ELSEVIER Journal of Chromatography A, 788 (1997) 1–49

JOURNAL OF CHROMATOGRAPHY A

Review

Analytical procedures for the determination of organotin compounds in sediment and biota: a critical review

Manuela Abalos[a], Josep-Maria Bayona[a], Ramon Compañó[b,*], Mercè Granados[b], Carmen Leal[b], Maria-Dolors Prat[b]

[a]Environmental Chemistry Department, CID-CSIC, Jordi Girona 18–26, E-08034 Barcelona, Spain
[b]Analytical Chemistry Department, University of Barcelona, Diagonal 647, E-08028 Barcelona, Spain

Received 3 April 1997; received in revised form 5 June 1997; accepted 19 June 1997

Abstract

Analytical procedures reported over the last 10 years for the determination of organotin compounds in sediment and biota have been critically reviewed in terms of sample handling, sensitivity, analytical cost, environmental acceptance, accuracy and precision. Critical steps in the analytical procedures are identified. Finally, research needs in extraction and determination are suggested. © 1997 Elsevier Science B.V.

Keywords: Reviews; Sediment; Biota; Organotin compounds

Contents

1. Introduction 2
2. Analytical procedures 3
  2.1. Extraction techniques 3
    2.1.1. Non-polar solvents 3
    2.1.2. Non-polar solvents plus acid 5
    2.1.3. Polar solvents 18
    2.1.4. Supercritical fluid extraction 29
    2.1.5. Basic and enzymatic hydrolysis 32
    2.1.6. Use of complexing agents 32
  2.2. Derivatization techniques 32
    2.2.1. Alkylation reactions 33
    2.2.2. Hydridization reaction 33
  2.3. Clean-up 33
  2.4. Determination techniques 34
    2.4.1. Gas chromatography 34
    2.4.2. Liquid chromatography 35

---

*Corresponding author.

0021-9673/97/$17.00 © 1997 Elsevier Science B.V. All rights reserved.
PII S0021-9673(97)00733-4

2.4.3. Detection limits 36
3. Critical considerations 38
3.1. Storage and sample preparation 38
3.2. Spiking 39
3.3. Calibration 40
3.4. Accuracy 41
3.5. Precision 42
3.6. Environmental acceptance and analytical cost 43
4. Conclusions 44
5. List of abbreviations 45
Acknowledgements 46
References 46

1. Introduction

Speciation of organotin (OT) compounds is of primary interest due to their species-dependent toxicity and their widespread application as biocides [1,2]. Their use in antifouling paints has produced toxic effects to non-target aquatic species, and they are one of the most toxic class of contaminants intentionally released into the aquatic environment [3–6]. As a consequence, triphenyltin and tributyltin are included in the European Union pollutant list (EU, Directive 76/464), in the Rhine and Danube basin monitoring programmes and in the Barcelona Convention protocol for the Protection of the Mediterranean against land-based pollution sources. Environmental Quality Standards below 20 ng l^{-1} in waterways have been issued in several countries, since deleterious effects have been described below few ng l^{-1} [2]. Consequently, monitoring is currently carried out in order to find out the effectiveness of present regulations on OT application as biocides in antifouling paints [7–11].

A great number of OT monitoring programmes have focused on sediment and biota since they allow pollution to be evaluated at a longer time scale [10–14]. Unfortunately, analytical methods are less robust than those applied to aqueous matrices. The strong interaction between OTs and abiotic matrices [1,3] combined with the lability of some analytes (e.g., phenyl- and cyclohexyltins) can bias results. An additional difficulty is that the analytes are not volatile or may lack chromophore groups, which necessitates derivatization steps in most of the speciation techniques based either on gas chromatography (GC) or liquid chromatography (LC). Furthermore, derivatized OTs used as calibrants in GC are not yet commercially available. The assessment of accuracy for butyl- and phenyltin determination is also hampered by the lack of certified reference materials (CRMs) with concurrent certified values.

To date, most of the reviews about OTs have focused on environmental and toxicological aspects, and the analytical procedures were addressed only marginally [2–4,15–18]. Another group of reviews focuses on specific analytical techniques such as supercritical fluid extraction–supercritical fluid chromatography (SFE–SFC) [19,20], the determination of OTs as halides by GC [21], LC–indcutively coupled plasma mass spectrometry (ICP-MS) [22], GC–MS [23], hydride generation cold trapping quartz furnace atomic absorption spectrometry (HG-CT-QFAAS) [24], GC with optical spectrometric detection [25,26] and LC methods [27,28]. Very few comprehensive reviews covering the methodological aspects for environmental relevant matrices have been published [29,30]. However, critical aspects and shortcomings of the analytical methods are not described. Here we review the analytical procedures published over the last 10 years, up to July 1996. We have focused on OT speciation procedures for solid matrices, mostly sediment and biota, which are the most troublesome matrices from the analytical point of view.

The procedures have been grouped according to the polarity of the solvent used in the extraction (Section 2.1). Derivatization and clean-up steps are also described in the same section. Critical steps are identified in each group of extraction techniques. GC and LC techniques and their coupling to detection systems are discussed in terms of resolution, sensitivity and analysis time (Section 2.4). Finally, we also discuss handling, spiking, calibration, accuracy, precision and environmental acceptance of the analytical methods (Section 3).

2. Analytical procedures

OT compounds are found in the aquatic environment associated with a variety of counterions (carbonates, chlorides, sulfates, sulfides, hydroxides and biopolymers) or as oxides, and they can interact with abiotic matrices in different ways (e.g., ionic and/or hydrophobic). Analytical procedures for OT speciation generally attempt to preserve only the organic radical during extraction, whereas the counterion and other tin heteroatomic bonds are cleaved during extraction or derivatization. Most of the analytical procedures developed for OT speciation are based on chromatographic separation, either GC or LC, allowing the simultaneous determination of a variety of tin species.

Tables 1–8 summarise most of the relevant information about the analytical procedures. The tables contain three groups of methods based on the polarity of the solvent used to extract the sample. For practical reasons, the cut-off between solvent polarity is based on its miscibility with water. Additionally, in the case of biotic matrices a group containing the extraction procedures in which the tissue homogenate is dissolved before to the extraction (i.e., enzymatic digestion and basic hydrolysis) is considered. Further, for abiotic samples a group of methods using SFE has been introduced.

The column labelled "Sample treatment" includes all the steps taken before the determination, divided into four groups: (1) pre-treatment, (2) extraction, (3) derivatization and (4) clean-up. A pre-treatment step is included when there is a contact of at least 30 minutes between sample and some of the extracting reagents before the extraction. As extraction step has been strictly considered that in which analytes are isolated from the matrix. Information about derivatization is summarised in terms of the derivatizing agent used. Adsorbent and eluent are specified in relation to the clean-up step. The heading "Determination technique" specifies the separation and detection techniques, columns in GC, columns and mobile phases in LC and packing materials in CT methods. Column entitled "Recovery" includes data from spiked and reference materials. When only one material at one spiking level was analysed, the recovery for each compound is expressed by a single value accompanied by its standard deviation. In contrast, when either different materials or different levels of spiking were analysed, the data are expressed as a range for both recovery and precision. The number of replicate determinations is also stated.

A column of comments includes information about the optimisation of experimental variables, the calibration method and an equation that summarises the steps of the analytical procedure in order to reflect the method complexity.

2.1. Extraction techniques

Extraction methods are described according to the categories outlined in Tables 1–8. However, because most of the reported methods are equally applicable to both biotic and abiotic matrices, extraction procedures are discussed together irrespective of the matrix. Furthermore a section concerning the use of complexing agents has also been added.

2.1.1. Non-polar solvents

These methods account for the 6 and 13% of extraction procedures described for biotic and abiotic matrices, respectively. Extraction is usually carried out on samples dried by freeze-drying, heating or chemical drying. In one analytical procedure, however, OTs are extracted in hexane from an aqueous slurry with an ion-pairing agent [31,32]. Organic solvents of low to medium polarity such as hexane [31–35], benzene [36], toluene [37–40] or dichloromethane (DCM) [12,41–44] are currently used. Extraction is usually performed by shaking and occasionally under reflux [32,36] or sonication [34,39]. Soxhlet extraction is also applied but only with volatile organic solvents (hexane, hexane–acetone, DCM) without complexing agents [32,33,44–46]. The efficiency with which butyltins are extracted from a spiked sediment with non-polar solvents in the presence of a complexing agent is satisfactory [34], as is the extraction of tributyltin (TBT) from a CRM [32]. In contrast, very poor recoveries were obtained for monobutyltin (MBT)

Table 1
Abiotic matrices: non-polar solvents

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked sediment	MBT DBT TBT DBDMeT TBMeT	(2) 1 g dry sample. Ex with 0.25% tropolone in benzene (100 ml, reflux, 2 h) (3) PeMgBr. Ev to 1 ml (4) Activated Florisil/Hexane. Ev to 1 ml	GC–FPD OV-225	Spiking level: 0.01–100 µg g^{-1} (n=3) MBT: 55–103 DBT: 98–180 TBT: 63–106 MeTBT: 94–104 DMeDBT: 34–71 RSD: 5–100%	Calibration: external standards 2Ex+1F+2Ev+CU+D	[36]
Spiked and incurred sediment	TBT	(1) 20 g wet sample+8 g silica+71 g Na_2SO_4 (2) Ex with hexane (400 ml, soxhlet, 48 h). Ev (3) HeMgBr. Ev to 0.1 ml (4) Florisil/hexane. Ev to 0.1 ml	cGC–FPD DB-5	Spiking level: 20–500 ng g^{-1} (n=5) TBT:92–106 RSD: 2–13%	Calibration: TPeT as surrogate P+2Ex+3Ev+CU+D	[33]
Incurred sediment	DBT TBT	(2) 12 g dry sample. Ex with 0.005% tropolone in toluene (10 ml, shaking, 15 h). Ev down to 2 ml	LC–GFAAS Nucleosil 5CN 7.5·10^{-4}% tropolene in toluene		Calibration: standard additions 1Ex+1F+1Ev	[37]
Incurred sediments	MBT DBT TBT	(2) 20 g dry sample. Ex with 0.2% tropolone in DCM (3×100 ml, 3 h). Ev to 10 ml. Addition of hexane. Heating at 60°C until DCM elimination (3) HeMgBr. Ev to 2 ml (4) Alumina–silica (1.5:1)/Pentane. Ev to 0.5 ml	cGC–FPD DB-5		Calibration: I.S. (TeBT) TPrT as surrogate 5Ex+3Ev+3C+D+CU	[12]
PACS-1	DBT TBT	(2) 1 g dry sample. Ex with 0.5% tropolone in hexane (20 ml, reflux, 2 h) (3) EtMgBr	GC–QFAAS	(n=4) DBT: 66+31 TBT: 85±17	Calibration: I.S. (nr) 2Ex+D	[32]
Spiked and incurred sediment	DBT TBT	(2) 0.1-1 g dry sample. Ex with 0.2% tropolone in toluene (5–10 ml, 1 h). Ev to near dryness. Solution in 0.5–1 ml 0.2% tropolone in toluene	LC–GFAAS Cyanopropyl bonded silica 0.001% tropolene in toluene	(a) Spiking level: 1000 ng g^{-1} (n=nr) TBT: 81±9 (b) Comparsion with with a HOAc Ex DBT: 89–107 TBT: 91–105	Extraction conditions were optimised Different columns and mobile phases were studied Calibration: external standards or standard additions 1Ex+1F+1Ev	[38] [40]
Spiked and incurred sediment	MBT DBT TBT	(2) Ex with DDC in hexane (sonication, 30 min). Ev to dryness. Solution in 250 µl n-octane (3) PeMgBr	GC–QFAAS	Spiking level: nr (n=nr) Butyltins: 95 RSD: 5%	Calibration: nr 1Ex+1Ev+D	[34]
Spiked and incurred sediment	TBT TPhT TCyT FBTO	(2) 3 g wet sample+15 g Na_2SO_4. Ex with hexane–acetone (9:1) (110 ml, soxhlet, 9 h). Ev to 1 ml (3) PeMgBr or MeMgI	cGC–MS cGC–AED SPB-1	Spiking level: nr (n=5) TBT: 44±20 TPhT: 80±3	Calibration: external standards 2Ex+2Ev+CU+D	[45]

Table 1. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
		(4) Activated basic alumina/hexane-Et$_2$O (8:2). Ev to 1 ml		TCyT: 85±11 FBTO: 94±5		
Spiked soils and sediments	TPhT TCyT FBTO	(2) 10 g dry sample. Ex with hexane–acetone (9:1) (soxhlet, 12 h). Ev to ca. 4 ml	LC–UV degradation Fluorimetry (morin) Rosil 3 μm cyanopropyl Hexane–THF–HOAc (96:2:2)	Sediment spiking level: 1–2.5 μg g^{-1} ($n=3$) TPhT: 65–105 TCyT: 125–130 FBTO: 100–135 Soils Spiking level: 2 –3 μg g^{-1} ($n=3$) TPhT: 44–60 TCyT: 95–100 FBTO: 91–93	Separation and detection systems were optimised Calibration: external standards 1Ex+1Ev+1F	[46]
Incurred sediments PACS-1F1	F1 MBT DBT TBT DCyHeT TCyHeT MPhT F3 DPhT TPhT	(2) 10g dry sample. Ex with 0.1% tropolone in DCM (2×80 ml, 30 min). Ev to dryness (3) PeMgBr (4) Activated silica gel/Eluent: -Fraction F1: hexane -Fraction F2: DCM–hexane (10:90) -Fraction F3: DCM–hexane (50:50) F1 and F3 evaporated to 1 ml Desulfuration (Cu). Ev to 0.1 ml.	cGC–MS RTx-5	PCAS-1 (n=nr) Recoveries for MBT, DBT and TBT within the 95% confidence interval RSD: nr	Calibration: I.S. (TeBT for fraction F1 and Chrysebe-d2 for fraction F3), DPrT as surrogate 2Ex+2F+3Ev+CU+D	[179]
Spiked and incurred sediments	MBT DBT TBT	(2) 2 g dry sample+20 ml water+6 g NaCl+1 g KI+2 g sodium benzoate. Ex with 0.5% tropolone in hexane (5 ml, 1 h) (3) Aliquot of 1 ml EtMgBr	cGC–QFAAS DB-1	Spiking level: 500 ng g^{-1} (n=nr) MBT: 33–82 DBT: 53–109 TBT: 76–106 RSD: nr	Calibration: external standards 2Ex+D	[31]
Spiked and incurred sediment	DBT TBT	(2) 20 g dry sample. Ex with DCM (200 ml, soxhlet, 6 h). Ev (3) Aliquot of 50% HeMgBr (4) Alumina-silica gel/hexane. Ev	cGC–FPD SE-30 or DB-1	Spiking level: 3 μg g^{-1} ($n=2$) TBT: 99±5	Calibration: I.S. (BTPeT). TPeT as surrogate. 1Ex+2Ev+D+CU	[44]

See List of abbreviations.

and dibutylyin (DBT) from a CRM, particularly in the absence of complexing agents. These results emphasise that matrix effects are evident when a non-polar solvent is used, and that complexing agents should be used to enhance the solubility of ionic OTs.

