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REVIEW

Analytical Methods for Speciation of Organotins in the Environment

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The growing awareness over the environmental fate of organotin compounds is reflected in the large number of analytical methods developed for their speciation. Organotin compounds have varying degrees of toxicological properties, depending on the nature and number of alkyl groups bonded to the tin atom. Most of the analytical speciation methods applied to actual environmental media have involved prior derivatization to transform organotin compounds into volatile hydrophobic analytes amenable to separation and identification by gas chromatography coupled to a sensitive and selective tin-detector. Evidence exists that members of the same homologous series are related by environmental degradation pathways. Chemical treatment prior to analysis, or high temperatures associated with gas chromatography separation, may alter the relative amounts of organotins in samples and blur the true environment picture. To avoid species redistribution that may occur during derivatization or gas speciation analysis, methods based on liquid chromatography and supercritical fluid chromatography have been investigated. This review documents analytical methods for determination of tin and speciation of organotin compounds, in the hope that it will be of value to those interested in initiating a programme for assessing the impact of such species on the environment.

Keywords: organotin compounds; tin; speciation

INTRODUCTION

The first commercial introduction of dialkyltin compounds was in the USA in the 1940s as stabilizers for PVC against the influence of heat and UV light; they were available in the UK in 1951 and in the rest of Europe and Japan in the mid-1950s. World production of organotin compounds, which was stated in 1950 to have been less than 50 tons,[1] had risen sharply to 35 000 tons in 1986.[2] The plastics industry is still responsible for the largest single usage of organotin compounds, amounting to approximately two-thirds of the consumption. Most of the remainder is accounted for by industrial organotin-based biocides for wood preservation, crop protection, antifouling paints and disinfection. The principal industrial applications of organotin compounds include:[3]

(1) *Monoalkyltins*: PVC stabilizers; homogenous catalysts in esterification reactions; water repellents and fire retardants for woollen and cotton fabrics and for surface treatment of glass.
(2) *Dialkyltins*: Stabilizers against effects of heat and light in PVC used in the construction industry; for roofing, cladding, piping and vinyl wall-coverings and for packaging of food, beverages, pharmaceuticals, cosmetics and giftware; catalysts in the production of polyurethane foams and room-temperature vulcanizing silicones; anthelmintics in poultry management and insecticides for sheep and cattle.
(3) *Trialkyltins*: Biocides in marine antifouling paints; fungicides, insecticides, miticides and antifeedants in agriculture; molluscicides for control of bilharzia; mosquito larvicides; for preservation of wood, paper and leather; moth proofing of textiles; protection of masonry structures; disinfection of industrial circulating water, hospitals and clothing; slime prevention in the paper industry.
(4) *Tetraorganotins*: Stabilizers for transformer oils and intermediates for other organotin compounds.

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Organotin compounds have a range of toxicity, the most toxic being trialkyltins as evident from their broad spectrum of application as biocides.

The increased consumption and widespread use of these chemicals, particularly as biocides, has resulted in their leakage into the environment. Organotin compounds have directly entered the marine and freshwater environment from their use as antifouling paints on ships and boats.[4–10] Other anthropogenic sources include municipal and industrial wastewater, sewage sludge and landfill leachates.[10,11] The active biocides in antifouling paints are mainly bis(tributyltin) oxide (TBTO), tributyltin fluoride (TBTF), tributyltin methacrylate and triphenyltin fluoride (TPTF). Their presence has been reported in a variety of natural waters as well as rainwater.[12–14]

Release of organotins, especially tributyltin (TBT) compounds into seawater as a result of leaching from antifouling paints on ships and boats, has been shown to cause deleterious effects in a variety of non-target organisms. The effects have taken the form of shell thickening, malformation and reduced growth in the Pacific oyster,[15–18] reproductive impairment in dog whelk (sea snail) and gastropods,[19,20] and acute mortality of larval mussels.[21] The lethal tributyltin concentration for sensitive species was reported to be in the range 0.04–16 $\mu g\ l^{-1}$ of Sn (equivalent to 0.1–39 $\mu g\ l^{-1}$ TBT.)[22] Acute effects on salt-water organisms were recorded at concentrations of 1 $\mu g\ l^{-1}$ of TBT; sublethal effects were observed even at concentrations as low as 10 $ng\ l^{-1}$ of TBT.[23] It is now recognized that water concentrations in the range 10–50 parts per trillion (ppt; $ng\ l^{-1}$) can exert lethal and sublethal effects on a wide variety of marine organisms, particularly the more juvenile life-forms.[24–27] TBT can also enter the food chain by accumulation in different marine species and plants destined for human consumption, such as oysters,[28–30] farmed salmon,[31,32] mussels,[33] clams, snails and seaweed.[34] This is especially true in poorly flushed water masses where the exchange rate with the open sea and tidal mixing are limited, and also in areas of high boating activity.[35–37] As a result of these findings, environmental regulations restricting the use of organotin compounds have been enforced in several countries.[38–40].

During the last two decades, the growing concern and awareness over the environmental fate of organotins has stimulated the development of a variety of analytical methods for their determination and speciation. The purpose of this paper is to provide a comprehensive review of the available methods for determination of tin and organotin compounds, in the hope that it will be of value to those interested in initiating a programme for assessing the impact of such species on the environment.

ANALYTICAL METHODS FOR DETERMINATION OF TIN

Tin in environmental samples is usually determined as tin(IV) oxide. Organotin compounds can be completely decomposed by concentrated sulphuric acid to which a small amount of nitric acid is added. After digestion, the sample is ignited to SnO_2. Alternatively, excess of nitric acid can be used followed by photometric determination or reduction of inorganic tin and subsequent titration of the tin(II) ion.[41–42]

Tin at low concentrations has largely been determined by spectrophotometric methods using various reagents such as cacotheline,[44] dithiol,[45,46] haematoxylin,[47] phenylfluorone,[48] 3,5-dinitrocatechol with Nile Blue,[49] Pyrocatechol Violet,[50] 2,6,7-trihydroxy-9-(3-pyridyl)fluorone,[51] Lumogallion[52] and quercitin.[53] Inorganic tin has also been determined spectrofluorimetrically using 3-hydroxyflavone as complexing agent.[54] Most of the reagents, however, lacked in sensitivity, with detection limits in the range 0.02–10 $mg\ l^{-1}$, and had poor selectivity for direct analysis, requiring elaborate extraction and separation procedures.

Atomic absorption spectrometry with a variety of flame types has been used for determination of tin owing to its selectivity,[55,56] but its sensitivity is poor and concentration and separation procedures are usually applied before determination.[57,58] The use of hydride generation followed by flame atomic absorption spectrometry[59–62] or plasma atomic emission spectrometry[63–68] has lowered the detection limit approximately 1000-fold to the 0.05–25 $\mu g\ l^{-1}$ range. A sensitive flame photometric detector selective for tin has been developed for analysis of volatile tin compounds by gas chromatography[69] with the absolute detection limit below 10^{-12} g (1 pg).

Other non-flame techniques have also been developed for determination of traces of tin, including graphite furnace atomic absorption spectrometry,[70–72] neutron activation analysis,[73] mass spectrometry,[74] X-ray fluorescence[75] and polarography.[76–78] A review citing 1067 references covering various analytical methods for determination of tin and other light and heavy metals has been published.[79]

There is no shortage of analytical methods for determination of trace amounts of inorganic tin in environmental samples, but tin metal and most inorganic tin compounds are relatively non-toxic; in fact, the use of tin metal in canning applications relies heavily on its safety in contact with food. However, formation of one or more tin–carbon bonds has a profound effect on its biological behaviour and organotin compounds exert very powerful biocidal activity with varying degrees of toxicity. The toxicological properties of organotin compounds are dependent upon the nature and number of organic groups attached to the tin atom.[80,81] For instance, in the series R_nSnX_{4-n} (R=organic group, X=inorganic anion), maximum biological activity occurs when $n = 3$ for triorganotins with the same alkyl group, regardless of the nature of the X goup, which does not usually influence the toxicity level especially when it is an inorganic group; while mono-organotin compounds have the lowest mammalian toxicity. Tetra-organotins are thought to have delayed-action toxicity, indicating that they may be metabolized into the triorganotin species, particularly in the liver.[82] Moreover, within the same series, a species-dependent toxicity pattern is exhibited according to the nature of the organic substituent. Thus, trimethyltin compounds show maximum biological activity against insects, triethyltin compounds have maximum toxicity for mammals and tributyltin compounds are most active against fungi, molluscs, Gram-positive bacteria, fish and plants. Triaryltin compounds exhibit the same biocidal activity as trialkyltins, but are less toxic to plants. Biological toxicity also decreases with increasing length of the alkyl chain.[3]

Because of such variability in the toxicological properties of organotin compounds, the effective evaluation of environmental risk associated with their usage cannot be achieved by conventional chemical determination of total tin. Analytical methods capable of speciation analysis must be employed.

