2002) 31.

[214] G. Zhai, J. Liu, L. Li, L. Cui, B. He, Q. Zhou, G. Jiang, Talanta 77 (2009) 1273.
[215] G. Yang, J. Xu, L. Xu, G. Chen, F. Fu, Talanta 80 (2010) 1913.
[216] X. Wang, H. Jin, L. Ding, H. Zhang, H. Zhang, C. Qu, A. Yu, Talanta 75 (2008) 556.
[217] Y.Z. Hua, J. Miao, W. Geng, Q.H. Mei, H.Y. Liang, W.X. Ru, Chin. J. Anal. Chem. 36 (2008) 1035.
[218] A.P. Birjandi, A. Bidari, F. Rezaei, M.R.M. Hosseini, Y. Assadi, J. Chromatogr. A 1193 (2008) 19.