2.1.2. Non-polar solvents plus acid

This category includes the largest number of extraction procedures evaluated either for abiotic (56%) or for biotic (53%) matrices. Traditionally, the sample is treated with hydrochloric acid with shaking or sonication, followed by sequential solvent extraction. This improves the extraction efficiency of MBT [47]. In spite of their improved ion-pairing properties, few authors use either hydrobromic or acetic acid [32,47–56] or a mixture [57,58]. Despite the variety of acid concentration, exposure time and

Table 2
Abiotic matrices: non-polar solvents plus acid

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked and incurred sediment	DBT TBT	(2) 20 g wet sample+50 ml water+5 ml conc. HCl. Ex with hexane (50 ml, 30 min). Ev of an aliquot to 0.1 ml Solution in ethanol (3) NaBH$_4$ (4) Silica gel/hexane. Ev to 1–5 ml	GC–ECD OV-17 and OV-1	Spiking level: 50-500 ng g^{-1} (n=5) DBT: 93–93 TBT: 86–98 R.S.D.: 1–3%	Composition of the extracting and clean-up step were optimised Calibration: external standards 2Ex+1C+2Ev+CU+D	[67]
Spiked and incurred sediment	MBT DBT TBT MpHT DPhT TPhT	(2) 20 g wet sample+50 ml water+5 ml conc. HCl. Ex with EtOAc (50 ml, 30 min). Ev of an aliquot just to dryness. Solution in ethanol (3) NaBH$_4$ (4) Silica gel/hexane. For MBT, no Ev. For the others: Ev to 1–5 ml	GC–ECD PEG 20 and OV-1	Spiking level: 50–500 ng g^{-1} (n=5) MBT: 70–73 DBT: 90–97 TBT: 90–96 MPhT: 72–86 DPhT: 77–85 TPhT: 74–81 R.S.D.: 2.4%	Composition of the extractant and clean-up step were optimised. Different columns were tested Calibration: external standards 2Ex+1C+2Ev+D+CU	[78]
Incurred sediment	MBT DBT TBT TPhT TCyHeT	(2) 1–20 g wet sample+HCl to pH 2–3. Ex with 0.25% tropolone in Et$_2$O(10+5+5 ml) (3) EtMgBr (4) Silica/hexane–EtO$_2$ (90:10)	cGC–FPD Pluronic L64 or PS 255		Effect of HCl digestion on stability of organotin compounds was examined. Reaction time in derivatization step were optimised Calbiration: DBHeT as surrogate 3Ex+3C+2Ev+D+CU	[100]
Incurred sediment	MBT DBT TBT	(2) wet sample+conc. HCl. Ex with tropolone in hexane. Ev to dryness. Solution in 0.2 ml 1.2·10^{-2} M HCl in ethanol (3) NaBH$_4$ (on-line)	HG-GC–AAS SP-2100		Calibration: TPrT as surrogate 1Ex+1Ev+D	[69]
Spiked sediment	TBT	(2) wet sample+10 ml 6 M HCl. Ex with DCM (20 g, 12–16 h). Ev to dryness. Solution in hexane. Washing with 3% NaOH. Ev to dryness. Digestion with 1 ml conc. HNO$_3$. Ev. Solution in 1 ml 3 M HNO$_3$	GFAAS	Spiking level: nr (n=nr) TBT: 72–99 R.S.D.: 4–10%	Calibration: external standards 2Ex+2C+3Ev	[101]
Spiked sediment	MBT DBT TBT	(1) 2g dry sample+20 ml water+5 ml conc. HCl (overnight) (2) Ex with 10 ml 0.05% tropolone in DCM. Ev to dryness. Solution with 0.5 ml ethanol (4) Silica gel (3) NaBEt$_4$	GC–QFAAS OV-101	Spiking level: nr (n=nr) Butyltins: 94 R.S.D.: nr	Calibration: TPrT as surrogate P+1Ex+1Ev+1F+D	[29]
PACS-1	TBT	(2) 4 g dry sample+4ml 10 M HCl+8 ml MeOH (sonication, 1h). Ex with isooctane (4 ml, 3 min) Dilution of 0.5 ml aliquot in 25 ml with FIA carrier	ISMS–MS FIA carrier: 1 mM NH$_4$OAc in MeOH	(n=5) TBT: 95±4	Calibration: standard additions to the solid 2Ex+1C	[75]

Table 2. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked MESS-1 and PACS-1	MBT DBT TBT	(2) 1 g dry sample+2 ml 10 *M*+HCl+1 ml MeOH (sonication, 1 h)+7 ml water. Ex with hexane–isobutyl acetate (80:20) (1 ml, 10 min) (3) HCl (on-column)	cGC–FPD DB-608	*PACS-1* (n=8) DBT: 92±29 TBT: 90±24	Calibration: standard additions to the solid 2Ex+1C	[108]
Spiked MESS-1 and PACS-1	MBT DBT TBT	(2) 1 g dry sample+2 ml 10 *M* HCl+1 ml MeOH (sonication, 1 h)+7 ml water. Ex with 1.5% tropolone in toluene–isobutyl acetate (80:20) (1 ml, 1 h) (3) HCl (on-column)	cGC–FPD DB-608	*MESS-1* Spiking level: nr (n=4) MBT: 86±4 DBT: 95±2 TBT: 94±5 *PACS-1* (n=6) DBT: 93±29 TBT: 87±30	Calibration: standard additions to the solid 2Ex+1C	[108]
Spiked and incurred seciment	MBT DBT TBT	(2) 5 g partially dried sample+10 ml 1.5 *M* HCl in MeOH. Ex with DCM (20 ml, 3 h). Ev of a 2 ml aliquot. Solution in hexane (3) HeMgBr (4) Florisil–Hexane. Ev to dryness. Solution in 0.2 ml hexane	cGC–FPD SPB-1	Spiking level: nr (n=nr) Butyltins: 93–130 R.S.D.: nr	Concentration of the extracts and drying time were optimised Calibration: I.S. (TPeT). TPrT as surrogate 2Ex+1C+2Ev+D+CU	[103]
Spiked sediment	MBT DBT TBT	(1) 2 g wet sample+5 ml conc. HCl+20 ml water (stand for overnight) (2) Ex with 0.05% tropolone in DCM (10 ml, 10 min). Shaking with 10 ml saturated aqueous solution of FeSO$_4$. Ev to dryness. Solution in ethanol (3) NaBEt$_4$ or NaBH$_4$	GC–MS OV-1 GC–QFAAS OV-101	Spiking level: 600 ng g^{-1} (n=2) TBT: 93–94 R.S.D.: nr	Study of the evaporation step Calibration: TPrT as surrogate P+2Ex+2F+1Ev+D	[102]
Incurred sediment	MBT DBT TBT TeBT	(2) 10 g wet sample+HCl to pH 2+50 g Na$_2$SO$_4$. Ex with 0.1% tropolone in DCM (100 ml, 16 h; 100 ml, 6 h) (3) HeMgBr (4) Silica–alumina/Pentane	cGC–MS DB-5		Reflux extraction was also tested Calibration: I.S. (hexamethylbenzene). TPeT as surrogate 2Ex+2F+1Ev+CU+D	[43]
PACS-1	MBT DBT TBT	*Procedure A* (for DBT and TBT): (1) 4 g dry sample+4 ml MeOH+8 ml HCl (sonication, 1h) (2) Ex with hexane–isobutyl acetate (80:20) (4 ml, 45 min). Ev of an aliquot to dryness. Solution with mobile phase *Procedure B* (for MBT, DBT and TBT): (1) 4 g dry sample+4 ml MeOH+8 ml HCl (sonication, 1 h) (2) Ex with 4 ml 1.5% tropolone in toluene–isobutyl acetate (80:20). Ev to dryness. Solution with mobile phase.	LC–ICP-MS Partisil-10 SCX (A) 0.18 *M* NH$_4$ citrate in MeOH–water (60:40) at pH 6.0 (B) 0.3 *M* NH$_4$ citrate in MeOH–water (60:40) with pH gradient, from 6 to 3.	*Procedure A* (n=7) DBT: 103 TBT: 93 R.S.D.: nr	Calibration: standard additons P+1Ex+1Ev	[109]

(*continued on page 8*)

Table 2. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Incurred sediment	MBT DBT TBT DMeBT MeDBT	(1) 5–25 g wet sample+40 ml conc. HCl (shaking, 2 h+stand for 2 h).+ 10 ml 48% HBr (stand for 15 min) (2) Ex with 0.05% tropolone in pentane (100 ml, 2 min) (3) PeMgBr. Washing with 3% NaOH. Ev to 1 ml	cGC–FPD BP-1		Volume of tropolone solution was optimised Calibration: I.S. (DMeDPeT). P+4Ex+2Ev+F+D	[57]
PACS-1	DBT TBT	(1) 1 g dry sample+5 ml 0.5 *M* HCl in MeOH (4 h) (2) +10 ml saturated NaCl solution. Ex with 0.5% tropolone in hexane (5 ml, 2 h) (3) EtMgBr	GC–QFAAS	(*n*=4) DBT: 84±9 TBT: 79±14	Calibration: I.S. (nr) P+2Ex+D	[32]
PACS-1	DBT TBT	(1) 1 g dry sample+10 ml 6 *M* HCl (1 h) (2) +6 g NaCl. Ex with DCM (5 ml, 4 h). Ev to dryness. Solution in hexane (3) EtMgBr	GC–QFAAS	(*n*=4) DBT: 117±16 TBT: 86±6	Calibration I.S. (nr) P+2Ex+1Ev+D	[32]
PACS-1	DBT TBT	(1) 1 g dry sample+2 ml 10 *M* HCl+1 ml MeOH (1 h) (2) Ex with hexane–isobutyl acetate (80:20) (2 ml, 30 min) (3) EtMgBr	GC–QFAAS	(*n*=4) DBT: 98±18 TBT: 105±5	Calibration I.S. (nr) P+2Ex+D	[32]
PACS-1	DBT TBT	(1) 1 g dry sample+5 ml pure HOAc (4 h) (2) 20 ml water. Ex with 0.5% tropolone in hexane (5 ml, 1 h) (3) EtMgBr	GC–QFAAS	(*n*=4) DBT: 94±10 TBT: 85±10	Calibration I.S. (nr) P+2Ex+D	[32]
Incurred sediments and sludges	MBT DBT TBT MPhT DPhT TPhT TCyT	(1) 5–15 g wet sample+HCl to pH 2 (stand for 30 min) (2) Ex with 0.25% tropolone in Et_2O (×3) Ev to 1–2 ml (3) EtMgBr. Ev (4) Silica gel/Hexane. Ev	cGC–FPD DB-5		Calibration: TPrT, MPeT DPeT, TPeT, TePeT as surrogates 4Ex+3C+3Ev+D+CU	[92] [93] [94]
Spiked and incurred sediments	MBT DBT TBT DPhT TPhT	(2) wet sample (15 g on dry weight basis)+conc. HCl up to pH 2–3. Ex with 0.25% tropolone in Et2O (3×15 ml). Ev to 1 ml (3) MeMgCl. Ev to 0.5 ml (4) Activated silica/Hexane–Et_2O (9:1). Ev	cGC–FPD SE-54	Spiking level: nr (*n*=nr) MBT: 30–110 DBT, TBT and TPhT: 60–91 RSD: nr	Calibration: I.S. (TeBT) 5Ex+1C+3Ev+D+CU	[91]
Spiked sediments	MBT DBT TBT MPhT DPhT TPhT	(2) 10 g wet sample+25 ml 1*M* HCl–THF (1:11). Ex with 0.1% tropolone in benzene (2×50 ml, 30 min). Ex with 500 ml NaCl 25%. Ex of the aqueous phase with 50 ml of 0.1% tropolone in benzene Desulfurization by washing with	cGC–FPD methylsilicone	Spiking level: 100 ng g^{-1} (*n*=3) MBT: 70±6 DBT: 95±5 TBT: 96±8 MPhT: 70±6 DPhT: 100±4	Solvent, % tropolone and %NaCl were optimised for water samples. Reaction time, derivatization reaction and detector response were studied.	[83]

Table 2. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
		3.3% tetrabutylammonium hydrogensulfate and 16% sodium sulfide. Ev to 0.5 ml (3) PrMgBr. Ev to 0.5 ml. Dilution to 5 ml with benzene (4) Florisil–hexane. Ev to 0.5 ml		TPhT: 92±6	Calibration: I.S. (HeTBT) 6Ex+1C+3Ev+D+CU	
Spiked and incurred sediments	Hexane-extractable tin	(1) 10–15 g wet sample+5 ml 2 M HCl (sonication, 1 h, 55°C) (2) Ex with 18 ml hexane. Washing with 3% NaOH. Addition of 1 ml conc. HNO$_3$. Ev. Solution in water	GFAAS	Spiking level: nr (n=nr) 90	Calibration: external standards P+2Ex+1 Ev	[42]
Spiked and incurred sewages and sludges	MBT DBT TBT	*Sludges:* (1) 150 ml sludge+10 ml conc. HCl (1–2 h). pH adjusted to 1–2 (shaking, 2 h) (2) +60 g NaCl. Ex with 0.5% tropolone in toluene (20 ml, 4 h). Ev to near dryness. Solution in hexane (3) EtMgBr (4) 5% activated silica gel-hexane *Sewages:* (2) 200 ml sewage (acidified to pH 1 at time of collection). +60 g NaCl. Ex with 0.5% tropolone in toluene (20 ml, 4 h). Ev to near dryness. Solution in hexane (3) EtMgBr (4) 5% activated silica gel/hexane–Et$_2$O (9:10)	cGC–QFAAS dimethylpolysiloxane	*Sludges* Spiking level: 10–50 ng ml^{-1} (n=2) MBT: 96–103 DBT: 89–95 TBT: 91–114 R.S.D.: 8–9% *Sewages* Spiking level 5–25 ng ml^{-1} (n=2) MBT: 101–109 DBT: 99–109 TBT: 90–104 R.S.D.: 6–8%	Extraction and clean-up conditions were optimised P+2Ex+2Ev+D+CU	[88] [89]
Incurred sediments	MMeT DMeT TMeT TPrT MBT DBT TBT	(2) 5 g sample+20 ml 96% HOAc+10 ml water+3 ml DDC in pentane. Ex with hexane (2×25 ml). Ev (3) PeMgBr	cGC–AED HP-1		Calibration: I.S. (TPrPeT) 4Ex+1Ev+D	[55]
Spiked and incurred sediments and sludges	TBT TeBT	(2) Sample+1 ml conc. HCl. Ex with benzene (50 ml, reflux, 30–40 min)	cGC–AED DB-1	Spiking level: nr (n=3) *Sediment:* TBT: 98±1 TeBT: 93±2 *Sludge:* TBT: 80±1 TeBT: 85±1	Calibration: external standards 2Ex+C	[58]
Spiked and incurred sediments and sludges	TMeT MBT DBT TBT	(1) 5–10 g wet sample+10 ml 1 *M* HCl (1–2 h) (2) +0.1 g ascorbic acid+0.5 ml tropolone solution. Ex with hexane	cGC–AED HP-5	Spiking level: nr (n=2–6) MBT: 10±16 DBT: 33±22	Effect of the number of extractions on the recoveries was studied. Calibration: I.S. (TOcT).	[70]

(continued on page 10)

Table 2. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
	DPhT	(5 ml, sonication) (3) PhMgBr or EtMgBr		TBT: 55±10 DPhT: 12±10 TOcT: 23±9 With 3 extractions: TBT: 90 TOcT: 77	P+2Ex+1C+D	
Spiked and incurred sediments PACS-1 CRM-462	DMeT TMeT DBT TBT	(2) 1 g dry sample+4 ml water+1 ml glacial HOAc+1 ml DDC in pentane. Ex with hexane (25 ml, sonication, 30 min; 25 ml, 30 min). Ev to dryness. Solution in octane (3) PeMgBr (4) Basic alumina/Hexane–Et_2O (9:1). Ev to ca. 0.25 ml	cGC–QFAAS RSL150	Spiking level: 5000 ng g^{-1} (*n*=6) DBT: 103±5 TBT: 95±5 *CRM-462* (*n*=nr) DBT: 100±5 TBT: 93±12 *PACS-1* (*n*=nr) DBT: 134±11 TBT: 98±7	Extraction conditions were optimised. Spiking procedure was studied. Calibration: I.S. (TPrT) 3Ex+2Ev+1C+D+CU	[25]
Incurred sediments	TeBT TBT DBT MBT	(2+3) 5 g wet sample+5 ml water+1 ml conc. HCl. pH adjusted to 5. Addition of 10 ml hexane (shaking, 15 min)+$NaBEt_4$. (shaking, 30 min) Separation of the organic phase. Ev to 1 ml (4) Silica gel/Hexane.·Ev to 1 ml	GC–AAS GC–MS Column: nr		Calibration: nr 1Ex+1Ev+CU+D	[71]
Spiked sediments	DBT TBT	(1) 1 g sample+2 ml conc. HCl (sonication, 30 min) (2) +15 ml MeOH. Ex with isobuty acetate (5 ml, sonication, 30 min). +30 ml water. pH adjusted to 1.5 with NaOAc. Ex with isobutyl acetate (5 ml, sonication, 15 min). Ev to dryness. Solution in MeOH–HOAc	LC–MS (thermospray) Partisil-10 SCX 0.018 *M* NH_4OAc in acetonitrile–water–HOAc (60:35:5)	Spiking level: nr (*n*=nr) DBT: 55 TBT: 67 TPeT: 74 R.S.D.: nr	Effect of pH was studied Solvent selection was made Calibration: TPeT as surrogate P+2Ex+2C+1Ev	[80]
PACS-1	MBT DBT TBT	(2) 5 g sample+10 ml 1% tropolone in water+20 ml HOAc. Ex with hexane (2×25 ml, sonication, 30 min). Ev. Solution in mobile phase	LC–ICP–MS TSK gel ODS 80 TM 0.1% tropolone in MeOH–water HOAc (80:14:6)	(*n*=10) MBT: 0 DBT: 43±40 TBT: 65±17	Calibration: nr 2Ex+Ev	[51]
PACS-1 and spiked PACS-1	TMeT TEtT TPrT TBT TPhT	(2) 0.5 g dry sample+1.25 ml 1 *M* HCl–THF (1+11). Ex with 0.1% tropolone in benzene (2.5 ml, 30 min). Addition of 5 ml 25% NaCl solution+0.1% tropolone in benzene. (2.5 ml, shaking, 30 min). Ev of 2 ml aliquot to dryness. Solution with 5 ml of mobile phase	LC–ICP–MS C_8 $5\cdot10^{-3}$ *M* sodium 1-pentanesulfonate in MeOH–water–HOAc (50:45:5)	Spiking level: 5 $\mu g g^{-1}$ (*n*=nr) TPrT: 106±9 TBT: 108±12 TPhT: 104±6	Calibration: standard addition 2Ex+1C+1Ev	[85]
PACS-1 CRM-462 RM-424 and other	MBT DBT TBT	(2) 1 g dry sample+2 ml conc.HCl+8 ml water. Ex with 0.05% tropolone in-hexane–EtOAc (1:1) (25 ml, sonication, 1 h). Ev to dryness	cGC–AED HP-1 or cGC–QFAAS RSL-150 or	*PACS-1* (*n*=5) MBT: 336±6 DBT: 97±4 TBT: 87±5	Type of acid and solvent were optimised Calibration: I.S. (TPeEtT).	[47]