ANALYTICAL METHODS FOR SPECIATION OF ORGANOTIN COMPOUNDS

Earlier methods for analysis of organotin compounds were based on photometric determinations at mg l^{-1} (ppm) concentration levels, after extraction with a suitable solvent. Trialkyltin, dialkyltin and diaryltin compounds have been determined photometrically after complexation with dithizone,[83,84] diphenylcarbazone,[85] Catechol Violet[86,87] and 4-(2-pyridylazo)resorcinol.[88] Detection limits were lowered to μg l^{-1} (ppb) levels by the use of fluorimetric and polarographic methods. Thus, triphenyltin compounds, extracted with benzene from potatoes, have been determined spectrofluorimetrically after complexation with 3-hydoxyflavone;[89] and they have also been determined in toluene extracts of water, tap water, canal water and synthetic seawater,[90] with detection limits of 4 μg l^{-1}. Anodic stripping voltammetry has been utilized 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[91,92] at the 10 μg l^{-1} level. Morin (2′, 3, 4′, 5, 7-pentahydroxyflavone) has been used as a fluorescence reagent for determination of sub-μg l^{-1} concentrations of organotins, especially dialkyltin compounds, in aqueous and rat tissue samples after solvent extraction.[93] Most of the methods did not offer adequate sensitivity for detection of organotin compounds existing in natural waters at ng l^{-1} (ppt) concentration levels, and were limited in selectivity either to specific or to a narrow range of compounds. The need to develop more sensitive analytical methods for speciation of a broader range of organotin compounds was soon recognized. Several reviews covering speciation of organometallics, including organotin compounds in the aquatic environment, have been published.[94–96]

The methods currently in use utilize hyphenated analytical instruments involving a separation technique such as gas chromatography (GC), liquid chromatography (LC) or supercritical fluid chromatography (SFC). This is coupled to tin-selective detection methods such as atomic absorption, emission or fluorescence spectrometry (AAS, AES, FL); flame photometric detection (FPD); mass spectrometry or inductively coupled and microwave-induced plasma/mass spectrome-

try (MS, ICPMS, MIPMS).[97,98] Liquid-chromatographic[99] as well as gas-chromatographic[100] separation methods for organotins have been reviewed. The potential of different LC separation modes, including reverse-phase, ion-pair, ion-exchange and size-exclusion chromatography, as well as capillary SFC, for speciation of metals and organometallics with particular reference to their interfacing with inductively coupled plasma–mass spectrometry (ICPMS), has also been presented.[101]

Almost all of the available methodologies fall under two basic categories:

(1) *Indirect methods* requiring prior formation of volatile alkyltin derivatives, by either:
   (a) *in situ* derivatization using $NaBH_4$ with on-line cryogenic trappng of derivatized analytes followed by evaporative or gas-chromatographic separation and detection; or
   (b) Prior extraction of ionic organotin compounds by organic solvents, either native or after complexation, followed by derivatization using an alkylating reagent, such as Grignard reagents, and subsequent gas-chromatographic separation and detection.
(2) *Direct methods* based on solution speciation by liquid or supercritical-fluid chromatography.

(1) Formation of volatile alkyltin derivatives

The most sensitive analytical methods for speciation of organotin compounds in environmental matrices are based on derivatization of analytes in the sample prior to separation and measurement with a tin-selective detector. Derivatization to increase the vapour pressure of analytes stems from the need to transform the compounds into volatile forms amenable to separation by evaporative or gas-chromatographic methods, to separate them from the matrix in order to reduce interferences from concomitants in the sample and to concentrate the analytes in order to improve detection limits. Derivatization is achieved, as stated earlier, by two different techniques: (a) hydride formation and (b) alkylation.

(a) Hydride formation

Tin and organotin compounds react with sodium borohydride ($NaBH_4$) in acidic conditions to yield the corresponding volatile hydrides [Eqn [1]).

$$R_nSn_{aq}^{(4-n)+} \xrightarrow[H^+]{NaBH_4} R_nSnH_{(4-n)} + H_2 \uparrow \quad [1]$$

$$n = 1, 2, 3$$
$$R = \text{organic group}$$

The reaction was originally utilized for generation of trace amounts of stannane (SnH_4) from aqueous solutions of tin and determination by atomic absorption spectrometry.[59] The sample is usually mixed and allowed to react with an acidic solution of $NaBH_4$ in a reaction chamber, 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 on the basis of 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.[102]

A number of tin-selective detectors have been successfully interfaced to the hydride generation system for speciation of organotin compounds. These include the flame photometric detector (FPD),[103,104] quartz-furnace atomic absorption spectrometry (QFAAS),[14,105–117] graphite-furnace atomic absorption spectrometry (GFAAS),[103] atomic fluorescence spectrometry[118] and mass spectrometry,[119] other non-specific detectors such as the flame ionization detector (FID)[120] have been used. Hydride generation has been utilized for derivatization of organotins from HPLC and GC effluents prior to detection by QFAAS.[121]

Parts per trillion concentrations (ppt, ng l^{-1} or pg ml^{-1}) of tin and methyltin compounds have been determined by emission spectrometry, using a tin-selective flame photometric detector (FPD) after on-line hydride generation with 1% sodium borohydride ($NaBH_4$) at pH 6.5, in a variety of natural samples including rainwater, estuarine water, tap water, seawater, human urine, digested chicken shell and sea shell.[13] The hydrides were scrubbed by helium gas and cryogenically trapped, by liquid nitrogen (−196 °C), in a glass U-trap packed with 20% w/w OV-3 silicone oil on Chromosorb-W. They were then volatilized by controlled warming and separated on the basis of their boiling points (SnH_4 −52 °C, $MeSnH_3$

1.4 °C; Me_2SnH_2 35 °C; Me_3SnH 59 °C). The volatilized hydrides were swept by the carrier gas into a quartz burner supporting a hydrogen-rich hydrogen–air flame, and detected utilizing the emission band of SnH at 610 nm.

Atomic absorption spectrometry using a hydrogen–air flame supported in a quartz T-tube was used for determination of ng l^{-1} concentrations of Sn(IV), dimethyltin (DMT), trimethyltin (TMT), diethyltin (DEtT), triethyltin (TEtT), monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT) and monophenyltin (MPhT) in seawater, lake water and digested marine algae and sediment.[14] The quartz-tube burner was located axially in the beam path of a tin hollow cathode lamp used for the atomic absorption measurements at a wavelength of 286.3 nm. Organotin compounds with boiling temperatures above 100 °C, such as dibutyltin dihydride (b.p. 150 °C), diphenyltin hydride (b.p. 250 °C) and n-tributyltin hydride (b.p. 280 °C) were volatilized by immersing the trap in a hot-water bath.

An electrothermally heated quartz furnace was also utilized for speciation of organotin compounds produced by the hydride generation technique. It was electrically heated to a temperature of 900–950 °C in the presence of a hydrogen–air mixture. The method was applied for speciation of alkyltin compounds in different compartments of estuarine waters, salt marsh water, river water, ocean water, industrial closed water systems and sediments, with detection limits at the sub-ng l^{-1} level.[105–113]

The graphite furnace of an atomic absorption spectrometer was coupled to a hydride generation system for determination of organotins in seawater samples.[103] The generated hydrides were cryogenically trapped on a packing of 15% OV-3 silicone oil on 60/80 mesh Chromosorb W-AW DMCS for separation of stannane and methylstannanes, and on silanized glass wool for speciation of butyltin stannanes. They were then purged into the internal purge opening of the graphite furnace, which was held at an atomization temperature of 2450 °C. Detection limits obtained were 0.75 ng l^{-1} as Sn, compared to 0.75 ng l^{-1} and 0.3 ng l^{-1} by electrothermal quartz-tube burner atomic absorption spectrometry (QFAAS) and flame emission spectrometry respectively (FPD).

A gas chromatography–flame ionization detector (GC–FID) was coupled to the hydride generation system for speciation of various organotin compounds [$(R_3Sn)_2O$ and R_nSnX_{4-n}: R=Me, Et, Bu, Ph; X=Cl, Br, OH, OMe; $n = 2, 3$] in aqueous samples.[120]

A method utilizing hydride generation coupled to the automatic purge-and-trap sampling system of a GC–FPD was developed, which permitted speciation of both volatile and nonvolatile organotin compounds in aqueous samples. Volatile organotin compounds were purged from the sample solution before addition of 4% $NaBH_4$, while the nonvolatile organotins were purged after hydridization with $NaBH_4$. Both volatile and nonvolatile derivatives were collected, on-line, at ambient temperature in a trap packed with the material Tenax-GC, followed by thermal desorption into a GC–FPD with nitrogen as carrier gas. Tetramethytin, which would have been otherwise undetected, was found in bay-water samples.[104]

Gas chromatography and liquid chromatography have been interfaced to a continuously operated hydride generation system coupled with an electrothermal quartz-tube firebrick-furnace atomic absorption spectrometer for speciation of methytins and ethyltins, with detection limits in the range 8.2–14.0 pg for HPLC–HG–QFAAS with 50 ml injection and 1.5–6.5 pg for GC–HG–QFAAS with 10 µl injection.[121] On-column redistribution of methyltin trichloride and tetramethyltin chloride was observed, precluding the analysis of all four methyltin compounds in admixture.

The hydride generation technique has been well established as a routine method for speciation of organotin compounds. It is especially useful for determination of organotin compounds which form volatile or low-boiling-point hydrides. Difficulties arise in the quantitative determination of organotins which form hydrides of higher boiling points such as di- and tri-phenyltin compounds, because they either remain in the reaction vessel or are caught in the trap, even if the trap is immersed in boiling water.[14] Generated hydrides including high-boiling-point-derivatives can also be extracted, off-line, by suitable organic solvents. Thus hydridized organotins were extracted with hexane from river water and sediment samples[122] and with dichloromethane from water samples,[123, 124] then concentrated and analysed by gas chromatography–electron capture detection (GC–ECD). Hydridized organotins were extracted from water samples with diethyl ether and analysed by GC–FID.[120] They were also extracted with dichloromethane from estuarine and seawater samples,[108, 125, 126] and with hexane

from shellfish tissue and sediment extracts,[126] and analysed by GC–FPD.

Selected methods for speciation of organotin compounds in environmental media by hydride generation are presented in Table 1 (water) and in Table 2 (sediment and biological material).

(b) Alkylation

Chemical derivatization 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, in environmental samples, into their corresponding non-polar tetrasubstituted compounds:

$$R_nSn^{(4-n)+} \xrightarrow[\text{solvent}]{R'MgX} R_nSnR'_{(4-n)} \qquad [2]$$

$$n = 1, 2, 3$$
$$R, R' = \text{organic groups}$$

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) derivatization; (d) clean-up and preconcentration; and (e) analysis.

Acidification is usually accomplished with HBr or HCl to transform the organotin species into a form suitable for extraction by an organic solvent and/or to dissolve solid phases or particles in order to release the compounds from inclusions in the sample, e.g. from biological tissue and suspended particulates in water or inorganic matter in sediment and sludge. Extraction with an organic solvent is necessary because reaction with the Grignard reagent has to be carried out in aprotic solvents, usually 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 derivatization step because they react with the reagent. A complexation agent, such as tropolone or diethyldithiocarbamate, is incorporated in the organic solvent to recover inorganic tin and organotin compounds with fewer and shorter alkyl chains attached to the tin atom, because they exhibit higher solubilities in aqueous solutions, like monobutyltins.[127] Methyltins which are highly solvated in aqueous solution are usually extracted after saturating the aqueous samples with sodium chloride to increase the ionic strength and induce 'salting out'.[128–130] Derivatization of organotin compounds to tetrasubstituted species requires care in handling of the Grignard reagents because they are extremely reactive. After alkylation the excess reagent is destroyed by addition of water or dilute acid solution and the extract dried with a suitable drying agent. Finally, after a clean-up step using alumina, silica gel, or Sep-Pak C_{18} columns, the sample is concentrated by evaporation under a gentle stream of nitrogen and the organotin compounds separated by gas chromatography and detected by a tin-selective detector.

A number of Grignard reagents have been used to convert the ionic organotins in environmental samples into volatile tetrasubstituted alkytin derivatives; they include methyl,[131–135] ethyl-[9, 11, 128, 136, 137] propyl-,[33, 129] butyl-,[130] pentyl-[12, 68, 138–144] and hexyl-magnesium chlorides/bromides.[145–147] The choice of alkylating reagent depends on the analytes being sought. Ethylation and pentylation are usually employed as they allow the determination of methyl-, propyl-, butyl- and phenyl-tin species which are of environmental concern. Specific detectors used for identification of alkyltin derivatives after GC separation include mass spectrometry (MS),[131, 133–136, 147] the flame photometric detector (FPD),[9, 11, 13, 129, 133, 134, 136, 137, 144, 147] quartz-furnace atomic absorption spectrometry (QFAAS)[12, 128, 130, 140, 142, 143] microwave-induced plasma–atomic emission spectrometry (MIPAES)[68, 139] and the nonspecific flame ionization detector (FID).[132, 145]

Tri, di-, and mono-butyltin species from HBr-acidified seawater samples have been extracted with organic solvents such as benzene, chloroform or dichloromethane containing tropolone, followed by methylation using MeMgBr and detection by GC–MS.[122] With 0.05% tropolone as a complexing agent added in the organic solvent, recoveries were improved and $BuSnBr_3$ and inorganic $SnBr_4$ species were also extracted. The benzene extract was subjected to Grignard alkylation without further purification, while chloroform and dichloromethane extracts were concentrated almost to complete dryness and then replaced with benzene or diethyl ether prior to alkylation because these solvents react with the reagent. A typical alkylation procedure used 3 ml of 2.5 M solution of MeMgBr in diethyl ether added to the benzene extract followed by stirring

Table 1 Selected methods for speciation analysis of organotins in water by formation of hydrides

Sample type (size)	Extraction reagents (solvent) and derivatization agent	Instrumental set-up (detection limit, ng l^{-1} as Sn)	Species (recovery, %)	Reference
Seawater, river water, lake water, rainwater, tap water (100 ml)	$NaBH_4$, 2 M Tris/HCl buffer, pH 6.5.	HG–CT–FPD (0.01). Cryo-trap: 20% OV-3 on Chromosorb-W.	MMT, DMT, TMT (96–109).	13
Seawater (100 ml)	$NaBH_4$, 5 M HNO_3, pH 2.	HG–CT–FPD (0.3). Water trap: dry ice/isopropanol. Cryo-trap: 15% OV-3 on Chromosorb-W. HG–CT–GFAAS (0.75).	MMT, DMT, TMT, MBT, DBT, TBT (100–105).	103
Seawater (10 ml)	$NaBH_4$	HG–P/T–GC–FPD (10). P/T trap: Temax GC Column: (2 mm× 6 ft) a glass-packed with 3% SP-2041 and 10% SP-2100.	MMT, DMT, TMT, tetramethyltin, MBT, DBT, TBT, MPhT.	104
Lake water, seawater (100 ml)	$NaBH_4$, 2 M acetic acid.	HG–CT–QFAAS (4–10). Cryo-trap: glass wool.	MMT, DMT, TMT, DEtT, TEtT, MBT, DBT, TBT, MPhT.	14
Seawater, freshwater, sewage treatment effluent (100 ml)	$NaBH_4$, pH 2, 5 M HNO_3. HCl or 65% HNO_3.	HG–CT–QFAAS (0.2–2). Cryo-trap: 3% SP-2100, Chromosorb-G.	MMT, DMT, TMT, MBT, DBT, TBT (75–90).	105–107, 113
Seawater (100 ml)	$NaBH_4$, 2 M acetic acid, pH 5–5.5.	HG–CT–QFAAS (2). Cryo-trap: 3% OV-1 on Chromosorb-W.	DBT, TBT	108–110
Seawater (100 ml)	$NaBH_4$ (dichloromethane).	GC–FPD (2). Column (2 mm×6 ft)[a] glass, 1.5% OV-101 on Chromosorb-G.	DBT, TBT.	108, 125
Seawater (2 l)	$NaBH_4$ (dichloromethane).	GC–FPD (1). Column: (0.32 mm× 25 m) fused silica, 5% cross-linked phenyl methyl silicone.	MBT, DBT, TBT (83.6–88).	125, 126
Seawater (200ml)	$NaBH_4$, acetic acid.	HG–CT–QFAAS (0.2–3). Cryo-trap: 10% OV-101, Chromosorb-G.	MMT, DMT, TMT, MBT, DBT.	111, 112
Water (1 l)	$NaBH_4$, 1 M acetic acid for HG–CT–FID then extraction (diethyl ether) for GC–FID.	HG–CT–GC–FID and GC–FID (2). Cryo-trap: Chromosorb-W. Column: quartz (0.2 mm×20 m), SE-30.	DMT, TMT, DEtT, DBT, TBT, DPhT, TPhT.	120
Seawater (50 ml)	$NaBH_4$, acetic acid.	HG–CT–QFAAS (0.6–1.2). Cryo-trap: 3% SP 2100, Chromosorb-G.	MBT, DBT, TBT (89–112).	114
River water (500 ml)	NaCl–HCl (benzene, then replaced by hexane) ethanolic $NaBH_4$.	GC–ECD (0.4–0.8 μg l^{-1}). Column: 2% OV-17 on Gas Chrom-Q. Organotins determined separately.	TPrT, DBT, TPhT, TBT, (66.6–95.1).	122
Rice-field water (200 ml)	Acetic acid–acetate buffer (dichloromethane, then replaced by hexane), $LiAlH_4$.	GC–ECD (0.34–6). Column: 3% OV-17 on Gas Chrom-Q. Organotins determined separately.	MPht DPhT, TPhT, (<35 for MPt, 62, 108).	123, 124