Table 2. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
incurred sediments		(3) NaBEt$_4$ (4) Basic alumina/Et$_2$O. Ev	HP-1	*CRM-462* (n=5) MBT: 125±16 ng DBT: 114±19 TBT: 91±9 *RM-424* (n=5) DBT: 107±19 TBT: 79±11	2Ex+1C+2Ev+D+CU	
PACS1 CRM-462 RM-424 and other incurred sediments	DBT TBT	(2) 1 g dry sample+4 ml water+1 ml pure HOAc+1 ml DDC in pentane. Ex with hexane (25 ml, sonication, 30 min; 25 ml, magnetic stirring, 30 min), Ev to dryness (3) PeMgBr (4) Basic alumina/Et$_2$O. Ev	cGC–AED HP-1 cGC–QFAAS HP-1	*PACS-1* (n=5) DBT: 132±11 TBT: 98±7 *CRM-462* (n=5) DBT: 100±5 TBT: 93±12 *RM-424* (n=5) DBT: 54±10 TBT: 60±33	Type of acid and solvent were optimised. Calibration: I.S. (TPrPeT). 2Ex+1C+2Ev+D+CU	[47]
Spiked and incurred sediments	TBT	(2) 10–15 g wet sample+5 ml 2M HCl. Ex with 18 ml hexane. Washing with 3% NaOH. Addition of 1 ml conc. HNO$_3$. Ev of hexane. Dilution with water	GFAAS	Spiking level: nr (n=nr) TBT: 90 R.S.D.: nr	Calibration: nr 2Ex+1Ev	[66]
Incurred sediments	DBT TBT TPhT	(2) 20–30 g wet sample+conc. HCl to pH 2–3. Ex with 0.25% tropolone in Et$_2$O (3×15 ml, 30 min). Ev to 5 ml (3) HeMgBr. Ev to 1 ml (4) Silica gel-8% water deactivated Florisil/hexane -Et$_2$O (85:15)	cGC–FPD DB1, DB5 or DB-1701 cGC–MS HP Ultra 2	Spiking level: nr (n=8) DBT: 83±9 TBT: 99±10 TPhT: 96±9	Calibration: external standards (prepared exactly as the samples including clean-up step) 5Ex+3C+2Ev+D+CU	[99]
Spiked and incurred sediments	MBT DBT TBT MPhT DPhT TPhT	(1) 20 g wet sample+50 ml water–HBr (2:3) (1 h) (2) Ex with 0.02% tropolone in pentane (100 ml, 2 h). Ev to ca. 0.5 ml (3) PeMgBr. Ev to 1 ml (4) Florisil/Pentane. Ev to 0.5 or 0.2 ml	cGC–FPD SPB-1	Spiking level: nr (n=5) Butyltins: 100 MPhT: 85 DPhT: 98 TPhT: 100 R.S.D.: 4–10%	Extraction conditions were optimised Calibration: I.S. (DMeDPeT) P+2Ex+1C+3Ev+D+CU	[53]
Spiked sediments PACS-1 CRM-426	MBT DBT TBT TeBT	(2+3) 1 g dry sample+20 ml water. pH adjusted to 4+10 ml hexane+NaBEt$_4$. Ex with hexane. Ev to 1 ml (4) 3% water deactivated silica/Hexane. Ev to 1 ml	cGC–QFAAS DB-1701	Spiking level: 500 ng g^{-1} (n=5) MBT: 76±5 DBT: 86±4 TBT: 92±4 TeBT: 86±4 *PACS-1* (n=3) MBT: 186±54 DBT: 113±18 TBT: 91±16 *CRM-462* (n=3) DBT: 82±15 TBT: 87±13	Calibration: matrix matched standards 1Ex+2Ev+CU+D	[72]

(continued on page 12)

Table 2. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Incurred sediments	TeMT TEtT MBT DBT TBT	(1) 2 g sample+5 g crushed ice+1 ml HCl. Mixed every 10 min for 1 h (2+3) pH adjusted to 5. Ex with hexane and 0.25 ml 10% $NaBEt_4$ (3×10 ml) (4) Activated silica gel/nr	cGC–ICP-MS DB-5		Calibration: nr P+3Ex+CU+D	[73]
Incurred sediment	MBT DBT TBT MPhT DPhT TPhT	(2) 0.5–1 g dry sample+2 ml conc. HCl +10 ml water. Ex with 0.05% tropolone in hexane–EtOAc (1:1) 25 ml, sonication, 1 h). Ev to dryness. Solution with 0.5 ml hexane (3) $NaBEt_4$ (4) Optional clean-up	cGC–FPD HP-1		Calibration: I.S. (TPeEtT) 2Ex+1C+1Ev+D(+CU)	[107]
Spiked sediment and PACS-1	MBT DBT TBT DPhT TPhT TPeT DCyT TCyT MOcT DOcT	(2) 2 g sample+20 ml glacial HOAc+ 20 ml water+8 g NaCl. Ex with 15 ml 0.3% tropolone in toluene. Ev to dryness. Solution in hexane (3) EtMgBr (4) 5% water deactivated silica gel/ Hexane	cGC–AED SPB-1	Spiking level: 250 ng g^{-1} ($n=3$) MBT: 85±6 DBT: 101±3 TBT: 88±2 DPhT: 77±1 TPhT: 88±1 TPeT: 101±5 DCyT: 90±2 TCyT: 84±1 MOcT: 89±2 DOcT: 91±2 *PACS-1:* MBT: 368±4 DBT: 91±8 TBT: 92±3	Various acids and organic solvents were examined. Extraction time was optimised Calibration: I.S. (TPeT) 1Ex+1Ev+D+CU	[50]
Incurred sediment and PACS-1	TBT	(1) 5 g dry sample+40 ml glacial HOAc (stirring, 3 h) (2) Ex with 100 ml pentane. Washing with 3% NaOH. Ev to dryness. Solution with MeOH–HNO_3 (9:1)	GFAAS	(n=nr) 95±3	Calibration: external standards P+2Ex+Ev	[56]

See List of abbreviations.

shaking mechanism, all these procedures are carried out at room temperature. Recently, sonication has become the most widely used stirring method for abiotic matrices, whereas low energy mixing methods are used for biota (e.g., stirring, tumbling etc.). It can be attributed to a higher energy of interaction in case of solid abiotic matrices, whereas OTs in the biota are assumed to be embedded in tissues.

Although medium polarity solvents are usually preferred to extract ionic OTs from abiotic matrices, some authors have questioned this due to their lack of selectivity, which impairs the derivatization reactions because the amount of substances coextracted increase with solvent polarity [47]. Therefore, there is no agreement on the solvents applied for extraction from the matrix. Among them pentane [53,56,57,59], hexane [25,32,42,47,51,55,60–74], isooctane [32,75]; ethyl acetate [76–79], isobutyl acetate [80], benzene [7,48,52,58,74,81–87], toluene [49,50,88,89], diethyl ether [49,50,88–100] and DCM [29,32,43,90,101–106] have been used. Solvent mixtures such as hexane–ethyl acetate [47,67,107], hexane–isobutyl acetate [32,108,109], chloroform–ethyl acetate [110], toluene–isobutyl acetate [108,109], hexane–diethyl ether [91,111–115] have been proposed. Sequential extraction with

Table 3
Abiotic matrices: polar solvents

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked and incurred sediment	TBT	(2) 1 g wet sample. Ex with 1-butanol (3 ml, sonication, 30 min)	LC-flame LEI Partisil-10 SCX 0.05 M NH$_4$OAc in MeOH–water (75:25) pH=5.1	Spiking level: 3000 ng g^{-1} (n=7) TBT: 97 R.S.D.: 8%	Calibration: external standards 1Ex+1C+1F	[157]
Spiked sediment	DBT TBT TPhT	(2) 10 g wet sample. Ex with conc. HCl–MeOH (5:95) (50 ml, reflux, 30 min, 70–80°C). Addition of 100 ml water+10 g NaCl. Ex with benzene (2×50 ml). Ev to 0.5 ml. Dilution with 10 ml hexane (4) Silica impregnated with HCl/Eluent: Trialkyltin: hexane–EtOAc (4:1) Dialkyltin: hexane–EtOAc (2:1) Ev to ca. 0.5 ml (3) NaBH$_4$	GC–ECD OV-17	Spiking level: 2000 ng g^{-1} (n=4) TPrT: 93±3 DBT: 76±4 TBT: 93±2 TPhT: 68±1	Derivatization (time and effect of EtOAc) and clean-up step were optimised Calibration: external standards 1F+5Ex+2Ev+D+CU	[132]
Spiked and incurred sediment	MMeT DMeT TMeT MBT DBT TBT	(2) 1 g dry sample. Ex with 10 ml 2.5 *M* CaCl$_2$–2.5 *M* HCl (15 h) (3) 0.5 ml of supernatant. NaBH$_4$	HG–CT–QFAAS CT packing material nr	Spiking level: 1 μg g^{-1} (n=2) MMeT: 93±21 DMeT: 103±25 TMeT: 96±12 MBT: 70±10 DBT: 93±20 TBT: 97±5	Calibration: I.S. (TeMeT) 1Ex+1F+D	[121]
Spiked and incurred sediment	DBT TBT	(2) 2–4 g wet sample+0.5 ml conc. HCl+25 ml MeOH (30 min, reflux, 80°C). Ex of 1 ml supernatant with cyclohexane (2×1 ml, 5 min). Ev to 1 ml (3) NaBH$_4$	GC–FPD OV-101	Spiking level: 300–1200 ng g^{-1} (n=3) TBT: 79–140 R.S.D.: nr	Extraction time was optimised Calibration: standard additions. DPrT or TPrT as surrogates. 4Ex+1C+D	[129] [130]
Incurred sediment	MMeT DMeT TMeT MBT DBT TBT	(2) 10 g wet sample. Ex with (0.5 ml conc. HCl+20 ml MeOH, 1 h, 80°C (3) 1.5 ml of supernatant. NaBH$_4$	HG–CT–QFAAS SP-2100 or OV-101 on Chromosorb GAW		Calibration: standard additions. TEtT as surrogate. 1Ex+1C+D	[131] [133]
Incurred sediment	MBT DBT TBT	(2) 1 g dry sample. Ex with HOAc (20 ml, shaking, 15 h) (3) 1 ml of supernatant. NaBH$_4$	HG–CT–QFAAS OV-101 on Chromosorb GAW		Calibration: standard additions 1Ex+1C+D	[37]
Incurred sediment	MBT DBT TBT	(2) 0.1–1g dry sample. Ex with 0.1 *M* HCl or 2 *M* HCl or 8 *M* HCl in MeOH or HOAc (20 ml, 4 h) (3) 0.1–1 ml of supernatant. NaBH$_4$	HG–CT–QFAAS Chromosorb GAW		Acid concentration and type were optimised Calibration: standard additions 1Ex+1C+D	[123]

(*continued on page 14*)

Table 3. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
PACS-1	TBT	(2) 4 g dry sample. Ex with 1-butanol (8 ml, 1 h, sonication). Dilution of 1 ml aliquot in 25 ml with FIA carier	ISMS–MS FIA carrier: 1 mM NH_4OAc in MeOH	(n=5) TBT: 97±6	Calibration: standard additions to the solid 1Ex+1C	[75]
Incurred sediment	MBT DBT TBT	(2) 1 g dry sample. Ex with pure HOAc (20 ml, shaking overnight+ sonication, 30 min) (3) 1–2 ml supernatant. $NaBH_4$	HG–CT–GFAAS SP-2100 on Chromosorb GNAW		Calibration: standard addition 1Ex+1C+D	[146] [147]
Spiked and incurred sediment	MMeT DMeT TMeT MBT DBT TBT	(2) 3 g dry sample. Ex with 2% HCl in MeOH (25–100 ml, shaking, 30–40 min) (3) $NaBH_4$	HG–CT–QFAAS SP-2100 on Chromosorb GAW–DMCS	Spiking level: 35–119 ng g^{-1} (n=2) MMeT: 45 DMeT: 83 TMeT: 95 MBT: 55 DBT: 101 TBT: 142 R.S.D.: nr	Calibration: standard additions. TEtT as surrogate 1Ex+1C+D	[142] [143]
Incurred sediment	MMeT DMeT TMeT MBT DBT TBT	(2) 10 g wet sample. Ex with HOAc (20 ml, 15 h) (3) $NaBH_4$	HG–CT–QFAAS OV-101 on Chromosorb G		Calibration: nr 1Ex+1C+D	[148,149] [150,151]
Incurred sediment and PACS-1	TBT	(2) 0.5–2 g dry sample. Ex with pure HOAc (20 ml, 4 h to overnight) (3) 2 ml supernatant. $NaBH_4$	HG–CT–QFAAS OVA-101 on Chromosorb GAW	(n=nr) 97±19	Calibration: standard additions (different possibilities were discussed) 1Ex+1C+D	[152]
Spiked sediment	MMeT DMeT TMeT MBT DBT TBT	(2) 1.5 g dry sample. Ex with 0.48 *M* HCl in MeOH (25 ml, sonication, 1 h) (3) 0.1 or 0.5 ml supernatant, $NaBH_4$	HG–CT–QFAAS SP2100 on Chromosorb GAW DMCS	Spiking level: 544 ng g^{-1} (n=2) TBT: 130±18	% HCl, sonication time and amount of $NaBH_4$ were optimised 1Ex+1C+D	[137]
Spiked and incurred sediment	MBT DBT TBT	(2) 1 g dry sample. Ex with 0.5 *M* HCl in MeOH (15–100 ml, sonication, 2 h) (3) (a) 0.1–0.4 ml of supernatant. $NaBH_4$ (b) 0.1–16 ml of supernatant. $NaBEt_4$ (on-line)	(a) HG–CT–QFAAS (b) CT–QFAAS SP2100 on Chromosorb GAW DMCS	Spiking level: 388–1000 ng g^{-1} (n=4) (a) MBT: 136±5 DBT: 124±5 (b) MBT: 29±6 DBT: 123±25 TBT: 92±11	HCl conc. was optimised. Ethylation conditions were also optimised Recoveries obtained by the variable extraction volume method Calibration: standard additions 1Ex+1C+D	[134,135] [136]
Spiked and incurred	MBT DBT	(2) 0.5 g dry sample. Ex with 0.05% tropolone in MeOH (2×15 ml,	cGC–FPD DB-1	Spiking level: 150–900 ng g^{-1}	Extracting solvent was optimised	[159]