[a] 6 ft ≃ 1.83 m.

Table 2 Selected methods for speciation analysis of organotins in sediment and biological tissue by formation of hydrides

Sample type (size)	Extraction reagents (solvent) and derivatization agent	Instrumental set-up (detection limit, ng g^{-1} as Sn)	Species (recovery, %)	Reference
Sediment, algae (1 g)	$HClO_4$–HNO_3 for algae, HF–HCl for sediment, final in 2 m HNO_3. Acetic acid, $NaBH_4$ 65% HNO_3.	HG–CT–QFAAS (0.4–1). Cryo-trap: glass wool.	MMT, DMT, TMT, DEtT, TEtT, MBT, DBT, MPhT.	14
Sediment (3 g)	MeOH–HCl reflux in water bath (MeOH). $NaBH_4$, 65% HNO_3	HG–CT–QFAAS (0.07–0.1). Cryo-trap: 3% SP 2100, Chromosorb-G.	MMT, DMT, TMT, MBT, DBT, TBT (45–42).	107
Sediment (10 g)	Acetic acid 15 hr in the dark. $NaBH_4$	HG–CT–QFAAS (0.2–3). Cryo-trap: 10% OV-101, Chromosorb-G.	MMT, DMT, TMT, MBT, DBT.	111, 112
Sediment (10 g)	MeOH–HCl reflux in water bath (MeOH–HCl). Water, NaCl (benzene, replaced by hexane). Ethanolic $NaBH_4$.	GC–ECD (0.4–0.8 μg l^{-1}). Column: 2% OV-17 on Gas Chrom-Q. Organotins determined seperately.	TPrT, DBT, TPhT, TBT (68.2–93.5).	121
Sediment, shellfish tissue (1–2 g)	MeOH–NaOH 45 min, $NaBH_4$ (hexane) or for tissue: (MeOH–dichloromethane, replaced by hexane). $NaBH_4$.	GC–FPD (10). Column: (0.32 mm×25 m) fused silica, 5% cross-linked phenyl methyl silicone.	MBT, DBT, TBT (99.6)	126
Sediment, mussel tissue, algae (0.2–0.5 g)	Acetic acid, overnight or 30 min ultrasonication. $NaBH_4$.	HG–CT–QFAAS (0.5–1.8). Cryo-trap: 3% SP 2100, Chromosorb-G.	MBT, DBT, TBT (algae: 25–44) (mussel: 62–101) (sediment: 6–109).	114
Sediment (1 g)	Acetic acid, overnight. $NaBH_4$.	HG–CT–QFAAS (0.6–1.8). Cryo-trap: 10% Ov-101, Chromosorb-G.	MMT, DMT, TMT, MBT, DBT, TBT (113).	115
Sediment (1.5 g)	MeOH–HCl, ultrasonicate(MeOH). 65% HNO_3 , $NaBH_4$.	HG–CT–QFAAS. Cryo-trap: 3% SP-2100, Chromosorb-G.	MMT, DMT, TMT, MBT, DBT, TBT (80–130).	116
Oyster, mussel, fish tissue (1 g)	MeOH–HCl, 1 hr ultrasonication (MeOH). Acetic acid, $NaBH_4$.	HG–CT–QFAAS (1.8–8.8). Cryo-trap: 10% OV-101, Chromosorb-W.	MBT, DBT, TBT (66–96 fot. TBT)	117

for 0.5 h at room temperature and subsequent treatment with 25 ml of 0.5 M H_2SO_4 solution to destroy excess reagent. The organic phase containing tetra-alkyl species (Bu_3SnMe, Bu_2SnMe_2, $BuSnMe_3$ and Me_4Sn) was decanted and concentrated at reduced pressure for GC–MS speciation by recording the fragment ions at m/z 135 corresponding to $[Me^{120}Sn]^+$, which was common to all organotin species and at m/z 139 for $[MeBuH^{[120]}Sn]^+$, which was common to Bu_2SnMe_2 and Bu_3SnMe species.

Methylation has also been utilized for derivatization of triphenyltin hydroxide, triphenyltin chloride, diphenyltin dichloride, phenyltin trichloride and bis(triphenyltin) oxides in water from rice-fields,[132] and for TBT in seawater, sediment and mussel tissue,[133] followed by GC–FPD determination of the hexane extract.

Ethylation using ethylmagnesium bromide has been utilized for derivatization of trace amounts of butyltin, phenyltin and cyclohexyltin species in rain, seawater, surface water and municipal wastewater, after addition of ascorbic acid and extraction on a tropolone–C_{18} silica cartridge, and in sediment and sludge samples after acid digestion and extraction with diethyl ether/tropolone solution,[11, 136] as well as in sediment and tissue of fish and mussels from freshwater marinas.[9] The alkylethyltin derivatives were determined by GC–FPD. Detection limits for

phenyl- and butyl-tin compounds were 1–10 ng l^{-1} in water, 0.05–2 mg g^{-1} in dry sediment and 9–23 ng g^{-1} in wet biological tissue samples.[9] EtMgBr was also used for derivatization of MBT, DBT, TBT, tripropyltin (TPrT) and TPhT in sediment after supercritical fluid extraction, followed by GC–FPD speciation;[137] and for tin, MBT, DBT, TBT and dioctyltin (diOctT) in sewage sludge followed by gas chromatography GC–quartz furnace–atomic absorption speciation (GC–QFAAS).[128]

Propylmagnesium bromide was used for derivatization of butyltin and phenyltin compounds in mussel tissue,[33, 129] and in freshwater, river water, seawater and sediment.[129]

Butylation was used for derivatization of methyltin compounds and inorganic tin in water from lakes, rivers, marinas and harbours. Experiments were carried out on 100 ml water samples saturated with sodium chloride to improve the recovery of the highly polar and volatile methyltins and acidified with 10 ml of HBr to prevent hydrolysis and adsorption of Sn(IV) species on the container walls. Extraction was performed with 5 ml of 0.1% tropolone–benzene and butylation was carried out with BuMgCl. The butylated methyltin species were analysed by GC–QFAAS.[130]

Butyltin species were determined in water samples from lakes, rivers and harbours after reaction of the tropolone–benzene extract with pentylmagnesium bromide and analysis by GC–FPD, with a detection limit of 0.02 μg l^{-1} for an 8 l extracted sample.[12] Lake sediments were analysed for butyltin compounds after refluxing 1 g samples with a solution of 0.25 g of tropolone in 100 ml benzene, followed by reflux derivatization of the extract with 10 ml of pentylmagnesium bromide. The excess reagent was destroyed with sulphuric acid and the organic layer separated, concentrated by drying and cleaned-up on activated Florisil with hexane as the eluent. The final solution was concentrated and analysed by GC–FPD. Results showed highest concentrations of butyltin species in sediments from areas with extensive boating and shipping activities.[138] Pentylation was also used for alkylation of butyltin compounds from water and sediment extracts followed by determination using gas chromatography coupled to a microwave-induced plasma atomic emission spectrometer (GC–MIPAES), with an absolute detection limit of 0.5 pg.[139–142] TBT in salmon reared in sea pens treated with tri-(n-butyl)tin was determined after digesting the salmon muscle tissue with HCl, extraction with hexane, then alkylation with pentylmagnesium bromide. The final hexane concentrate was analysed using GC–QFAAS with a detection limit of 15 ng TBT g^{-1} wet weight. All of the salmon reared in TBT-treated sea pens, but non in the untreated sea pens, were found to contain detectable concentrations of TBT in their muscle tissues.[22, 143]

Hexylmagnesium bromide has been utilized for alkylation/determination of butyltin compounds in shellfish tissue by GC–FID,[145] in oyster and mussel tissues by GC–FPD[146] and in estuarine waters by GC–FPD with confirmation by GC–chemical ionization–MS.[147]

Selected methods for speciation of organotin compounds in environmental media by alkylation are presented in Table 3 (water) and Table 4 (sediment and biological material).

(2) Direct methods

There is ample evidence that organotin species found in environmental samples are related by environmental degradation pathways.[148] A large number of studies have been conducted on degradation of organotins in soils and water, demonstrating the progressive degradation of triorganotins to di-, mono- and inorganic tin species. Ultraviolet breakdown is one of the most significant modes of degradation in the environment. Certain fungi and bacteria are able to break down organotins, particularly tributyltin and triphenyltin compounds, and also to biomethylate inorganic tin.[3, 149, 150] It is well known that organotin compounds in environmental media are not sufficiently volatile or inert for successful direct GC separation. In fact, most organotins (except the neutral tetraorganotins) are either strongly complexed by natural ligands present in environmental media, such as saline fluids, or behave as classical solvated metal ions.[148]

The earliest work on GC of organotin species was on separation of organotin halides[151, 152] and it was quite apparent that on-column adsorption and degradation, particularly of the more ionic mono- and di-butyltin chlorides, were appreciable and required extensive silylation/deactivation to be carried out.[152] In speciation analysis of methyltin chlorides by GC–QFAAS, it was also observed that on-column rearrangement[153] can occur between methyltin trichloride and tetra-

Table 3 Selected methods for speciation analysis of organotins in water by alkylation

Sample type (size)	Extraction reagents (solvent) and derivatization agent	Instrumental set-up (detection limit, ng l^{-1} as Sn)	Species (recovery, %)	Reference
Seawater (1 l)	HCl, pH 2, tropolone (hexane). MeMgCl.	GC–FPD (0.5–3.5). Column: silica (25 m× 0.2 mm) SE-54 or (30 m×0.25 mm) DB-5. GC–MS : EI–SIM mode.	TBT(61–93), DBT, MBT TPhT (56–89), DPhT	133, 134
Seawater (500 ml)	HBr, tropolone (benzene, chloroform or dichlormethane, replaced by benzene). MeMgBr	GC–MS (10 mg l^{-1}). Column: glass (1.2 m×2 mm), 3% OV-101, OV-101 on Supelcoport. EI–MS multiple peak scanning at *m/z*: 135, 193.	MBT, DBT, TBT (70–195)	131
Rice-field water	(dichloromethane, replaced by hexane). MeMgCl	GC–FPD. Column: capillary (12 m×0.22 mm) OV-101.	MPhT, DPhT, TPhT	132
Rain and surface water, freshwater marina, wastewater (100–500 ml)	HCl, ascorbic acid, Sep-Pak C_{18} cartridge tropolone (diethyl ether–hexane). EtMgBr.	GC–FPD (1–10). Column: glass (30 m×0.3 mm), PS 255, or Pluronic L64 and silica, DB-5.	MBT, DBT, TBT (50–98) MPhT, DPhT, TPhT MCyhT, DCyhT, TCyhT	9, 11, 136
Sewage (200 ml)	HCl, pH1, NaCl, tropolone reflux (toluene, replaced by hexane). EtMgBr	GC–QFAAS (40). Column: silica (30 mm×0.53 mm) coated with dimethylpolysiloxane.	MBT, DBT, TBT (90–109)	128
River water (10–50 ml)	Flow injection. C_{18} microcolumn (citrate–ammonia, pH 9). $NaBEt_4$ on-column ethylation (MeOH).	On-column ethylation–GC–MIPAES (0.1–0.2). Tenax trap. Column: HP-1 capillary (25 m×0.32 mm).	MBT, DBT, TBT, MPhT DPhT, TPhT (80–100)	200
Seawater, freshwater, river water (1 l)	HCl–THF, NaCl, tropolone (benzene). PrMgBr.	GC–FPD (3). Column: capillary (30 m×0.25 mm) coated with methylsilicone.	MBT, DBT, TBT, MPhT DPhT, TPhT (84–99)	129
Bay, harbour and lake water (100 ml–5 l)	HBr, NaCl, tropolone (benzene). BuMgCl.	GC–QFAAS (0.04–2 μg l^{-1}). Column: glass (1.8 m×6 mm) 3% OV-1 on Chromosorb.	MMT, DMT, TMT (85–117)	130
Water (1 l)	Carbopack or LC_{18}, water, tropolone (MeOH). PeMgBr.	GC–FPD (2).	MBT, DBT, TBT (98–100)	144
River water, lake water (8 l)	HCl, pH 1, tropolone (benzene). PeMgBr.	GC–QFAAS (0.02 mg l^{-1}). Column: glass, 3% OV-225.	MBT, DBT, TBT (96–103)	12
River water (1.5 l)	Citric acid–phosphate, pH 5, DDTC (pentane, replaced by iso-octane). PeMgBr(hexane).	GC–MIPAES (0.2). Column: HP-1; (25 m×0.32 mm).	MMT, DMT, TMT, MBT DBT, TBT (>95)	139
River water, seawater (500 ml)	Citric acid–phosphate, pH 5, DDTC (pentane, replaced by iso-octane). PeMgBr	GC—QFAAS (4–10) Column: wide bore (15 m×0.53 mm) RSL 150.	MMT, DMT, TMT, MBT DBT, TBT (101–106)	140, 142
Estuarine water (2 l)	HCl, pH 2, tropolone (hexane). HexylMgBr.	GC–FPD (1). Column: capillary (20 m×0.32 mm) SE-52. GC–MS by Cl for confirmation.	MMT, DMT, TMT MBT, DBT, TBT (32–93)	147

Table 4 Selected methods for speciation analysis of organotins in sediment and biological tissue by alkylation

Sample type (size)	Extraction reagents (solvent) and derivatization agent	Instrumental set-up (detection limit, ng g^{-1} as Sn)	Species (recovery, %)	Reference
Sediment (15 g) and biota (5 g)	Sediment: HCl, pH 2, tropolone (diethyl ether). Biota: MeOH–HCl, NaCl, tropolone (diethyl ether/hexane). MeMgCl.	GC–FPD (0.1–2.0 and 0.4–8.0 for biota). Column: silica (25 m×0.2 mm) SE-54 or (30 m×0.25 mm) DB-5. GC–MS EI–SIM mode.	TBT (61–93), DBT, MBT, TPhT (56–89), DPhT	133, 134
Mussel (2 g)	Saponification: NaOH–MeOH, NaCl (diethyl ether/pentane). Acidic: HCl, NaCl, tropolone (diethyl ether), Extracts replaced (by hexane). MeMgl.	GC–MS (2–8) tri-cyclohexyltin (20). Column: capillary (30 m×0.2 mm) DB5-MS quantitation using optimized *m/z* for each organotin. GC–FPD also used.	MBT(69), MPhT(58), DBT, TBT, FBT, di- and tri-cyclohexyltin, DPhT, TPhT (72–93)	135
Lake sediment (5–15 g), mussel (1 g), fish (8 g)	HCl, pH 2, tropolone (diethylether). EtMgBr	GC–FPD (0.05–2 and 9–23 for biota). Column: fused silica (30 m×0.32 mm) DB-5.	MBT, DBT, TBT (60–95), MPhT, DPhT, TPhT, mono-, di- and tri-cyclohexyltin	9, 11, 136
Sludge (150 ml)	HCl, pH 1, 4 h. NaCl, tropolone (toluene replaced by hexane). EtMgBr.	GC–QFAAS (2 dry mass). Column: silica (30 mm×0.53 mm) coated with dimethylpolysiloxane.	MBT, DBT, TBT (89–114)	128
Sediment (1–3 g)	Supercritical fluid (SFE) extraction (CO_2, MeOH–HCl modifier). Extract collected (iso-octane, replaced by hexane). EtMgCl.	GC–FPD. Column: fused silica (2.5 m×0.32 m) DB-5.	TBT (69.4–82)	137
River sediment (1 g)	MeOH–HCl serial extraction (MeOH), acetate buffer, pH 4.1. $NaBEt_4$.	Ethylation–CT–QFAAS (0.9–1.2 for butyltins). Cryo-trap: 3% SP-2100 on Chromosorb-G.	MMT, DMT, TMT, MBT(29), DBT(123), TBT(92)	199
Sediment	HCl, tropolone (dichloromethane). $NaBEt_4$.	GC–QFAAS.	TBT, DBT, MBT (94), TPhT, DPhT, MPhT	197
Sediment and mussel (10 g)	HCl–THF, NaCl, tropolone (benzene), tetrabutyltammonium–HSO_4/sodium sulphide (benzene). PrMgBr.	GC–FPD (0.5). Column: capillary (30 m×0.25 mm) coated with methylsilicone.	DBT, TBT, TPhT, DPhT (90–100), MBT (70), MPhT (70–100)	129
Mussel (4 g)	HBr–EtOH, ascorbic acid, tropolone (benzene). NaBr (benzene). PrMgBr.	GC–FPD (< 10). Column: fused silica DB-5.	MBT, DBT, TBT, MPhT,DPhT, TPhT	33
Sediment (1 g)	HCl, tropolone reflux (benzene). PeMgBr (replaced by hexane).	GC–FPD (5). Column: 3% OV-225 and 3% OV-1.	TBMT, DBDMT (34–104), MBT, DBT, TBT (55–119)	138
Sediment (5 g)	Acetic acid, water, DDTC in pentane (hexane, replaced by iso-octane). PeMgBr (hexane).	GC–MIPAES (0.05). Column: HP-1 (25 m×0.32 mm).	MMT, DMT, TMT, MBT, DBT, TBT (> 95)	139
Fish tissue (5 g)	HCl digest (hexane). PeMgBr.	GC–QFAAS (5.5). Column: fused silica, dimethylsilicone.	TBT (87–101)	143