Table 3. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
sediment	TBT MPhT DPhT TPhT	sonication, 15 min). Addition of 150 ml water. Ex with 30 ml DCM. Ev. Solution in 1 ml isooctane (3) PeMgBr. Ev to 1 ml (4) Silica gel/Hexane–benzene (1:1) Ev	cGC–MS HP-5	(n=5) MBT: 80–85 DBT: 89–88 TBT: 91–94 MPhT: 78–81 DPhT: 87–91 TPhT: 92–90 R.S.D.: 7–16%	Calibration: TPrT as surrogate 4Ex+3Ev+D+CU	
PACS-1	MBT DBT TBT	(2) 2 g dry sample. Ex with pure HOAc (20 ml, overnight). Ev to dryness Solution in mobile phase	LC–GFAAS Spherisorb SCX-5 μm 0.18 *M* diammonium citrate in MeOH–water (60:40) with pH gradient from 6.5 to 4.0	(n=nr) MBT: 210±10 DBT: 70±9 TBT: 72±10	Mobile phase (pH, ionic strength) was optimised Calibration: external standards 1Ex+1C+1Ev	[153]
Incurred sediment	MBT DBT TBT	(2) 5 g dry sample. Ex with MeOH-HCl (8.5%) (2×15 ml). Ex with 10 ml 0.1% tropolone in DCM (3) $NaBH_4$	cGC–FPD Ultra-1	Spiking level 40 ng g^{-1} (n=5) MBT: 73±7 DBT: 89±8 TBT: 89±17	Calibration: I.S. (DPrT) 4Ex+1Ev+D	[138]
Spiked and incurred sediment	MMeT DMeT TMeT MBT DBT TBT	(2) 1 g dry sample. Ex with 0.5 *M* NaOH in MeOH (15–100 ml, sonication, 2 h) (3) $NaBEt_4$ (on-line)	CT–QFAAS SP2100 on Chromosorb GAW DMCS	Spiking level: 449–1000 ng g^{-1} (n=4) TBT: 92±5	Ethylation conditions were optimised Recoveries obtained by the variable extraction volume method Calibration: standard additions 1Ex+C+D	[135]
Spiked and incurred sediment PACS-1	MBT DBT TBT	(2) 0.1–2 g dry sample. Ex with HOAc (20 ml, 4h) (3) $NaBH_4$	HG-CT-QFAAS	Spiking level: 1000 ng g^{-1} (n=2) MBT: 97±12 DBT: 100±5 TBT: 100±3 *PACS-1* (n=2) MBT: 143±32 DBT: 88±23 TBT: 98±10	Calibration: standard additions 1Ex+1C+D	[154]
PACS-1 CRM-462	MBT DBT TBT	(2) 2 g sample. Ex with pure HOAc (20 ml, shaking, overnight). Ev to 0.5 ml. Dilution in mobile phase	LC–ICP-MS TSK gel ODS 80 TM 0.1% tropolone in MeOH–water–HOAc (80:14:6)	*PACS-1* (n=5) MBT: 80±13 DBT: 67±20 TBT: 257±22 *CRM-462* (n=5) MBT: 87±4 DBT: 101±15 TBT: 198±15	Different extraction methods previously reported were assayed Calibration: standard additions 1Ex+1C+1Ev	[51]

(*continued on page 16*)

Table 3. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked and incurred sediments	DBT TBT	(2+3) 4 g wet sample+8–16 ml 0.1% NaOH in MeOH (45 min). NaBH$_4$. Ex with hexane (2 ml)	cGC–FPD Phenyl–methylsilicone	Spiking level: nr (*n*=nr) DBT: 90–97 TBT: 90–97 R.S.D.: nr	Calibration: I.S. (TPrT) 1Ex+1C+D	[163]
Spiked sediment	TBT TPhT	(2) 1 g dry sample. Ex with MeOH (2×5 ml, sonication, 15 min)	LC-fluorimetry (fisetin) Partisil-10 SCX 0.15 *M* NH$_4$OAc in MeOH–water (80:20)	Spiking level: 450 ng g^{-1} (*n*=3) TBT: 68 TPhT: 87 R.S.D.: 3%	Calibration: external standards 2Ex+2C	[160]
Spiked and incurred sediment PACS-1 CRM-462	MBT DBT TBT MPhT DPhT TPhT	(2) 0.1–1 g+0.5 *M* HAcO in MeOH (10 ml, microwaves, 3 min, 70 W) Dilution to 100 ml with water (3) NaBEt$_4$. Ex with isooctane. Desulfurization by addition of propan-2-ol, tetrabutylammonium sulfate and sodium sulfite	cGC–FPD CP-Sil-8CB	*PACS-1* (*n*=6) MBT: 133±27 DBT: 94±7 TBT: 95±9 *CRM-462* (*n*=6) DBT: 84±10 TBT: 100±6	Extraction conditions were optimised Calibration: TPrT as surrogate 3Ex+D	[139] [140]
PACS-1	MBT DBT TBT	*Procedure A:* (2) 1 g wet sample (or 0.3–1 g dry sample)+0.5 *M* HOAc (a) or 0.5 *M* HCl (b) in methanol (10 ml, sonication, 1 h, 50°C) (3) 0.1–0.5 ml supernatant. NaBEt$_4$ (on-column) *Procedure B:* (2) 1 g wet sample (or 0.3–1 g dry sample)+0.5 *M* HOAc in methanol (10 ml, microwave, 3 min, 60 W) (3) 0.1–0.5 ml supernatant. NaBEt$_4$ (on-column)	CT–QFAAS SP-2100 on Chromosorb GAW DMCS	(*n*=nr) *Procedure A:* (a) MBT: 76±5 DBT: 86±4 TBT: 92±4 (b) MBT: 72±20 DBT: 101±3 TBT: 93±6 *Procedure B:* MBT: 136±21 DBT: 92±8 TBT: 93±4	Calibration: nr 1Ex+1C+D	[122]
Spiked sediments	MBT DBT TBT	(1) 2 g sample. Ex with HOAc (2×25 ml). Dilution with water (2) +A few drops of 4 *M* NaOH Ex with toluene (3±10 ml). Ev to dryness Solution with mobile phase	LC–ICP–MS Partisil-10 SCX (a) NH$_4$ citrate–citric acid in MeOH–water (70:30) pH 5.8 (b) NH$_4$ citrate–citric acid, from MeOH–water (70:30) at pH 5.8 to MeOH–water (85:15) pH 3.4.	Spiking level: 125 ng g^{-1} (*n*=nr) MBT: 12±4 DBT: 33±3 TPhT: 103±25	Calibration: nr P+7Ex+2C+1Ev	[155]

See List of abbreviations.

Table 4
Abiotic matrices: supercritical fluids

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked soil	TeEtT TEtPeT DMeDPeT TeBT TBPeT MBTPeT	(2) 5 g dry sample. SFE: CO_2, 80°C, 100 atm, 10 min (dynamic) (1.5 ml min^{-1}). Collection in 5 ml hexane	cGC–AED HP-5	Spiking level: 2 $\mu g\ g^{-1}$ (n=2) TeEtT: 90 TEtPeT: 90 DMeDPeT: 90 TeBT: 62 TBPeT: 48 MBTPeT: 30 R.S.D.: nr	Extraction conditions were optimised Calibration: external standards 1 SFE	[169]
Spiked and incurred sediment PACS-1 CRM-462 RM-424	MBT DBT TBT MPhT DPhT TPhT	(2+3) HeMgBr in extraction cell. SFE: CO_2, 40°C, 350 atm, 10 min (static)+10 ml CO_2 (dynamic) (5–7 min) (1–1.5 ml min^{-1}). Collection in 5 ml hexane	cGC–FPD cGC–MS (confirmation) DB-17	Spiking level: 91–331 ng g^{-1} (n=6) MBT: 15±7 MPhT: 40±34 DBT: 76±7 DPhT: 106±12 TBT: 111±2 TPhT: 114±10 *PACS-1* (n=6) DBT: 38±4 TBT: 78±6 *CRM-462* (n=2) DBT: 63±7 TBT: 91±16	Calibration: I.S. (TeBT). TPeHeT as surrogate 1 SFE+2Ev	[170]
Spiked soil	DMeT TMeT TEtT MBT DBT TBT DPhT	(2) 5 g dry sample. SFE: DDC, CO_2 (5% MeOH), 80°C, 450 atm, 30 min (static)+20 min (dynamic) (1.5 ml min^{-1}). Collection in 5 ml MeOH. Addition of 5 ml MeOH (3) 0.5 ml aliquot. PeMgBr. Dilution to 10 ml with octane	cGC–AED HP-5	Spiking level: 50 $\mu g\ g^{-1}$ (n=3) DMeT: 72±23 TMeT: 76±7 TEtT: 87±6 MBT: 48±45 DBT: 92±15 TBT: 81±7 DPhT: 41±6	Extraction conditions were optimised Calibration: external standards 1SFE+5Ex+D	[169]
Spiked soils and spiked reference materials PACS-1 CRM-462 RM-424	MMeT DMeT TMeT DEtT TEtT MBT DBT TBT TeBT DPhT TPhT TePhT TeCyT	(2) 5–2 g soil or 1g dry sediment. SFE: DEA–DDC, CO_2 (5% MeOH), 60°C, 450 atm, 20 min (static)+30 min (dynamic) (1.5–2 ml min^{-1}) Collection in 15 ml DCM (3) PeMgBr	cGC–AED HP-7	Spiking level: 1.25 $\mu g\ g^{-1}$ (n=4) MMeT: <5–48 MBT: <5 DMeT: <5–82 DEtT; 9–94 DBT: 37–106 DPhT: 10–34 TMeT: 96–106 TEtT: 100–132 TBT: 94–106 TPhT: 75–108 TeBT: 77–123 TeCyT: 79–103 TePhT: 76–106 *PACS-1* (n=3)	Extraction conditions were optimised Calibration: external standards 1SFE+3Ex+2Ev+D	[167,168]

(continued on page 18)

Table 4. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
				MBT: 8.9±26 DBT: 95±6 TBT: 108±6 *CRM-462* (*n*=8) DBT: 45±26 TBT: 104±32		
Spiked sediment PACS-1 CRM-462 RM-424	TBT	(2) 1–3 g dry sample. SFE: CO_2 (20% MeOH–HCl), 60°C, 350 atm, 30 min (2 ml min^{-1}). Collection in 2 ml isooctane (3) EtMgCl	cGC–FPD DB-5	Spiking level: nr (*n*=2) TBT: 82±9 *PACS-1* (*n*=5) TBT: 69±7	Extracting composition, P, T and extraction time were optimised Calibration: I.S. (TPrT) 1SFE+2Ex+D	[166]
Spiked sediment PACS-1	MBT DBT TBT	(2) 0.5 g dry sample. SFE: DDC in extraction cell, CO_2 (10% MeOH), 70°C, 500 atm, 30 min (1200 ml min^{-1} as gas). Collection in 2 ml DCM–MeOH (50:50) (3) EtMgBr	cGC–AED HP-5	Spiking level: 500 ng g^{-1} (*n*=4) MBT: 62±5 DBT: 91±3 TBT: 93±4 *PACS-1* (*n*=3) MBT: 146 DBT: 79 TBT: 85 R.S.D.: nr	SFE extraction cond. (P, presence of DDC) were optimised Calibration: I.S. (TPeT) 1SFE+D	[118]

(1) 1 atm=101/325 Pa.
See List of abbreviations.

hexane and diethyl ether has also been used [116]. Low-to-medium polarity solvents such as toluene in the presence of complexing acids [i.e., acetic acid (HOAc)] provide a compromise between extraction efficiency and selectivity for OTs from sediments allowing the application of classical derivatization methods [50,117].

The salting out effect or ion-pairing with NaCl are used to increase the efficiency of the extraction of OTs from the aqueous phase to the organic phase when HCl is used, especially for biotic samples and sometimes for abiotic samples [32,83,85,88,89, 116,118].

Several procedures have been developed for the "selective" extraction of OTs in the presence of inorganic tin followed by graphite furnaceatomic absorption spectrometry (GFAAS) determination without any chromatographic separation. While organic tin is extracted with hexane after HCl treatment, inorganic tin is determined after digestion with nitric acid [68]. Other procedures isolate TBT from the solvent extract (DCM, HCl–hexane) by NaOH wash, removing MBT and DBT [56,59,60,63, 74,101]. However, several authors have questioned the extraction selectivity of these procedures and the term hexane-extractable tin has been coined [42,65,66].

2.1.3. Polar solvents

Extraction with polar solvents accounts for 25% of the analytical procedures for both biotic and abiotic matrices. Extraction is usually performed by: (i) aqueous HCl [119–123]; (ii) HCl or HOAc in polar organic solvents (MeOH, acetone) [112,122–143]; (iii) acetic acid [37,51,123,144–155]; (iv) net polar organic solvents (MeOH, DCM–MeOH, butanol, MeOH–EtOAc) [75,119,128,156–162] or (v) polar organic solvents in basic conditions [135,163]. Sonication is used in most procedures. Very recently, a focused microwave field has been introduced to reduce extraction time from hours to several minutes [139,164].

In some cases after the acid or polar solvent extraction, a liquid–liquid extraction (LLE) with a

Table 5
Biotic matrices: non-polar solvents

Sample	Analyte	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked oysters	TBT	(1) 20 g wet sample+8 g silica+70 g Na_2SO_4 (overnight, 15°C) (2) Ex with hexane (400 ml, soxhlet, 24 h) (3) HeMgBr. Ev to 1 ml (4) Florisil–Hexane (300 ml). Ev to 0.1 ml	cGC–FPD DB-5	Spiking level: 20–1000 ng g^{-1} (n=5) TBT: 86–102 R.S.D.: nr	Calibration: I.S. (TPeT) P+2Ex+3Ev+CU+D	[33]
Spiked and Incurred bivalves tissues	MBT DBT TBT	(2) 15 g wet sample+40 g Na_2SO_4. Ex with 0.2% tropolone in DCM (3×75 ml, 3 min). Ev to 10 ml. Addition of hexane. Heating at 60°C until DCM elimination (3) HeMgBr. Ev to 2 ml (4) Alumina-silica gel/Hexane. Ev to 0.5 ml	cGC–FPD DB-5	Spiking level: 2.3–2.5 μg (n=8) MBT: 40±23 DBT: 97±16 TBT: 94±7	Calibration: I.S. (TeBT) 5Ex+3C+4Ev+D+CU	[41]
Spiked and incurred oxysters and fish	MBT DBT TBT TeBT	(2) 3 g sample+20 g Na_2SO_4 anh. Ex with 0.1% tropolone in DCM (2×25 ml). Solvent exchange to 5 ml hexane (3) HeMgBr (4a) Silica–alumina/Pentane (4b) Amino Sep–Pak/Pentane. Ev to 1 ml	cGC–MS DB-5	Spiking level: 400 ng g^{-1} (n=4) MBT: 72±22 DBT: 93±19 TBT: 80±13 TeBT: 74±17	Calibration: I.S. (hexamethylbenzene). TPeT and TPrT as surrogates 4Ex+F+3Ev+D+2CU	[43]
Incurred mussels	MBT DBT TBT	(2) 0.5 g dry sample. Ex with 0.02% tropolone in toluene (2×30 ml, sonication, 30 min). Ev to near dryness. Solution with 4 ml hexane (3) PeMgBr (4) Florisil-alumina/Hexane (140 ml). Ev to 0.3 ml	cGC–FPD DB-608		A FPD based on quartz surface-induced luminescence was reported. Calibration: I.S. (TPrT) 2Ex+3C+2Ev+CU+F+D	[39]
Incurred bivalves	MBT DBT TBT TeBT	(2) 30 g wet sample+Na_2SO_4. Ex with hexane-tropolone (3) PeMgBr (4) Florisil-silica gel/Hexane. Ev to 0.5 ml	cGC–FPD DB-5		Calibration: I.S. (DPrDPeT). TPrT as surrogate 1Ex+1Ev+D+CU	[35]
NIES-11	TBT TPhT	(2) 0.14 g dry sample. SFE: CO_2 (10% MeOH), 100°C, 600 psi, 3 min (static)+17 (dynamic) (0.5=65 ml min^{-1}. Collection in 5 g MeOH	LC–ICP–MS PRP-1 0.004 M sodium pentane–sulfonate in MeOH–water–OAc buffer (94:5:1), pH 6	(n=3) TBT: 44±1 TPhT: 23±1	Supercritical extraction conditions were optimised Calibration: nr 1Ex	[79]

(1) 1 p.s.i.=6894.76 Pa.
See List of abbreviations.