Table 4 *Continued*

Sample type (size)	Extraction reagents (solvent) and derivatization agent	Instrumental set-up (detection limit, ng l^{-1} as Sn)	Species (recovery, %)	Reference
Sediment (5 g)	Acetic acid, water, DDTC in pentane (hexane, replaced by iso-octane). PeMgBr.	GC—QFAAS (0.45). Column: wide bore (15 m×0.53 mm) RLS 150.	MBT, DBT, TBT (95–107)	142
Oyster and mussel (15 g)	Sodium sulphate, tropolone in (dichloromethane, replaced by hexane). HexylMgBr.	GC–FPD (5). Column; capillary (25 m×0.25 mm) DB-5. GC–MS for confirmation. EI–SIM mode.	DBT (94), TBT (97), MBT (40)	146
Oyster and mussel (7–10 g)	HCl, NaCl (dichloromethane, replaced by hexane). HexylMgBr.	GC–FID. Column: capillary (30 m×0.32 mm) SE-30.	DBT, TBT (50–80)	145

methyltin chloride, precluding the analysis of all four methyltin compounds in admixture.[121]

Gas chromatography coupled to a helium microwave-induced plasma mass spectrometry (GC–MIPMS) has been utilized for speciation of a mixture of tetra- and tri-vinyl, ethyl and butyltin halides dissolved in dichloromethane.[154] Even though the achieved absolute detection limits (0.09–0.35 pg) were better than values reported by various chromatographic detection methods, by at least one order of magnitude, the chromatogram obtained for the mixture of the tetraorganotins, as shown in the report, revealed three other unknown peaks which eluted with the same retention times as the triorganotin halides, indicating degradation of tetraorganotins to triorganotins. On-column adsorption and degradation of tri-, di- and mono-organotin halides during GC analysis has been improved by hydrogen-halide doping whereby hydrogen halide, either in solution or gaseous form, is injected into the carrier stream of the chromatograph. The presence of a large excess of hydrogen halide shifts the equilibrium in favour or organotin halides, thus minimizing their degradation. This method allowed separation of microgram amounts of mono-, di- and tri-butyltin halides and detection of 1 pg of tripropyltin and tributyltin chlorides.[155] It was successfully applied to GC–FPD determination of butyltin chlorides in sediment extracts, with absolute detection limits of 30 pg tin.[156]

The most sensitive methods for speciation of organotins, as mentioned earlier in this review, rely upon digestion or extraction combined with various chemical means for derivatization to form hydrophobic organotin analytes representative of the original tin-containing species, and of sufficient volatility for speciation by gas chromatography coupled to a sensitive tin-specific detector. However, any chemical manipulation can alter the relative amounts of tin and organotin compounds present in the sample, hence blurring their true environmental impact.

The need to minimize the risk of decomposition at high temperatures associated with GC analysis, and to avoid derivatization which introduces additional handling steps that augment experimental error, has encouraged many investigators to seek alternative methods based on direct solution speciation of organotin compounds. High-performance liquid chromatography is an appropriate tool, provided a sensitive and selective detector is used. The popularity of LC in the speciation of organometallic compounds is well recognized. It offers the possibility of separating ionic, polar and non-polar compounds by a variety of separation techniques, including normal and reverse-phase liquid chromatography (RPLC), reverse-phase ion-pair chromatography (IPLC), size-exclusion chromatography (SEC) and ion-exchange chromatography (IEC).[157] The compatibility of liquid flow rates from LC columns with traditional sample introduction devices makes it easy to interface LC with a variety of sensitive and specific liquid detection systems for direct excitation of the HPLC effluent stream.

Silica columns, which are used extensively with organic and to some extent with organometallic compounds, are unsuitable for separation of the highly polar organotins, which are almost completely adsorbed on the silica.[158] Silanized, C_2, C_8, C_{18} reverse-bonded-phase silica columns

(RPLC) were used for speciation of organotin chlorides with acetone–pentane (normal phase)[121, 159] as mobile phase and also with methanol (reverse phase) followed by GFAAS detection.[160, 161] Reverse-phase ion-pair liquid chromatography (IPLC), which utilizes the same columns and eluents as RPLC, with the exception that a counterion of opposite charge to the analytes is added to the mobile phase, has also been used for separation of tin, TMT, TPhT and TBT in methanolic solutions.[162] The method employed a Spherisorb ODS-2 C_{18} column and a mobile phase of methanol/water/acetic acid (80 : 19 : 1) at pH 3.00, containing 4 mM sodium pentanesulphonate as counterion, followed by detection with ICP–AES at the tin atomic line of 284.00 nm and by ICP–MS at the major tin isotope mass of 120. Detection limits for TMT, TPhT and TBT were 200 ng, 1300 ng and 1700 ng for ICP–AES and 0.4 ng, 1 ng and 0.7 ng for ICP–MS, respectively, utilizing a 200 µl loop.

Micellar liquid chromatography (which is essentially the same as IPLC but uses a detergent as the counterion), coupled to ICP–MS has also been employed for separation of triorganotin compounds on a C_{18} reverse-bonded column. The mobile phase consisted of 3% (v/v) acetic acid, 3% (v/v) propanol, with 0.1 M sodium dodecylsulphate (SDS; negatively charged) as the counterion in water.[156] Using the same C_{18} column, but with 0.05 M SDS and 5 mM KF it was possible to separate mono-, di- and trimethyltin species. Detection limits, with a 100 µl injection loop, were 25 pg, 51 pg and 111 pg for TMT, TET and TPrT chlorides and 46 pg, 26 pg and 126 pg for MMT, DMT and TMT chlorides, respectively.[163]

Cyanopropyl-bonded silica columns were used for speciation of dialkyltin compounds. (DOctT, DBT, DPrT, DPhT, DEtT and DMT) as the chlorides with n-hexane–ethyl acetate (95 : 5) containing 5% acetic acid as eluent[164] and as morin complexes using toluene containing 1–5% acetic acid, 1–5% methanol or ethanol and 0.0015% morin.[165] In the former case, morin was used for post-column derivatization, and the dialkyltin complexes were detected by fluorescence spectrophotometry with excitation and emission at 420 and 500 nm respectively. Detection limits ranged from 1.5 pg for DPhT to 6.0 pg for DMT for 10 µl injection.[165] Monoalkyltin (MBT, MEtT and MMT) chlorides in hexane solution were also separated on a cyano-bonded-phase silica column with toluene containing 5% acetic acid, 2% methanol, 5% acetonitrile and 5 mM morin, followed by fluorescence detection as the morin complexes and trialkyltin (TBT, TEtT, TMT, TPrT and TPhT) chlorides were separated on the same column with hexane containing 0–5% acetic acid and 0–5% ethyl acetate and detected by a refractive index detector.[66]