Table 6
Biotic matrices: non-polar solvents plus acid

Sample	Analyte	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked rabbit tissues	TeEtT TePrT TeBT	(2) 1–5 g wet sample+10 ml water+8 ml conc. HCl+2 g NaCl. Ex with hexane (3×20 ml, 5 min) (4) Silica gel/Hexane. Ev	GC–FID PEG 20M	Spiking level: 4–6 μg g^{-1} (n=5) TeEtT: 100–104 TePrT: 102–103 TeBT: 97–100 R.S.D.: 1–2%	Various extractants were examined. Several stationary phases were tested Calibration: external standards. TeEtPb as surrogate 3Ex+3C+CU+1Ev	[61]
Spiked rabbit and rat tissues	TMeT TEtT TPrT TBT	(2) 5 g wet sample+10 ml water+8 ml conc. HCl+2 g NaCl. Ex with EtOAc (2×20 ml, 5 min). Ev to 0.5–1 ml. Addition of 10 ml hexane. Ev to 0.5–1 ml (4) Silica gel/Hexane–EtOAc (4:1) Ev	GC–ECD DEGS–HG	Spiking level: 10–100 ng g^{-1} (n=5) TEtT: 98–104 TPrT: 97–106 TBT: 98–104 R.S.D.: 2%	Calibration: I.S. (TPrT, TEtT or methylmercury) P+3Ex+3C+3Ev+CU	[76]
Spiked rat tissues	DMeT DEtT DPrT DBT DOcT	(2) 1–5 g wet sample+10 ml normal saline solution+8 ml conc. HCl (5 min).+2 g NaCl. Ex with EtOAc (2×200 ml). Ev to 0.5–1 ml. Addition of 10 ml hexane. Ev	LC-Fluorometry (morin) Unisil QCN 5% HOAc in hexane–EtOAc (95:5)	Spiking level 2–3 μg (n=5) DMeT: 91–92 DEtT: 92–93 DPrT: 95–97 DBT: 98–99 DOcT: 96–98 R.S.D.: 0.2–1%	Mobile phase was optimised Calibration: other dialkyltins as surrogates 2Ex+2C+2Ev+1F	[77]
Spiked tuna fish	MMeT DMeT TMeT	(2) 5 g sample homogenised in normal saline sol.+10 ml conc. HCl.+2 g NaCl. Ex with EtOAc (3×20 ml, 3 min). Ex with petroleum ether (2×10 ml). Combined organic phases backextracted with 0.02 M H_2SO_4 (2×5 ml+10 ml). (3) $NaBH_4$ on-line	LC–HG-DCP PRP-1 0.003 M hexane sulfonic acid+0.003 M KF+2.5% HOAc in 0.01 M H_2SO_4	Spiking level: 10–75 μg (n=3) MMeT: 88–70 DMeT: 94–102 TMeT: 96±95 R.S.D.: 1–4%	Several aspects of the detection were optimised Calibration: external standards 8Ex+3C+D	[116]
Spiked fish muscle and shellfish tissue	DBT TBT	(2) 10 g wet sample+100 ml water+15 g NaCl+10 ml HCl. Ex with EtOAc–hexane (3:2) (50 ml, 30 min). Ev to 0.1 ml. Addition of 1 ml ethanol (3) $NaBH_4$ (4) Silica gel/Hexane. Ev to 1–5 ml	GC–ECD OV-17 or OV-1	Spiking level: 100–1000 ng g^{-1} (n=5) DBT: 76–96 TBT: 85–93 R.S.D.: 1–6%	Several extractants were examined. Elution patterns from the silica gel column were investigated Calibration: external standards 2Ex+1C+2Ev+D+CU	[67]
Spiked and Incurred fish tissues	MBT DBT TBT	(1) 5–200 g wet sample+10 ml conc. HCl per g of sample (magnetic stirring, 2 h). Five-fold dilution with water (2) Ex with 1% tropolone in benzene (2×25 ml) (3) PeMgBr	GC-QFAAS OV-225	Spiking level: 20–100 ng g^{-1} (n=nr) MBT: 55–63 DBT: 66–83 TBT: 94–104 R.S.D.: 2–20%	Calibration: external standards P+1Ex+D+CU	[7]

Table 6. Continued

Sample	Analyte	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
		(4) 3% water-deactivated silica gel/ Hexane				
Tissues from OTs treated rats	MEtT DEtT TEtT	(1) 1 ml 10% sample homogenate in 6 *M* ultrapure HCl (4 h) (2) Ex with 2 ml chloroform-EtOAc (1:1)	LC-GFAAS Partisil-10 SCX 0.5 *M* NH_4 citrate in MeOH-water (70:30)	Spiking level: 0.2–0.5 m gl^{-1} (*n*=3) DEtT: 88–106 TEtT: 85–93 R.S.D.: 6–20%	Several acid treatments and extraction conditions were examined. Various LC columhns were tested Calbiration: matrix-matched standards P+1Ex	[110]
Incurred oxysters	MBT DBT TBT	(2) 15 g sample+15 ml 6 *M* HCl (10 min)+2 g NaCl. Ex with 50 ml DCE. (4h). Ev to dryness. Solution in (a) hexane or (b) ethanol (3) (a) PeMgBr or (b) $NaBH_4$	GC–FID OV-17 on Chromosorb W		Calibration: I.S. (hexadecane) 1P+1Ex+1Ev+D	[104]
Spiked fish tissue	MBT DBT TBT MPhT DPhT TPhT	(2) 10 g wet sample+100 ml water+15 g NaCl+10 ml conc. HCl. Ex with EtOAc (50 ml, 30 min). Ev to dryness. Solution in ethanol (3) $NaBH_4$ (4) Silica gel/Hexane. Ev to 1–5 ml	GC–ECD PEG 20M	Spiking level: 100–1000 μg g^{-1} (*n*=5) MBT: 87–95 DBT: 86–99 TBT: 88–100 MPhT: 75–85 DPhT: 86–88 TPhT: 86–81 R.S.D.: 2–7%	Elution patterns from silica gel were studied. Several column packings were investigated Calibration: external standards 2Ex+1C+2Ev+D+CU	[78]
Spiked and incurred salmons	TBT	*GFAAS method* (1) 5 g wet sample+10–50 ml conc. HCl (2 h) (2) Ex with hexane (2×25 ml). Washing with 3% NaOH. Ev to dryness. Solution in HNO_3–HOAc (2:98) *cGC-AAS method* (1) 1–5 g wet sample+10–50 ml conc. HCl (2 h) (2) Ex with hexane (2×25 ml). Ev (3) PeMgBr. Ev to 2 ml (4) Deactivated silica gel/Hexane. Ev to 0.2 ml	GFAAS cGC–QFAAS dimethyl silicone	Spiking level: nr (*n*=4–8) TBT: 87–101 R.S.D.: 6–50%	*GFAAS method* Calibration: external standards P+2Ex+1Ev *cGC-AAS method* Calibration: I.S. (TeBT) P+3Ex+3Ev+D+CU	[60]
Spiked and incurred oysters and salmons	TBT	(1) 1 g wet sample+40 ml HCl (shaking, 90–120 min) (2) Ex with 100 ml hexane (45–50 min). Washing with 3% NaOH. Aliquot of 50 ml+10 ml conc. HNO_3. Ev to 4–6 ml. Dilution to 25 ml with water	GFAAS	Spiking level: 200 ng g^{-1} (*n*=3) TBT: 100±16	Calibration: external standards P+2Ex+1Ev	[68]
Spiked mussels	TBT	(2) 5–10 g wet sample (or 0.3–0.4 g dry sample)+5–10 ml water+10 ml 6 *M*	GFAAS	Spiking level: 2.5–7.5 μg	Calibration: external standards	[101]

(*continued on page 22*)

Table 6. Continued

Sample	Analyte	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
oysters and fish		HCl. Ex with 20 g DCM (12–16 h). Ev to dryness. Solution in hexane. Washing with 3% NaOH. Ev to dryness. Digestion with 1 ml of conc. HNO_3. Ev. Solution with 1 ml of 3 *M* HNO_3		(n=5) TBT: 99–111 R.S.D.: 9–24%	2Ex+2C+3Ev	
Spiked and incurred fish tissues	DBT TBT	(2) Sample homogenised (1:2) with MeOH. 15 g homogenate+10 g NaCl+50 ml 3 *M* HCl. Ex with Et_2O–hexane (3:2) (2×100 ml). Washing with $NaHCO_3$. Ev to 2 ml. (3) EtMgBr. Ev near to dryness (4) Silica gel/Hexane. Ev to dryness. Solution in 2 ml hexane	cGC–FPD CBP-10	Spiking level: 800 ng g^{-1} (n=2–3) DBT: 91–94 TBT: 83–96 R.S.D.: 1–7%	Effect of solvent used in sample homogenisation was studied Calibration: external standards subjected to the extraction procedure except the clean-up 5Ex+2C+3Ev+D+CU	[111]
Spiked and Incurred fish tissues	DBT TBT TPhT	(2) Sample homogenised (1:2) with MeOH. 15 g homogenate+10 g NaCl+50 ml 3 *M* HCl. Ex with Et_2O–hexane (3:2) (2×100 ml). Ev to dryness. Solution in Et_2O (4a) Florisil. HOAc–Et_2O (1:99). Ev near to dryness. Solution in Et_2O (3) EtMgBr. Ev near to dryness (4b) Florisil/Hexane–Et_2O (99:1). Ev to 2 ml	cGC–FPD CBP-10	Spiking level: 500 ng g^{-1} (n=3) DBT: 85–94 TBT: 83–91 TPhT: 88–107 R.S.D.: 3–8%	Extraction conditions were optimised. Clean-up method was also optimised. Effect of fish type on the recoveries was evaluated Calibration: external standards subjected to the extraction procedure 4Ex+2C+4Ev+2CU+D	[113]
Spiked and incurred musels	MBT DBT TBT	(2) 5 g wet sample+10 ml 1.5 *M* HCl. Ex with 20 ml DCM (3h). Ev of a 2 ml aliquot. Solution in hexane (3) HeMgBr (4) Florisil/Hexane. Ev to dryness. Solution in 0.2 ml hexane	cGC–FPD SPB-1	Spiking level: 0.1–3 μg ml^{-1} (n=4) TBT: 83–108 R.S.D.: nr	Extraction and derivatization were optimised Calibration: I.S. (TPeT) 2Ex+1C+2Ev+D+CU	[103]
Spiked mussels and oysters	DBT TBT	(2) 7–10 g wet sample+15 ml 6 *M* HCl+15 ml sat. NaCl Ex with 15 ml DCM (1 h). Ev (3) HeMgBr. Ev to 1 ml (4) Deactivated silica/Hexane. Ev to 0.2–0.5 ml	cGC–FID SE-30	Spiking level: 600–1200 ng g^{-1} (n=6) TBT: 101 R.S.D.: 10%	Calibration: I.S. (BTPeT). TPeT as surrogate 2Ex+2C+3Ev+D+CU	[105]
Spiked and incurred mussels	TBT	*GFAAS method* (1) 1–5 g wet sample+10–50 ml conc. HCl (2 h) (2) Ex with hexane. Washing with 3% NaOH. Ev to dryness. Solution in HNO_3–HOAc (2:98) *cGC-AAS method* (1) 1–5 g wet sample+10–50 ml conc. HCl (2 h) (2) Ex with 0.25% tropolone in benzene. Ev (3) PeMgBr (4) Deactivated silica gel/nr. Ev to 0.1 ml	GFAAS cGC–QFAAS dimethyl silicone	Spiking level: nr (n=15) TBT: 89–101 R.S.D.: nr	*GFAAS method:* Calibration: standard additions P+2Ex+1Ev *cGc-AAS method:* Calibration: I.S. (TeBT) P+1Ex+2Ev+D+CU	[74]

Table 6. Continued

Sample	Analyte	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked and incurred oysters	TBT	(2) 10 g wet sample+10 ml HCl+30 ml sat. NaCl. Ex with DCM (70+50 ml, 30+10 min). Ev to dryness. Solution in 10 ml DCM (4) Silica/DCM. Ev to dryness (3) $NaBH_4$	cGC–MS HP-1	Spiking level: 100–500 ng g^{-1} n=nr TBT: 87–91	Calibration: external standards 3Ex+2C+2Ev+CU+D	[106]
Incurred and spiked oysters	DBT TBT	(1) 3–22 g wet sample+30 ml conc. HCl (30 min) (2) Ex with hexane (50 ml, 60 min) Stand for overnight. Ev to dryness. Solution in 5 ml MeOH	LC-FAAS Partisil-10 SCX 0.1 M NH_4OAc in MeOH-water (70:30)	Spiking level: nr (n=nr) DBT: 49±3 TBT: 61±2	Calibration: external standards P+1Ex+1Ev	[62]
Spiked and incurred oysters	TBT	(1) 5 g wet sample+25 ml conc. HCl (rotation, 90 min) (2) Ex with hexane (50 ml, 50 min). Washing with 3% NaOH (×2). Ev. Digestion with HNO_3	GFAAS	Spiking level: 20–200 ng g^{-1} (n=8) TBT: 80–101 R.S.D.: 4%	Calibration: external standards P+3Ex+1Ev+Digestion	[63]
Spiked and incurred oysters	TBT	(2) 5 g wet sample+2.5 ml 6 M HCl +15 g Na_2SO_4. Ex with 0.05% tropolone in hexane (3×20 ml, 8 min). Ev to 5 ml (4) C_{18} cartridge/0.05% tropolone in hexane (3) $NaBH_4$ in a packed reactor inside the injection port of the gas chromatograph	cGC–FPD DB-1	Spiking levels: 25–125 ng g^{-1} (n=7) TBT: 97–107 R.S.D.: 5–7%	Some changes in the temperature program of the GC separation were proposed Calibration: TPrT as surrogate 3Ex+1F+1Ev+CU+D	[64]
Spiked and incurred oysters. Tissues of rats treated with TPhT	MBT DBT TBT MPhT DPhT TPhT	(2) 5 g wet sample+1.5 g NaCl+0.5 ml conc. HCl. Ex with 0.05% tropolone in benzene (2×10 ml, 20 min) (3) PeMgBr or BMgCl. Ev to dryness. Solution in 5 ml toluene	cGC–FPD Ultra-1	Spiking levels: 100–600 ng g^{-1} (n=6) MBT: 71–72 DBT: 72–74 TBT: 72–73 MPhT: 70–74 DPhT: 72–73 TPhT: 70–74 R.S.D.: 1–10%	Calibration: external standards 4Ex+2C+1Ev+D	[81] [82]
Spiked and incurred bivalves tissues	MBT DBT TBT DCyT	*LC method* (2) 34–220 g wet sample+100 ml water+20 g NaCl+50 ml conc. HCl. Ex with DCM (100+2×50 ml, 30 min). Ev to dryness. Solution in hexane *GC method* (2) The same as the LC method using Et_2O in place of DCM (3) MeMgBr (4) Silica gel/Pentane. Ev to 0.4 ml	LC–GFAAS LC–MS C_{18} 2% HOAc in THF–acetone (98:2) cGC–MS DB-1	LC–GFAAS Spiking levels: 50–150 μg g^{-1} (n=nr) DBT: 80–92 TBT: 90–97 R.S.D.: 3%	*LC method:* Calibration: external standards for TBT and standard additions for DBT 3Ex+1C+1Ev+1F *GC method:* Calibration: I.S. (TeBT) 4Ex+1C+2Ev+F+D+CU	[90]
Spiked and incurred mussels	MBT DBT TBT	(2) Wet sample (5 g in dry wt. basis)+ 25 ml MeOH+17 ml conc. HCl. Saturation with NaCl. Ex with	cGC–FPD cGC–ECD cGC–MS	Spiking level: low ppb (n=6)	Several detection systems coupled to cGC and LC were compared	[91]

(continued on page 24)

Table 6. Continued

Sample	Analyte	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
	DPhT TPhT	0.25% tropolone in Et_2O–hexane (3:2) (3×40 ml). Ev to 1 ml (3) MeMgCl. Ev to 0.5 ml (4) Activated silica/Hexane–Et_2O (9:1)	SE-54 LC–MS 0.05 *M* NH_4OAc in MeOH–water (50:50)	TBT: 61–93 TPhT: 56–89 R.S.D.: (cGC–FPD): 3–8%	Calibration: I.S. (TeBT) 5Ex+3C+3Ev+D+CU	
Spiked and incurred salmon tissues	MBT DBT TBT	(1) 5 g wet sample+40 ml conc. HCl (shaking, 2 h; stand for 2 h)+10 ml conc. HBr (stand for 15 min) (2) Ex with 0.05% tropolone in pentane (100 ml, 2 min) (3) PeMgBr. Washing with 3% NaOH (stand for overnight). Ev to 1 ml.	cGC–FPD BP-1	Spiking level: 800 ng g^{-1} ($n=5$) MBT: 95±13 DBT: 100±3 TBT: 72±8	Derivatization under reflux was proposed. The chromatographic conditions were optimised Calibration: I.S. (DMDPeT) P+4Ex+D+1F+2Ev	[57]
Incurred mussels and fish tissue	MBT DBT TBT MPhT DPhT TPhT	(2) 1 g mussels or 8 g fish+HCl to pH=2. Ex with 0.25% tropolone in Et_2O (10 ml+2×5 ml). Ev to 2 ml (3) EtMgBr. Ev to 0.5 ml (4) Silica gel/Hexane–Et_2O	cGC–FPD DB-5		Calibration: TPrT, MPeT, DPeT and TPeT as surrogates 3Ex+2Ev+1F+D+CU	[93] [94]
Incurred mussels	MBT DBT TBT MPhT DPhT TPhT	(2) 4 g wet sample+10 ml 1 *M* HBr in ethanol containing L-ascorbic acid. Ex with 0.5% tropolone in benzene (10+5 ml, sonication, 30 min) Washing with 2 *M* NaBr. Ev to 2 ml (3) PrMgBr. Ev to 1 ml (4) Silica gel/nr	cGC–FPD DB-5		Calibration: I.S. (TePeT). TPeT as surrogate 3Ex+2C+2Ev+D+CU	[48]
Spiked shellfish	MBT DBT TBT TeBT	(2) 20 g wet sample+75 g Na_2SO_4 anh.+5 ml conc. HBr. Ex with 0.05% tropolone in toluene (2×60 ml, 5 min). Solvent exchange to hexane (3) PeMgBr. Ev to 4 ml (4) Florisil-1% deactivated silica gel (2:1)/Hexane. Ev to 0.5 ml	cGC–FPD DB-5	Spiking levels: 10–1000 ng g^{-1} ($n=4$) MBT: 66–109 DBT: 65–104 TBT: 66–100 TeBT: 61–75 R.S.D.: 2–18%	Calibration: I.S. (DPrDPeT). TPrT as surrogate 4Ex+3C+5Ev+D+CU	[49]
Incurred mussels	TBT TeBT	(1) 12 g wet sample+40 ml conc. HCl (shaking, 2 h; stand for 2 h)+ 10 ml conc. HBr (stand for 15 min) (2) Ex with benzene (100 ml, 5 min)	cGC–AED DB-1		Calibration: external standards P+1Ex	[58]
Incurred oysters and spiked bivalves	Hexane-extractable tin	(1) 10–15 g wet sample+5 ml 2 *M* HCl (sonification, 1 h, 55°C) (2) Ex with 18 ml hexane. Washing of an aliquot with 3% NaOH. Addition of 0.5 ml HNO_3. Ev of hexane. Dilution with water of 5 ml	GFAAS	Spiking level: nr (n=nr) 91±5	Calibration: external standards P+2Ex+1Ev	[42] [65]
Spiked and incurred mussels	MBT DBT TBT MPhT	(2) 10 g wet sample+25 ml 1 *M* HCl–THF (1:11). Ex with 0.1% tropolone in benzene (2×50 ml, 5 min). Shaking with 500 ml 25% NaCl. Ex	cGC–FPD methylsilicone	Spiking level: 100 ng g^{-1} ($n=3$) MBT: 70±1 DBT: 96±8	Reaction time of the propylation reaction was optimised Calibration: I.S. (HeTBT)	[83]

Table 6. Continued

Sample	Analyte	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
	DPhT TPhT	of the aqueous layer with 50 ml of 0.1% tropolone in benzene. Ev to 0.5 ml (3) PrMgBr. Ev to 0.5 ml. Dilution to 5 ml with benzene (4) Florisil/Hexane. Ev to 0.5 ml. Dilution to 5 ml		TBT: 94±11 MPhT: 100±4 DPhT: 93±5 TPhT: 90±11	5Ex+1C+2Ev+D+CU	
Incurred mussels	MPhT DPhT TPhT	(2) 4 g wet sample+10 ml 1 *M* HBr in ethanol. Ex with 10 ml 0.1% tropolone in benzene (2×10 ml, sonication, 30 min). Washing with 2M NaBr. Solvent exchange to hexane–MeOH. Collection of the MeOH phase. Solvent exchange to benzene (3) PrMgBr (4) Silica gel/Benzene. Ev to 1 ml	cGC–FPD TC-5		Calibration: I.S. (TePeT). TPeT as surrogate 6Ex+3C+5Ev+CU+D	[52]
Spiked and incurred oysters. Dab fish Eggs	MBT DBT TBT DPhT TPhT	(2) 5 g wet sample+10 ml 0.9% saline solution+12 ml conc. HCl (stand for 10 min).+2 g NaCl. Ex with Et_2O (20 ml×3, 10 min). Exchange to hexane saturated with acetonitrile. Ex with 20 ml acetonitrile saturated hexane (×2). Exchange to Et_2O (4a) Florisil/HOAc–Et_2O (1:99). Exchange to hexane–EtOAc (2:1) (4b) HCl-treated silica gel/Hexane–EtOAc (2:1). Exchange to Et_2O (3) MeMgBr. Ev to 2 ml	(a) cGC-FPD DB-5 (b) cGC–AED HP-1 or DB-5 cGC–MS–SIM cross-linked methylsilicone	Spiking level: 100 μg g^{-1} (n=3) MBT: 58±2 DBT: 97±6 TBT: 94±12 DPhT: 60±2 TPhT: 72±10	Calibration: external standards P+5Ex+2C+5Ev+2CU+D	[97] [98]
Spiked fish tissues NIES-11	TMeT TBT TPhT	(2) 2.5 g wet sample+25 ml water+3.75 g NaCl+2.5 ml 6 *M* HCl. Ex with 12.5 ml EtOAc (30 min). Ev to near dryness. Solution in MeOH	LC–ICP-MS ODS-2 and PRP-1 0.004 *M* sodiumpentanesulfonate in MeOH–water–OAc buffer (94:5:1)	*NIES-11* (n=3) TBT: 94±4 TPhT: 99±4 *Tuna fish* Spiking level: 100 ng g^{-1} (n=3) TBT: 65±2 TPhT: 64±5	Separation on a polymeric column was optimised Calibration: external standards 1Ex+1C+1Ev	[79]
Spiked and incurred bivalves and mussels NIES-11	TBT	(1) 5 g sample (or 1 g NIES-11)+40 ml conc. HCl (stirring, 3 h)+10 ml water (stirring, 10 min) (2) Ex with 100 ml pentane. Washing with 3% NaOH. Ev to dryness. Solution with MeOH–water (3:2) (4) C_{18}/MeOH–HNO_3	GFAAS	Spiking level: 20–200 ng g^{-1} (n=3) TBT: 92–105 R.S.D.: 5–9% *NIES-11* (n=3) TBT: 108 R.S.D.: nr	Calibration: external standards and standard additions P+2Ex+1Ev+CU	[56] [59]
Spiked and incurred zebra	DBT TBT	(2) 6 g wet sample+10 ml water+40 ml MeOH+17 ml conc. HCl+10 g NaCl (stand for 15 min). Ex with	cGC–FPD DB-1	Spiking level: nr (n=12) DBT: 46±11	Calibration: nr P+4Ex+3C+1Ev+CU+D	[115]

(continued on page 26)

Table 6. Continued

Sample	Analyte	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
mussels		0.25% tropolone in Et_2O–hexane (3:2) (30 ml, 1 min; 2×20 ml, 30 min; 4°C) (3) HeMgBr. Ev to 1 ml (4) Silica gel-8% water deactivated florisil/Hexane–Et_2O (90:10)		TBT: 84±8		
Spiked and incurred marine mammals	MBT DBT TBT	(2) 1–2 g sample+10 ml 1 *M* HCl+40 ml 0.1% tropolone in acetone+500 ml 25% NaCl. Ex with 100 ml 0.1% tropolone in benzene. Exchange to hexane (3) PrMgBr. Ev to near dryness (4a) Dry florisil, (nitrogen stream during 3 h)/Acetonitrile–water (80:20) (4b) Wet florisil/Hexane–benzene (90:10)	cGC–FPD DB-1	Spiking level: 20 $\mu g\ g^{-1}$ ($n=3$) MBT: 97±26 DBT: 102±9 TBT: 91±14	Calibration: I.S. (HeTBT) 3Ex+2Ev+2CU+D	[84] [87]
Spiked and incurred zebra mussels	MBT DBT TBT MPhT DPhT TPhT DCyT TCyT FBTO	(2) 2 g wet sample+0.3 ml 1 *M* HCl to pH=2.0+0.5 g NaCl. Ex with 0.3% tropolone in Et_2O (2×6 ml, sonication, 5 min). Ev to dryness Solution to 1 ml Et_2O. (3) MeMgI. Ev to 1 or 2 ml (4) Basic alumina/Hexane–Et_2O (80:20). Ev to 0.4–0.6 ml	cGC–MS cGC–AED DB5-MS	Spiking level: 100 $ng\ g^{-1}$ ($n=13$) MBT: 69±18 DBT: 93±23 TBT: 79±25 MPhT: 58±12 DPhT: 72±17 TPhT: 83±18 DCyt: 84±14 TCyT: 88±19 FBTO: 82±16	Parameters related with derivatization were investigated. Three clean-up systems were examined Calibration: I.S. (MPhTEtT, EtTBT, DPhDEtT, TPhEtT). PCB 103 as an additional I.S. 3Ex+3C+3Ev+CU+D	[95] [96]
Incurred bivalves	MBT DBT TBT TPhT	(2) wet sample (5 g dry weight basis) +25 ml MeOH+17 ml conc. HCl (stand for 10 min)+NaCl. Ex with 0.24% tropolone in Et_2O–hexane (3:2)(3×40 ml) (3) MeMgCl. Ev to 0.5 ml (4) Activated silica/Hexane–Et_2O (90:10). Ev	cGC–FPD SE-54		Calibration: I.S. (TeBT) 3Ex+3C+1Ev+CU+D	[114]
Spiked horseshoe crabs	MPhT DPhT TPhT	(2) 2–3 g sample+10 ml 1 *M* HCl+40 ml 0.1% tropolone in acetone. Ex with 0.1% tropolone in benzene. Ev Addition of 70 ml hexane-saturated acetonitrile+10 ml hexane. Ex with 100 ml hexane–benzene (90:10). Ev to 5 ml (3) PrMgBr. Ev. Solution with 5 ml hexane (4) Florisil/Hexane–benzene (90:10)	cGC–FPD DB-1	Spiking level: 300 ng (n=nr) MPhT: <10 DPhT: 107 TPhT: 80 R.S.D.: nr	Calibration: external standards subjected to the whole analytical procedure 5Ex+3Ev+CU+D	[86]

See List of abbreviations.

Table 7
Biotic matrices: polar solvents

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked oysters	MMeT DMeT TMeT MBT DBT TBT	(2+3) 0.2–0.5 g wet sample+1 ml MeOH. Ex with 8.5 *M* HCl (5 ml, sonication, 1 h, 60°C). NaBH$_4$. (2 ml of supernatant)	HG-CT QFAAS SP2100 on Chromosorb GAW–DMCS	Spiking level: 10–100 ng g^{-1} ($n=3$) 93–113 R.S.D.: 1–18%	OTs stability under extracting conditions was studied Calibration: matrix matched standards+I.S. (TEtT) 1Ex+1C+D	[124]
Spiked eelgrass	MMeT DMeT TMeT MBT DBT TBT	(2) 0.5 g wet sample. Ex with 6 *M* HCl (10 ml, sonication, 2 h, 50°C) (3) NaBH$_4$	HG–CT–QFAAS SP-2100 on Chromosorb GAW-DMCS	Spiking level: 1 μg g^{-1} ($n=3$) MMeT: 83±6 DMeT: 87±8 TMeT: 72±19 MBT: 65±12 DBT: 63±9 TBT: <5	Acid extraction not satisfactory for TBT Calibration: matrix matched standards 1Ex+1C+1Ev+D	[119]
Spiked and incurred fish tissues	DBT TBT	(2) Sample homogenised (1:1) with 0.5 *M* HCl in MeOH. 10 g homogenate. Ex with 0.5 *M* HCl–MeOH (3×30 ml). Ev to 30 ml. Addition of 100 ml sat. NaCl. Ex with hexane (3×40 ml). Washing with NaHCO$_3$. Ev just to dryness. Solution in DCM–cyclohexane (1:1) (4) GPC. Ev just to dryness. Solution in Et$_2$O (3) MeMgBr or PeMgBr. Addition of NaOH and Na$_2$S$_2$O$_3$. Ev just to dryness. Solution in 1 ml hexane	cGC-FPD CBP-10	Spiking level: 200–1000 ng g^{-1} ($n=3$) DBT: 92–105 TBT: 80–104 R.S.D.: 2–8%	Clean up of the extracts by GPC was studied. Derivatization step was optimised Calibration: external standards P+4Ev+4Ex+1F+CU+D	[127]
Spiked and Incurred oyster tissues	MBT DBT TBT	(2) 1.6 g dry sample. Ex with 2 *M* HCl (45 ml, 12 h) (3) NaBH$_4$	HG-CT-GC-QFAAS OV-101 on Chromosorb 750	Spiking level: 600 ng g^{-1} ($n=3$) MBT: 88±7 DBT: 73±6 TBT: 69±10	Acid and alkaline leaching procedures were compared Calibration: standard additions 1Ex+1F+D	[120]
Spiked eelgrass	TBT	(2) 1 g wet sample. Ex with 10 ml DCM–MeOH (2:1) (sonication, 2 h 50°). Ev to dryness. Solution with Bu$_4$NBH$_4$ in DCM (3) HG: first with Bu$_4$NBH$_4$ and after with NaBH$_4$	HG–CT–QFAAS SP-2100 on Chromosorb GAW–DMCS	Spiking level: 0.5 μg g^{-1} ($n=3$) TBT: 77±12	HG in two step was proposed Calibration: standard additions 1Ex+1Ev+1C+D	[119]
Spiked and incurred salmon tissue	DBT TBT	(2) 40 g wet sample+80 ml MeOH. Ex with 0.005% tropolone in DCM (2×40 ml, 2 min). Washing with 160 ml water. Addition of hexane. Ev to 10 ml (4) Silica gel/DCM–MeOH (1:1) 0.02 *M* HCl (3) NaBH$_4$ (packed bed reactor)	cGC–FPD HP-5	Spiking levels: 25–125 ng g^{-1} ($n=4$–7) DBT: 73–125 TBT: 78–107 R.S.D.: nr	The derivatization step by means of a packed bed reactor was optimised Calibration: TPrT as surrogate 3Ex+1C+2Ev+CU=D	[128]

(*continued on page 28*)

Table 7. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked fish	MBT DBT TBT TeBT	(2) 50 g sample. Ex with 2% HCl in acetone (2×150 ml). Ev. Ex with hexane (150+50 ml). Ev to 5 ml. Saponification with 2 *M* KOH in MeOH. Ex with chloroform-DCM (1:1) (4×100 ml). Ev to dryness. Solution with 0.2 M HCl in actone (2–5 ml)	cGC–DCP–AED cGC–FPD DB-17	Spiking level: 50–200 ng g^{-1} (n=3) TBT: 93–99 R.S.D.: 1–4%	Calibration: nr 8Ex+2C+3Ev	[112]
Incurred mussels	MMeT DMeT TMeT MBT DBT TBT	(2) 0.5–1 g dry sample. Ex with HOAc (25 ml, 25 h). (3) NaBH$_4$ (0.1–1 ml supernatant)	HG–CT–QFAAS OV-101 on Chromosorb GAW–DMCS		Calibration: external standards 1Ex+1C+D	[144]
Incurred oysters	MBT DBT TBT	(2) 1 g dry sample. Ex with HOAc (20 ml, 4 h) (3) NaBH$_4$	HG–CT–QFAAS Chromosorb GAWHP		Four leaching procedures using HCl and/or HOAc were evaluated Calibration: standard additions 1Ex+1C+D	[123]
Incurred fish tissue (NIES-11)	TBT TPhT	(2) 1 g dry sample. Ex with 1 *M* HCl in MeOH–EtOAC (1:1) (50+20 ml, 30 min). Addition of 100 ml 10% NaCl. Ex with EtOAc–hexane (3:2) (2×30 ml). Shaking with 100 ml hexane. Ev to near dryness. Dilution with 10 ml ethanol (4) Anion exchange and cation exchange cartridges/1 *M* HCl in MeOH.+15 ml 10% NaCl. Ex with hexane–cyclohexane (1:1) (2×25 ml). Ev to 1 ml (3) PrMgBr	cGC–FPD Ultra-1		Calibration: I.S. (HeTBT) 9Ex+2F+2Ev+CU+D	[161]
Spiked and incurred mussels	MBT DBT TBT MPhT DPhT TPhT	(2) 0.1–0.5 g dry sample. Ex with 0.05% tropolone in MeOH (2× 15 ml, sonication, 15 min) Addition of 150 ml water. Ex with 30 ml DCM. Solvent exchange to isooctane (3) PeMgBr. Ev to 0.5–1 ml (4) Florisil/hexane–benzene (1:1). Ev to 1 ml	cGC–FPD DB-1 cGC–MS (Confirm.) HP-5	Spiking level: 240–620 ng g^{-1} (n=5) TBT: 91 DBT: 89 MBT: 85 TPhT: 92 DPhT: 85 MPhT: 82 R.S.D.: 10%	Different extraction solvents were tested Calibration: TPrT as surrogate 4Ex+3Ev+D+CU	[158] [159]
Spiked and incurred algae	MBT DBT TBT	(2) 0.5–0.5 g dry sample. Ex with HOAc (20 ml, stirring overnight+sonication, 30 min) (3) NaBH$_4$	HG–CT–QFAAS OV-101 on Chromosorb GNAW	Spiking level: 2–5 ng (n=nr) TBT: 25–38 DBT: 33–39 MBT: 31–44 R.S.D.: nr	Calibration: standard addition 1Ex+1C+D	[145]