Di- and tri-butyltin species (DBT and TBT) were separated as tropolone complexes on a cyanopropyl-bonded silica column and determined by GFAAS.[167–169] Monobutyltin did not elute because it was strongly retained on the column and tetrabutyltin eluted with tributyltin. Similar behaviour for MBT was observed with HPLC–ICPMS using a strong ion-exchange column.[170]

Size-exclusion liquid chromatography (SEC) and reverse-bonded chromatography coupled to GFAAS were utilized for analysis of experimental controlled-release biocidal polymers incorporating organotin moieties and organotin silicates in their backbone. The aim of the study was to determine the association of molecular-weight fractions with their tin content, which has important implications with respect to performance specifications of such controlled-release biocides.[171]

Considering the ionic character of organotin species in environmental media,[148] liquid chromatography by ion exchange has been utilized more than other techniques for speciation of organotins. Ion-exchange chromatography coupled to GFAAS, via a 'well sampler' interface, has been used for speciation of a broad range of organotins of industrial and environmental interest.[172] Separation was achieved using commercial, reverse-bonded-phase strong cation-exchange columns (Partisil SCX siloxane-bonded benzenesulphonic acid). Ammonium acetate or diammonium citrate in methanol–water mixtures were used as eluents. The polar organotin species behaved as classical cations in appropriate methanol–water mixtures and their ionic character was demonstrated by the similar capacity factor obtained from chromatograms of various R_3SnX compounds (X = OAc, F, Cl, Br, SO_4, $SnBu_3$, $SnBu_3$ and H). Complete separations were achieved for organotin, $R_nSn^{(4-n)+}$, by class ($n = 2, 3$), by functionality (R=aryl, alkyl, alicyclic) and by geometric isomers (R=n-butyl vs isobutyl; benzyl vs 4-tolyl). By varying the mobile-phase composition and ionic strength, optimized conditions for speciation of mixtures of commercial organotins

could be attained. Column performance varied with individual organotin analyte, as did detection limits in the range 5–30 ng as Sn for 100 µl injections. The method was applied for detection of di- and tri-butyltin in aqueous leachates of sandblasting grits from shipyard operations involving removal of paints from ships' hulls, and also for detection of tripropyl- and tributyltin in the leachate of a marine antifouling organometal polymer. Simultaneous speciation of mono, di- and tri-butyltin compounds was achieved on a Spherisorb SXC strong cation-exchange column coupled to GFAAS with 0.04% potassium dichromate in 2% nitric acid used as an oxidizing matrix modifier.[173] The eluent used was methanol–water solution 60 : 40, (v/v) containing 0.18 M diammonium citrate at pH 6.5 as eluent at a flow rate of 1 ml min^{-1} and a step change in the pH to 4.0 after 28 min. Detection limits for MBT, DBT and TBT were 0.5 ng, 1.1 ng and 0.8 ng (Sn), respectively. The method was applied for speciation of butyltin compounds in acetic acid leachates of sediment reference material.

Ion-exchange chromatography using a strong ion-exchange column (Adsorbosphere SXC) coupled to ICPAES and ICPMS was utilized for speciation of triorganotin compounds in methanolic solutions.[162] The mobile phase was 0.1 M ammonium citrate in 85% (v/v) methanol–water at a flow rate of 1 ml min^{-1}. Detection limits by ICPMS (TMTCl, 0.4 ng; TPhTCl, 1 ng; TBTCl 0.8 ng, with a 200 µl injection loop) were three orders of magnitude lower than those by ICPAES.

A comparable detection limit (0.7 ng of TBT acetate) was obtained for HPLC–ICPMS speciation of TBT on a Zorbax SCX column using an eluent with low methanol content: 30% methanol with 5% acetic acid and 0.05 M ammonium citrate.[174] The same column and eluent were also used for ion-exchange HPLC–fluorecence speciation of tributyltins after post-column derivatization with morin in Brij-35 [polyoxyethylene(23) dodecanol, a non-ionic surfactant] micellar solution.[174] The surfactant was used to allow spectrofluorimetric detection of the morin complex of TBT, which was not otherwise observable[175] along with MBT and DBT, because morin forms sensitive fluorescent chelates with inorganic tin and dialkyltins and the reaction is reported to be poorly sensitive to TBT.[93]

Sensitive detection techniques other than GFAAS, ICPAES, fluorescence, and ICPMS were also coupled to liquid chromatography systems for speciation of organotins. Thus, a laser-enhanced ionization (LEI) detector was interfaced to an ion-exchange chromatographic system for speciation of TBT, TEtT and TPhT in water and sediment, with detection limit of 0.06 ng for a 20 µl injection volume.[176] The LEI technique utilized two pulsed lasers to perform a double-resonance electronic excitation of tin atoms in a premixed air–acetylene flame as the HPLC effluent stream entered the flame region. The resulting excited tin atoms undergo rapid collisional ionization, which is detected by electrodes in the flame.[177, 178]

Laser-excited atomic fluorescence (LEAF) in an air–acetylene premixed flame was used for detection of organotins separated by HPLC on a Partisil SCX strong cation-exchange column, with a detection limit of 0.24 ng for a 20 µl injection.[179]

HPLC was interfaced with a sodium borohydride ($NaBH_4$) hydride generation system coupled to a quartz-tube firebrick-furnace atomic absorption spectrometer for speciation of Sn, MBT, DBT and TBT in methanolic solutions, using a Partisil SCX strong cation-exchange column with an eluent made of 50 mM citric acid, 50 mM LiOH and 4 mM oxalic acid in methanol.[180] The limits of detection were 0.32 ng, 0.48 ng and 0.37 ng for TBT, DBT and MBT respectively, using a 100 µl injection loop. The same arrangement has been used for speciation of methyltin and ethyltin compounds by normal-phase LC on an ODS Spherisorb S5W column with acetone–pentane as eluent.[121] Detection limits were 9.6 pg, 9.5 pg, 8.6 pg, 8.2 pg, 14.0 pg, 13.5 pg, 12.0 pg and 10.0 pg for tetramethyltin, TMT, DMT, MMT, tetraethyltin, TEtT, DEtT and MEtT respectively, using a 50 µl injection volume.

Liquid-chromatographic methods for direct speciation of organotin compounds are presented in Table 5.

Direct speciation of organotin compounds by supercritical fluid chromatography coupled to ICPMS has also been reported, with detection limits in the sub-picogram range (0.034 pg for tetrabutyltin and 0.047 pg for tetraphenyltin;[181] 0.26 pg, 0.80 pg, 0.57 pg and 0.20 pg for tetrabutyltin, TBT, TPhT and tetraphenyltin respectively).[182] TBT in a sediment reference material was determined using ion-spray mass spectrometry–mass spectrometry (MS/MS).[183] The sediment sample was extracted with iso-octane or 1-butanol, diluted with methanol containing 1 mM ammonium acetate, and delivered to the ion-spray tandem mass spectrometer using flow injection.