Table 7. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked shellfish	TBT	(2+3) 4 g sample+10 ml 0.1% NaOH in MeOH (45 min). Addition of NaBH$_4$. Ex with hexane (2 ml)	cGC–FPD Phenyl methyl silicone	Spiking level: nr (n=nr) TBT: 95–104 R.S.D.: nr	Calibration: standard additions. TPrT as surrogate 1Ex+1C+D	[163]
Spiked mollusc and salmon NIES-11	MBT DBT TBT	(2) 1 g wet sample+1 ml MeOH. Ex with HCl 0.1 *M* (5 ml, sonication, 1h) (3) NaBH$_4$	HG–CT–QFAAS OV-101 on Chromosorb W HP	Spiking level: 250–1250 ng g^{-1} (n=6) MBT: 98–99 DBT: 97–98 TBT: 96–97 R.S.D.: 5–9 *NIES-11* (n=nr) TBT: 70 R.S.D.: nr	Effect of drying sample and extraction conditions on stability and extraction of BTs were studied. NaBH$_4$ conc. for various matrices was optimised. Stability of NIES was questioned. Calibration: matrix matched standards 1Ex+1C+D	[125] [126]
Incurred oysters, cockles and mussels	MBT DBT TBT	(2) 5 g dry sample. Ex with 0.08% tropolone in MeOH (2×25 ml, sonication, 30°C, 15 min). Ev to 1 ml. Addition of 10 ml hexane. Ev to 1 ml (3) PeMgBr. Ev to 1 ml (4a) Florisil/nr. Addition of 25 ml 1 *M* NaOH (30 min, 40°C) (4b) Florisil/pentane. Ev to 0.5 ml	cGC–FPD SPB-1		Extraction conditions were optimised Calibration: I.S. (DMeDPeT) 4Ex+4C+4Ev+2CU+D	[156]
Incurred mussels	MBT DBT TBT TPhT	(2) 3 g wet sample. Ex with 0.05% tropolone in MeOH (2×15 ml, sonication).+100 ml water. Ex with 30 ml DCM. Ev to dryness Solution in MeOH	LC–HG–ICP–AED Partisil-10 SCX 0.1 *M* NH$_4$OAc, 0.1% tropolone in MeOH–water (80:20) at pH=7.4		Mobile phase and detection system were optimised Calibration: nr 1Ex+2C+1Ev	[162]
Mussel	MBT DBT TBT MPhT DPhT TPhT	(2) 0.5 g dry sample. Ex with tropolone in MeOH+HCl (×2, sonication, 15 min). Addition of 200 ml NaCl. Ex with DCM (2× 25 ml). Ev. Addition of 2 ml isooctane. Ev to near dryness (3) PeMgBr (4) Silica gel/hexane–benzene (1:1) Ev to 1 ml	cGC–MS Ultra-1	Spiking level: 320 ng g^{-1} (n=5) MBT: 85±15 DBT: 89±11 TBT: 91±9 MPhT: 82±17 DPhT: 85±14 TPhT: 92±9	Preparation candidate to reference material Calibration: TPrT as surrogate 3Ex+2C+3Ev+CU+D	[141]
Incurred eel NIES-11	MMeT DFeT TMeT MBT DBT TBT	(2) 1 g wet sample (or 0.3–1 g dry sample). Ex with (a) 0.5 *M* HCl or (b) HOAc in MeOH (sonication, 1 h, 50°C) (3) NaBEt$_4$	CT–QFAAS SP-2100 on Chromosorb GAW	*NIES-11* (n=nr) TBT: (a) 84 (b) 97 R.S.D.: 5–8%	Effect of drying was studied. Acid conc. was optimised Calibration: standard additions 1Ex+1C+D	[122]

See List of abbreviations.

non-miscible solvent (benzene, CHCl$_3$–DCM, EtOAc–MeOH, DCM, hexane, cyclohexane, toluene, hexane–EtOAc) is carried out to recover OTs from the extracts [112,127,129,130,132,141,155,156, 158,161,162]. Several authors have used tropolone and salting out effect to increase the solubility of OTs in the organic solvent.

2.1.4. Supercritical fluid extraction

The SFE and SFC methods for OTs extraction and

Table 8
Biotic matrices: basic and enzymatic hydrolysis

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked and incurred fish tissues	MMeT DMeT TMeT	(1) 2 g wet sample+5 ml 20% TMAH (1–2 h at 60°C, until tissue had dissolved) (2) Adjustment of pH to 6–8+2 g NaCl. Ex with 0.5% tropolone in benzene (3 ml, 1 h) (3) BMgBr (4) Silica gel/nr	GC–QFAAS OV-225	Spiking level: nr (n=nr) Recoveries were quantitative	Calibration: external standards P+1Ex+1Ev+D+CU	[7]
Spiked and incurred fish, shellfish	DBT TBT	(1) 5 g wet sample+500 mg Na_2SO_3 Enzymatic hydrolysis (protease, 24 h) (2)+NaCl+HCl. Ex with 0.05% tropolone in hexane (2×10 ml). Ev to 1 ml (3) MeMgCl	GC–QFAAS OV-73	Spiking level: 35–60 ng g^{-1} (n=4) DBT: 86–100 TBT: 75–99 R.S.D.: 1–6%	Various extraction methods were tested Calibration: external standards P+4Ex+1Ev+D	[175]
Spiked and incurred fish, shellfish	DMeT TMeT	(1) 5 g wet sample. Enzymatic hydrolysis (protease, 24 h) (2) Ex with 0.05% dithizone in DCM–hexane, back-extraction with HNO_3. Neutralisation and Ex with ditizone solution (×3). Ev to 1 ml (3) BMgCl	GC–QFAAS OV-73	Spiking level: 12–70 ng g^{-1} (n=4) DMeT: 97–100 TMeT: 78–87 R.S.D.: 3–12%	Calibration: external standards P+6Ex+1Ev+D	[175]
Spiked and incurred fish, shellfish	TeMeT TeEtT	(1) 5 g wet sample. Enzymatic hydrolysis (protease, 48 h) with 2 ml hexane present (2) Ex with hexane (2+1 ml)	GC–QFAAS OV-73	Spiking level: 5–75 ng g^{-1} (n=4–6) TeEtT: 72–100 TeMeT: 98–100 R.S.D.: 2–4%	Calibration: external standards P+2C	[175]
Spiked fish	DBT TBT TPhT	(1) 5 g wet sample+50 ml KOH in ethanol (60°C, 90 min) (2)+HCl+10 g NaCl. Ex with toluene (2×10 ml). Ev. Solution with ethanol (4) Ion-exchanger/1 *M* HCl in MeOH. Addition of NaCl. Ex with hexane (×2). Ev to 1 ml. (3) PrMgBr. Ev to 1 ml	GC–FPD OV-1	Spiking level: 200–2000 ng g^{-1} (n=5) DBT: 42–57 TBT: 84–95 TPhT: 91–96 R.S.D.: 2–6% (TBT and TPhT) 10–25% (DBT)	Effect of T and hydrolysis time on the stability of OTs were studied. Ion exchange process was examined Calibration: I.S. (HeTBT) P+6Ex+1C+3Ev+CU+D	[174]
Spiked mussels	MBT DBT TBT MPhT DPhT TPhT	(1) 2 g sample+6 ml 5 *M* NaOH in ethanol–water (1:1) (40°C, 20 min) (2)+HCl+2 g NaCl. Ex with Et_2O–pentane–tropolone (80:20:0.1) (2×12 ml) (3) MeMgI. Ev to 1 ml (4) Alumina/hexane–Et_2O (80:20). Ev to 0.5 ml	cGC–MS cGC–AED DB-5MS	Spiking level: 100 ng g^{-1} (n=nr) 69–88 for all OT except 58 for MPhT R.S.D.: nr	Parameters related with derivatization were investigated. Three clean-up systems were examined Calibration: I.S. (TEtPhT, EtTBT, DEtDPhT and EtTPhT) P2Ex+1C+3Ev+CU+D	[95]
Spiked and incurred mussels and fish tissues	MBT DBT TBT	(1) 5 g wet sample+10 ml 10% TMAH (60°C, 1–2 h). Adjustment to pH 8 (2) Ex with 0.5% tropolone in hexane (3 ml, 1 h) (3) EtMgBr (4) Silica gel/Hexane. Ev to 0.5 ml	cGC–QFAAS DB-1	Spiking level: 1 μg (n=nr) Recoveries over 80%	Calibration: external standards subjected to the whole analytical process P+2Ex+2Ev+D+CU	[31]

Table 8. Continued

Sample	Analytes	Sample treatment	Determination technique	Recoveries (%)	Comments	Ref.
Spiked marine biotissue NIES-11	MBT DBT TBT TPhT	(1+2) 0.1 g sample. Enzymatic hydrolysis (protease–lipase, 4 h, 37°C) (3) NaBEt$_4$. Ex with hexane (1 ml) (4) Alumina. Et$_2$O. Ev	cGC–AED HP-1	Spiking level: 1 μg g^{-1} (n=4) MBT: 73±6 DBT: 98±5 TBT: 93±5 TPhT: 60±11 *NIES-11* (n=5) TBT: 103±5 TPhT: 115±5	pH and hydrolysis time were optimised. Several clean-up methods were investigated Calibration: standard addition and I.S. (TPeEtT) P+1Ex+1C+CU+1Ev+D	[172]
Spiked marine biotissue NIES-11	MBT DBT TBT TPhT	(2+3) 0.1 g sample+5 ml 25% TMHA (4 h, 60°C). NaBEt$_4$. Ex with hexane (1 ml) (4) Alumina/Et$_2$O. Ev	cGC–AED HP-1	Spiking level: 1 μg g^{-1} MBT: 84±5 DBT: 91±4 TBT: 94±3 TPhT: 72±9 *NIES-11* TBT: 102±5 TPhT: 94±7	Several clean-up methods were investigated Calibration: standard addition and I.S. (TPeEtT) P+1Ex+1C+1Ev+CU+D	[172]
Spiked fish	TBT TPhT	(1) 1 g sample+30 ml 1.8 *M* KOH–ethanol–water (60°C, 90 min) (2)+35 ml water+6 g NaCl+5 ml HCl. Ex with toluene (2×5 ml, 10 min). Exchange solvent to ethanol (4) Anion and cation cartridge/1 *M* HCl–MeOH through the second cartridge. Addition of 5 ml 1.7 *M* NaCl. Ex with hexane (×2) (3) PrMgBr. Ev to 1 ml (4) Florisil/hexane–Et$_2$O (99:1). Ev to 0.2 ml	GC–FPD OV-1	Spiking level: 20–400 ng g^{-1} (n=5) TBT: 78–86 TPhT: 64–71 R.S.D.: 3–6%	Extraction and clean-up conditions were optimised Calibration: I.S. (HeTBT) P+6Ex+2C+4Ev+2CU+D	[173]
Spiked fish tissue	MBT DBT TBT TPhT	(2+3) 1 g wet sample+10 ml 20% TMAH solution (1 h, 60°C). NaBEt$_4$. Ex with 10 ml hexane. Ev to 1 ml (4) 3% water deactivated silica/ Hexane. Ev to 1 ml	cGC–QFAAS DB-1701	Spiking level: 500 ng g^{-1} (n=5) MBT: 80±4 DBT: 91±5 TBT: 94±4 TPhT: 91±6	Calibration: external standards P+1Ex+2Ev+CU+D	[72]
Spiked fish and mussel NIES-11	MMeT DMeT TMeT MBT DBT TBT	(2) 0.1–0.2 g dry sample (1–2 g wet sample)+5 ml 25% TMAH (microwave, 60 W, 3 min). Dilution with 15 ml water (3) NaBEt$_4$. Ex with isooctane (1 ml) (4) Alumina/nr	cGC–AED DB-210	Spiking level: 20–40 ng *Fish* (n=5) MBT: 53–66 DBT: 97–102 TBT: 85–95 R.S.D.: 5–8% *Spiked NIES-11* (n=5) TBT: 94±5 DBT: 98±6 MBT: 96±6 *NIES-11* (n=5) TBT: 94±6	Microwave field instead centrifugation to break up emulsions was proposed Calibration: I.S. (TeBT). TPrT as surrogate P+1Ex+D+CU	[164]

See List of abbreviations.

determination published before 1994 have been reviewed [20]. In this review, only the SFE methods developed for soils and sediments, accounting for 6% of the abiotic procedures reviewed, is discussed. Shorter extraction time and limited amounts of toxic solvents and acids used are the main advantages of the SFE methods. Although most OTs are soluble in carbon dioxide [165] an organic modifier is mandatory to extract native OTs from soils and sediments [166]. Two approaches have been evaluated to improve the extraction efficiency of mono- and diorganotin species: (i) the addition of complexing agents [e.g., diethylammonium–diethylthiocarbamate (DEA–DDC) or DDC] [118,167–169] and (ii) alkylation in the extraction cell with a Grignard reagent prior to the extraction [170]. Recoveries obtained by the first approach are satisfactory for di- and triorganotin species but a clean-up step is usually needed. On the other hand, the second method yields satisfactory recoveries only for TBT and triphenyltin (TPhT). Recently, chlorodifluoromethane at subcritical and supercritical conditions has been evaluated for the extraction of a variety of trialkyltins from soils [171]. Despite these approaches deserve interest, further developments are needed to bring these methodologies to routine analysis.

2.1.5. Basic and enzymatic hydrolysis

Basic and enzymatic hydrolysis methods, which are restricted to biotic samples, lead to a tissue solubilization. This makes the embedded OTs more available to the extracting agent. They account for 15% of the analytical procedures for biotic matrices. Tetramethylammonium (TMAH) hydrolysis is currently applied above room temperature (60°C) for several hours (e.g., 1–2 h) [7,31,72,172]. Again, TMAH hydrolysis time can be reduced from hours to minutes when the digestion is carried out under focused microwave irradiation [164]. OTs are isolated from the hydrolysed tissue by hexane LLE in the presence of tropolone [7,31]. Alternatively, simultaneous extraction–derivatization with sodium tetraethylborate ($NaBEt_4$) (see Section 2.2) after a pH adjustment reduces the number of LLE [72,164,172] compared to Grignard derivatization methods.

Alternatively, ethanolic KOH at 60°C for 90 min [173,174] or NaOH at 40°C for 20 min [95] followed by pH adjustment and LLE have also been applied to the determination of OTs from biotic matrices. The digestion time in basic extraction conditions is critical due to the lack of stability of mono- and diorganotin compounds [1].

Up to now, very few analytical procedures using enzymatic hydrolysis for the extraction of OTs from biota tissues have been published. A lipase–protease mixture buffered at pH 7.5 is held at 37°C for 24 h [172,175]. Extraction is performed either following $NaBEt_4$ derivatization with a small volume of hexane [172], or before the derivatization with Grignard reagents [175].

2.1.6. Use of complexing agents

Tropolone in a variety of non-protic solvents (e.g., DCM, benzene, diethyl ether, toluene and hexane) has been extensively used to improve the solubility of mono- and disubstituted OTs within low polarity extracting solvents or supercritical fluids (see Section 2.1.4). No significant differences in the extraction efficiency according to tropolone concentration from 0.01 to 0.5% have been found [53]. The use of tropolone in the extraction of OTs with liquid solvents from biotic and abiotic matrices enhances the solubility of coextracted compounds; a clean-up step prior to the GC determination is mandatory [47]. DDC [25,34,55] and ditizone [175] have been rarely used [47]. Furthermore, a variety of complexing agents (e.g., DDC, DEA–DDC) have been evaluated to improve the solubility of OTs in supercritical carbon dioxide [118,167,169]. However, up to now no systematic study on the solubility and stability of the complexing agents in this fluid has been reported.

2.2. Derivatization techniques

GC methods generally need to include a derivatization reaction to produce volatile OT compounds to perform their separation. Separation of OT halides by GC without previous derivatization [21,108] can be considered as an exception, but their thermal lability strongly limits these methods. Underivatized OT halides can also be analysed by SFC with CO_2 at low temperatures [165], however, this approach still requires further developments. Derivatization methods are based on alkylation or hydridization reactions, which are commented in the following sections.