Table 5 Selected LC methods for direct speciation of organotin compounds

Species (detection limit, ng ml^{-1})	Column used	Mobile phase	Instrumental set-up	Reference
DOcT, DBT, DPrT, DPhT,DEtT, DMT (0.15–6).	Cyanopropyl-bonded silica (250 or 100 mm×4.6 mm).	1–5% Acetic acid +1–5% MeOH or EtOH+0.0015% morin, in toluene.	HPLC–Fluorescence.	165
DOcT, DBT, DPrT, DEtT, DMT, (0.1–1 ng).	Cyanopropyl-bonded silica (250 mm×4 mm) Unisil QCN.	5% Acetic acid in n-hexane–ethylacetate (95 : 5).	HPLC–Fluorescence. Post-column reagent: 0.005% morin in EtOH.	164
MMT, MBT, MEtT, TEtT, DBT, TBT.	Cyanopropyl-bonded silica (250 or 100×4.6 mm).	5% Acetonitrile, 2% MeOH, 5% acetic acid with 5 mM morin in toluene for MMT, MEtT and MBT. 8% acetonitrile in same for DBT, MBT, MMT. 1% Acetic acid, 1% ethyl acetate in hexane for TBT, BT, TMT, TetT and DBT with RI detection.	HPLC–fluorescence for monoalkyltins. HPLC–RI for trialkyltins.	166
TMT, TEtT, TBT, TPrT, TPhT, n-DBT, i-DBT, tricyclohexyltin, D(4-tolyl)T, D BeT, (25–130)	Partisil-10 SCX (250 mm× 4.6 mm).	0.01–0.06 M Ammonium acetate or 0.06–0.0075 M ammonium citrate in MeOH–water (70 : 30).	HPLC–GFAAS.	172, 160
MBT, DBT, TBT (5–11)	Spherisorb SCX (250 mm×4.6 mm).	0.18 M Ammonium citrate in MeOH–water (60 : 40), pH gradient 6.5 to 4.0.	HPLC–GFAAS. Matrix modifier: 0.04% $K_2Cr_2O_7$ in 2% HNO_3.	183
TBT (1), DBT	Nucleosil CH5 (150 mm×4.6 mm).	0.001% Tropolone in toluene.	HPLC–GFAAS. Modifier: 0.01% picric acid.	167–169, 186
TBT (0.2), DBT (0.4)	Pattisil-SCX-10 (250 mm×4.6 mm).	0.18 M Amonium acetate in MeOH–water (60 : 40).	HPLC–ICPMS.	170
TBT (9), TPhT	Partisil-SCX-10 (250 mm×4.6 mm).	0.1 M Ammonium acetate in MeOH–water (80 : 20).	HPLC–ICPMS.	195
MBT, DBT, TBT (2), TBT (15)	Zorbax SCX-10 (250 mm×4.6 mm).	0.05 M Ammonium citrate in MeOH–water (70 : 30).	HPLC–ICPMS. HPLC–Fluorescence. Post-column reagent: 0.005% morin with 0.6% Brij-35 in EtOH.	174, 175
TBT (8), TPhT (10), TMT (4), TBT (8 ppm), TPhT (15 ppm), TMT (2 ppm)	Absorbosphere SCX-5 (250 mm×4.6 mm).	0.1 M Ammonium acetate in water–acetonitrile (15 : 85).	HPLC–ICPMS. HPLC–ICPAES.	162
TBT (7), TPhT (10), TMT (4), TBT (17 ppm), TPh (13 ppm), TMT (2 ppm)	Spherisorb ODS-2 (C_{18}) (250 mm×4.6 mm).	0.004 M Sodium pentanesulphonate in MeOH–water–acetic acid (80 : 19 : 1).	HPLC–ICPMS. HPLC–ICPAES.	162
MBT, DBT, TBT (3.2–4.8)	PRP-X 200 (250 mm×4.1 mm).	0.05 mM citric acid+0.05 mM LiOH+4 mM oxalic acid in MeOH.	HPLC–HG–GFAAS.	180
Tetramethyltin, TMT, DMT, MMT (0.17–0.19) tetraethyltin, TEtT DEtT, MEtT (0.2–0.28)	ODS Spherisorb S5W.	Acetone–pentane (60 : 40). Acetone-pentane (70:30).	HPLC–HG–QFAAS.	121

Table 5 *Continued*

Species (detection limit, ng ml^{-1})	Column used	Mobile phase	Instrumental set-up	Reference
MMT, DMT, TMT, MBT, DBT, TBT (25), DPhT, TPhT	TSK gel ODS-80TM (250 mm×4.6 mm).	8% Acetic acid +0.2% tropolone +54% THF in water.	HPLC–Flame AAS.	193
TMT (0.13), TEtT (0.26), TPrT (0.56), MMT (0.23), DMT (0.13), TMT (0.63)	Spherisorb ODS-2 (C_{18}) (250 mm × 4.6 mm).	8% Acetic acid, 3% propanol, 0.01–0.1 M sodium dodecylsulphate (SDS), 5 mM KF.	HPLC–ICPMS.	163
TBT (3), TPrT, TEtT, TMT	Partisil-10 SCX.	005 M Ammonium acetate, pH 5.1, in MeOH–water (75 : 25).	HPLC–LEI (laser-enhanced ionization). Atom reservoir: all–acetylene flame	176
TBT (35), TEtT, TMT	Partisil-10 SCX.	0.2 M Ammonium acetate pH 4 in MeOH–water (80 : 20).	HPLC–LEAF (Laser-enhanced atomic fluorescence). Atom reservoir: air–acetylene flame.	179

TBT was quantitated by means of selected reaction monitoring of the daughter/parent pair, $BuSnH_2^+/TBT^+$, corresponding to *m/z* 179/291, with a detection limit of 5 pg. The potential of tandem mass spectrometry (MS/MS) for speciation of organotin compounds was demonstrated by monitoring parent–daughter ion relationships for various organotin compounds. Results obtained were sufficiently characteristic to allow direct identification of individual compounds in a mixture without the need for prior derivatization or chromatographic separation.[184]

DISCUSSION

It is quite clear from the preceding survey and tables that both the hydride generation technique and derivatization by alkylation have been successfully utilized for speciation of organotins in environmental samples, with comparable detection limits and recoveries. Alkylation, however, has been applied to far more diverse sample types, including natural waters, wastewater, sludge, sediment and biological materials.

With alkylation, the resulting tetrasubstituted organotin compounds can be purified and concentrated, which is necessary for trace analysis and for determinations carried out on complex matrices. The procedure, however, can only be applied to completely water-free media. Organotin species in aqueous samples including water and sediment have to be extracted into an organic phase and must be dried before alkylation. This introduces several critical handling steps which affect the accuracy and precision of determinations and should be systematically checked during analysis, in order to verify that the final analyical sample remains representative.[185] Such complexity can introduce hindrance to routine analyses.

In the hydride generation technique, the number of steps is reduced, since enrichment and clean-up of samples by cryogenic trapping and thermal desorption is conducted *in situ*. The hydride generation technique has become an established tool in analytical procedures used for speciation of organotin compounds in aqueous samples. This fact is evident from an inter-laboratory study conducted on split samples to compare two different methods for speciation of organotins in estuarine and marine waters, both of which utilized hydride generation as a common step in the procedures.[108] The methods were (1) hydride generation followed by purge-and-trap with boiling-point separation and atomic absorption detection using the hydrogen–air flame quartz burner,[109, 110] an adaptation of methods described in Refs 13 and 14, and (2) simultaneous hydride generation–dichloromethane extraction followed by gas-chromatographic separation with flame-photometric tin-selective detection.[125] Values obtained by the two methods were in good agreement with the theoretical slope of 1.0 for

analysis of di- and tri-butyltin compounds at ng l^{-1} levels in marine and estuarine water samples. Moreover, from the standpoint of routine analysis, the hydride generation technique, as well as direct high-performance liquid chromatography, better fulfil the criteria of simplicity and safety. The hydride generation technique due to its higher sensitivity, offers lower detection limits for analysis of environmental samples and has been incorporated in standard analytical methods for determination of total tin and organotin compounds in marine water, sediment and animal tissue.[127] The technique will still require some care in optimizing the amount of $NaBH_4$ needed for each type of matrix, because organic-rich matrices such as biological tissue and oil-contaminated sediment require more $NaBH_4$ for derivatization than water samples, as the reagent can be used up in reducing the organic matter.[186, 187]

In order for direct liquid-chromatography methods to achieve comparable detection limits, a preconcentration step must be employed. Different extractants from water samples have been proposed in the presence[12, 134] or absence of tropolone.[188–190] The best recoveries seem to be obtained with toluene or hexane.[191]

Solid-phase extraction, using silica-bonded stationary phases which simplify the sample preparation, can also be applied. Silica-gel C_{18}-bonded-phase cartridges have been used for preconcentration of MMT, DMT, TMT, MBT, DBT, TBT DPhT and TPhT from natural waters with various extraction/elution solvents.[9, 11, 136, 174, 192, 193] The performance of cartridges with different polar and non-polar stationary phases (C_{18}, C_8, C_2, phenyl) for quantitative separation of butyltin and phenyltin species has been investigated.[194]

To avoid the complexity of alkylation with reactive Grignard reagents and the lability of generated hydrides, another derivatization reagent, sodium tetraethylborate ($NaBEt_4$), has been introduced. It acts as an ethylation reagent, quantitatively transferring ethyl anions to organotins in aqueous media. Unlike the analogous Grignard reagents and the Sn–C_2H_5 bond, once formed, is more thermally stable than the Sn–H bond. $NaBEt_4$ has been successfully used for ethylation of methyltins and butyltins,[195] phenyltins and cyclohexyltins[196] in sediment extracts followed by GC–QFAAS analysis, and for derivatization of octyltin compounds in water.[197] It has also been utilized for determination of tin, MMT, DMT, TMT, MBT, DBT and TBT in sediment samples by on-line ethylation–cryogenic trapping–QFAAS.[198] It has been incorporated in a semi-automated flow-injection system for on-column preconcentration, ethylation and determination of tin, MBT, DBT, TBT, MPhT, DPhT and TPhT in river water, by GC–MIPAES with detection limits in the sub-ng l^{-1} level.[199]

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