2.2.1. Alkylation reactions

Alkylation with a variety of Grignard reagents (e.g., methylation, ethylation, propylation, pentylation and hexylation) is the most widely used derivatization technique, accounting for 53 and 81% for sediment and biota, respectively of analytical procedures in which derivatization is performed. However, the method is time consuming, and requires strict anhydrous conditions and non-protic solvents, which necessitates solvent exchange when polar solvents are used as extracting agents. Furthermore, a LLE step becomes necessary to isolate the derivatized OTs. Stäb et al. [95] found that the derivatization yield of Grignard reactions is not affected by the OT counterion (i.e., halide, acetate), but it is strongly dependent of the elapsed time in solution for mono- and diorganotin compounds. Cai et al. [170] found the formation of dialkyl mono- and disulfides when the derivatization was performed in situ on a sediment sample before the SFE, which necessitates large excess of derivatization reagents. Similar side reactions occur when the Grignard derivatization reaction is performed on the extracts. A wide range of reaction times are reported, but too long exposure of phenyltins to Grignard reagents can lead to deproportionation reactions [176]. Several authors [102,177] have reported substantial losses of the most volatile tin species when the derivatization is performed with methyl and ethyl Grignard reagents. It is thus advisable to avoid evaporation to dryness of derivatized OTs. Another limitation of the methyl derivatives is that they do not allow the determination of the naturally occurring methylbutyltins [36].

To minimise analysis time, sodium tetraethylborate derivatization has been developed. This allows one to carry out the reaction in an aqueous media under buffered conditions [102]. In spiked river sediments, the derivatization yield of MBT using $NaBEt_4$ is lower than that given by hydridization methods, but matrix effects are reduced [136]. The method is particularly successful for aqueous samples [178] but lower derivatization yields than those given by the Grignard reaction are observed in complex matrices containing large amounts of coextracted compounds. The $NaBEt_4$ procedure allows a simultaneous extraction–derivatization in a buffered medium. The ethylated derivatives are recovered with a non-polar solvent [71–73]. A similar approach has been followed using $NaBH_4$ in NaOH–MeOH [163].

2.2.2. Hydridization reaction

Hydride generation with $NaBH_4$ has seldom been used in off-line methods owing to the lack of hydride stability. However, these derivatization techniques combined with CT-QFAAS allow the determination of butyltins and highly volatile OTs (i.e., methyltin), which cannot be determined by most of off-line methods. However, phenyltins cannot be analysed with this method. The on-line HG-CT-QFAAS methodology allows to reduce the sample handling steps to a minimum, which makes this approach one of the most rapid alternatives for the analysis of OTs. The amount of derivatization reagent needs to be optimised according to the matrix characteristics [123,126] since the matrix can inhibit the hydridization reaction [145]. In this regard, Asbhy and Craig [102] reported that uncomplexed tropolone suppresses the hydride generation reaction. Sullivan et al. [128] developed a gas phase hydridization reaction by packing the injector port of the gas chromatograph with $NaBH_4$ blended with an inert GC packing. Although the method may reduce the analysis time, it leads to low repeatability when applied to environmental samples.

2.3. Clean-up

Most of the analytical procedures based on GC determination require a clean-up, usually after the derivatization step. Silica is the adsorbent most used (about 50%), other adsorbents are: Florisil [33,36,83,84,86,87,103,113,156,158,159,173], alumina [25,45,47,95,96,164,172], alumina–silica [12,41,43,44], amino [43] and C_{18} cartridges [56,59], Florisil–silica [35,49,99,115] and Florisil–alumina [39]. The adsorbent activity must be carefully monitored to obtain consistent results and a balance must be reached between the clean-up efficiency and the analyte recovery [67].

In most of the methods applied to sediments that use GC–MS or GC–flame photometric detection

(FPD), a desulfurization with activated copper following the clean-up step is performed [179]. However, alkylsulfides generated during the Grignard derivatization from elemental sulfur occurring in sediments are not removed by this procedure. Alternatively, other desulfurization reagents such as tetrabutyl ammonium hydrogensulfate and sodium sulfide [83,139,140] have been successfully applied. Florisil is the preferred adsorbent for biotic matrices with a high lipid content [84,86,87,156]. Indeed, some biotic samples need an extra clean-up step. In this regard, partitioning between hexane–methanol [52,86] or hexane–acetonitrile [98], a basic hydrolysis [57,156] or double Florisil clean-up at different stages of the analytical procedure [84,87,98,113] have been successfully applied. Hexane or hexane–Et_2O mixtures are the most widely used eluents during the clean-up step because they allow GC determination without evaporation to dryness. More volatile eluents such as pentane are used to minimise the evaporation losses of the most volatile species.

Other analytical procedures perform the clean-up step before derivatization. Florisil [97,98,113], silica [29,106,128,132], silica-HCl [78], C_{18} [64] cartridges have been applied. Since underivatized OTs have a strong interaction in these adsorbents, polar eluents are needed to achieve quantitative recovery, which leads to poor clean-up efficiency. Tropolone in hexane has been used as eluent in this case [64]. Gel permeation chromatography (GPC) [127] and anion/cation exchange cartridges [161] are other alternative clean-up methods used prior to derivatization.

2.4. Determination techniques

In most methods, OT speciation is based on chromatographic separation prior to the detection. GC methods constitute the 64% of the determination techniques reviewed, and CT and LC techniques are each described in 13% of the articles. Up to now, capillary electrophoresis (CE) has been applied almost exclusively to water samples and only one separation of triorganotins in soils by micellar electrokinetic chromatography (MEKC) has been proposed [171]. However, some analytical techniques allow TBT determination by GFAAS after a selective extraction [42,56,59,60,65,66,68,74,101]. In addition, Siu et al. [75] developed an ion spray mass spectrometry (ISMS)–MS technique for TBT determination in the presence of other butyltins.

Although HG-CT is not considered as a GC separation in this review, in the following it will be treated together with GC, as it uses stationary phases and detection systems common to some GC methods.

2.4.1. Gas chromatography

GC-based speciation techniques have been widely used since they give higher resolution than LC methods which allows the simultaneous determination of butyl-, phenyl-, cyclohexyl-, methyl-, ethyl- and octyltins [45,140,167,169]. Another advantage of GC over LC is the possibility of using several internal standards (I.S.s) and surrogates which allow the steps of the analytical procedure to be traced. The main disadvantage of GC methods is that they usually require production of volatile OT derivatives to perform their separation.

Packed columns were extensively used in chromatographic separations during the 1980's. Nowadays they are used almost exclusively in CT when hydride derivatization is carried out. The hydrides are purged with a helium stream and trapped in a U-shaped packed column cooled by liquid N_2. The column is then heated rapidly until the purging step is complete. This method is only successful for the determination of methyl- and butyltins.

On the other hand, capillary columns gained acceptance during the 1990's and nowadays they are commonly used rather than packed or megabore columns. Dirkx et al. [180] reported that peak shape and resolution are significantly improved using capillary columns, which leads to more sensitive detection of closely eluting compounds, almost irrespective of their concentration ratio. Nevertheless, some recent determinations in hyphenated systems still use megabore columns since the higher flow rate minimises the detector dead volume [47,50,53,156].

Samples are usually introduced into the column by splitless injection because non-volatile coinjected compounds are retained in the liner. Its limitation is the low sample capacity (up to 2 μl) and the discrimination of low-volatile OTs against the highly volatile tin species. Cold on-column and temperature programmable injectors avoid some of the limitations of the splitless mode and they allow up to 5 μl to be injected [172]. In order to prevent column contamination GC Tenax packing in the injection port [172] or uncoated deactivated tubing [91] have been used.

The high efficiency achieved by capillary GC (cGC) allows satisfactory resolution of OTs according to carbon number even with non-polar non-selective stationary phases, such as dimethylpolysiloxane or 5% diphenyldimethylpolysiloxane (DB-1, HP-1, Ultra-1, SPB-1, SE-30, DB-5, HP-5, Ultra-2, CP-Sil 8CB, RTx-5, SE-54). The application of such columns amounts 90% of the publications reviewed. Müller [100] found an interesting correlation between retention time and the number of carbons on the alkyl substituents: OTs with equal carbon number in the molecule coelute. Although mid-polarity stationary phases such as 50% diphenyldimethylpolysiloxanes (DB-17, OV-17) or 14% cyanopropylphenyl 86% methylpolysiloxanes (DB-1701) are more rarely used [67,72,99,104,111–113,127,132,170], they allow the resolution between specific OTs (phenyl- and cyclohexyltins) which are poorly resolved in non-polar or low-polarity columns. Recently a 50% trifluoropropylpolysiloxane stationary phase (DB-210) has been used to decrease the analysis time [164]. Analysis time can also be reduced by heating the column to 280°C at 20°C min^{-1}, this allows the determination of butyl- and phenyltins in ca. 10 min with a 25 m×0.32 mm I.D. column [172]. Butyltins can be measured with a shorter column (12 m) in less than 10 min [106].

From the detection point of view, GC is highly flexible. In this respect, the following detectors have been used for OTs speciation: flame ionization detection (FID), electron-capture detection (ECD), atomic absorption spectrometry (AAS), tin-selective FPD, atomic emission detection (AED) and MS. ECD and FID were used in the early speciation studies but seldom during this decade [61,67,76,78,104,105,132]. The lack of selectivity and/or sensitivity of those detection systems led to their replacement by more sensitive low cost detectors such as MS in the electron impact mode, FPD equipped with an interference filter at 610 nm or AAS. Unfortunately, the low-molecular-masses of diagnostic ions in the electron impact or chemical ionisation modes impair moderate selectivity in case of complex matrices [23]. Up to now, high-resolution MS has not been evaluated to improve the selectivity in OT speciation studies and isotopic dilution techniques have not been applied in the GC–MS techniques. Similarly, FPD suffers some interferences associated to coextracted sulfur species [170]. Dual-flame FPD was introduced to improve the selectivity and to minimise the signal quenching but it has not been very effective for OT due to a lower sensitivity than single-flame FPD [91]. AED is one of the most sensitive and selective detection systems coupled to GC used in OT speciation. However, the high cost and maintenance operation of the GC–microwave induced plasma (MIP)-AED system precludes its application to monitoring studies involving a large number of samples.

2.4.2. Liquid chromatography

An extensive review of LC in OT speciation [28] covers most of the methods published before April 1995. This work points that there are many methods for standards, but few for environmental samples. This reveals that, in spite of the advantage of avoiding a derivatization step, LC has some limitations arising from the insufficient sensitivity of the most common detectors for the levels found in environmental samples.

The number of species analysed in biota and sediments using LC are significantly lesser than the ones analysed using GC. Mainly, they are butyltins, and in some cases TPhT is also considered [46,79,80,160,162].

Among the different modes of LC used (ion-exchange, reversed-phase, normal-phase and ion-pair chromatography), ion-exchange has been the most applied [62,80,109,110,153,155,157,160,162], whereas reversed- and normal-phase, which have been extensively proposed for standards, have been scarcely applied to solid matrices [37,40,46,51,77,90]. In any case isocratic elution is the most common mode.

Ion-exchange chromatography is generally performed in silica based cation-exchange columns, mainly the Partisil-10 SCX (Whatman). Mobile phases consist of a mixture of methanol, or sometimes acetonitrile, and water, containing ammonium acetate or citrate. The separation between TBT and DBT or among different triorganotin compounds is achieved at the same pH value. In contrast, in order to elute MBT the pH must be lowered. This separation mode has been successfully applied by several researchers [109,153,155] but it is time-consuming since the column must be reequilibrated after each run. An alternative approach to separate the three butyltin compounds involves the addition of tropolone to the mobile phase [162].

Separations of di- and triorganotin compounds based on normal phase mode using different cyanopropyl columns have been described [37,40,46,77]. Mobile phases consist of a high percentage of hexane together with a more polar solvent, such as ethyl acetate or tetrahydrofurane (THF) and HOAc, which is necessary to avoid the adsorption of the OTs on the unreacted silanol groups of the stationary phase. A mobile phase consisting of tropolone in toluene has been also proposed, but it slowly degraded the column [37,40].

Reversed-phase with an octadecylsilane stationary phase (C_{18}) has been used in the separation of butyltin compounds in sediments using a polar mobile phase. In this case the addition of a complexing agent, such as tropolone, to the mobile phase is mandatory [51].

On the other hand the reversed-phase ion-pair approach has been used in the separation of triorganotin compounds [79,85] or methyltins [116]. Polymeric-based column (PRP-1) or octylsilane column were used, whereas sodium pentanesulfonate or hexanesulfonate were used as an ion-pair.

Several detectors or hyphenated techniques have been used in LC: AAS [37,40,62,90,110,153,162], ICP-MS [51,85,109,155], fluorimetry [46,77,160], MS [90], laser enhanced ionisation (LEI) [157] and ICP-atomic emission spectrometry (AES) [162].

Among different AAS modes, flame AAS with pulse nebulization [62] and off-line GFAAS were the earliest [90,110], but they did not provide limits of detection (LODs) low enough or did not allow continuous recording. Later, some automated coupling systems of GFAAS with LC were proposed, but chromatographic resolution was severely affected [37,40].

When ICP-MS is coupled to LC, pneumatic nebulizers and spray chambers are the most common systems for sample introduction. These conventional nebulizers introduce only 1–5% of the sample into the plasma and have large dead volumes that can cause band broadening. The use of more efficient nebulizers, such as ultrasonic types has also been reported for triorganotin speciation [85]. Nevertheless, they can also present additional extra-column dead volume in the gas phase. One option that shows promise is the use of a direct inject nebulization which must be coupled to micro LC systems, but to date it has been applied only to standards [181]. Moreover, ICP methods suffer from poor compatibility with most mobile phases.

ICP-AES has rarely been used in tin speciation, mainly because of the lack of sensitivity. Recently, a system based on a hydride generator device between the LC column and the detector has been described. Due to the separation of the organic eluent this HG-ICP-AES system avoids the torch instability and increases the instrumental sensitivity [162].

When fluorimetric detection is used, derivatization with a fluorogenic reagent is mandatory because OTs do not present native fluorescence. The reagents used are flavone derivatives [46,77,160] and the reaction is commonly performed after the chromatographic separation.

2.4.3. Detection limits

Selected absolute detection limits according to the analytical technique and analyte are listed in Table 9. Two major difficulties were found in drawing up this table: (i) the way in which the limits were calculated is seldom reported, and (ii) the mass units referred to are not in all cases clearly given (tin, compound, halide).

Despite these uncertainties, several features can be pointed out. Among the non-chromatographic techniques the ISMS–MS is ca. 4-orders of magnitude more sensitive than GFAAS. In the group of the GC detection techniques, AED, MS in the electron impact (selected ion monitoring) and FPD have detection limits in the sub-to-low picogram range. Intra-technique discrepancies can be attributable to the operation mode and to the dramatic improvements in the sensitivity of the commercially available instrumentation over the last decade. For instance, the FPD configuration (i.e., filterless, single vs. double flame) can lead to remarkable differences in its sensitivity [91]. Filterless operation and quartz surface-induced luminescence are the most sensitive detection modes of the FPD [39,91,100,107]. Un-

Table 9
Selected absolute detection limits for phenyl-, butyl- and methyltins (pg).

	Butyltins			Phenyltins			Methyltins
	MBT	DBT	TBT	MPhT	DPhT	TPhT	
GFAAS			30000 as Sn [68]				
ISMS/MS			5 as Sn [75]				
GC–ECD	20–50 [78]	20–50 [78]	1–50 [76,78,91]	50–100 [78]	50–100 [78]	50–300 [78,91]	TMeT:1 [76]
GC–QFAAS	400–1800 [69,102]	500–1400 [69,102]	700–1200 [69,102]				
	25 as Sn [72]	25–35 as Sn [34,72]	25–34 as Sn [34,72]				
GF–FPD							
Single flame	7–1500 [53,57,91,103, 113,140]	11–1500 [53,57,91,99, 103,113,127,140]	10–1500 [16,53,57,91,99, 103,113,127,140]	22–500 [53,140]	195–500 [53,91]	20–500 [53,91,99,140, 173]	MMeT: 4 [140]
	3.7 as Sn [170]	3–30 as Sn [108,170]	3.4–100 as Sn [108,128,170]	11.5 as Sn [170]	4.4 as Sn [170]	4.7 as Sn [170]	
Dual flame	270 [91]	180 [91]	160 [91]			455 [91]	
Filterless	8 [91]	14 [91]	3 [91,100]		24 [91]	12 [91]	
Quartz surface-induced luminiscence	0.8–3 as Sn [39,107]	0.7–3 as Sn [39,107]	0.8–3 as Sn [39,107]	0.8 as Sn [107]	2.3 as Sn [107]		
GC–MIP–AES	5–10 [97,169]	5–10 [97,169]	5–10 [97.169]		5 [169]	10 [97]	DMeT, TMeT: 5 [169]
	0.05–4 as Sn [45,55]	0.05–4 as Sn [45,55]	0.05–3 as Sn [45,55]	3–4 as Sn [45]	3–4 as Sn [45]	3–4 as Sn [45]	
GC–ACP–AES			880 as Sn [58]				
GC–MS		11 [91]	9 [91]			59 [91]	
	0.8–2 as Sn [45]	1–3 as Sn [45]	0.5–1 as Sn [45]	0.5–0.6 as Sn [45]	0.3–0.4 as Sn [45]	0.2–0.4 as Sn [45]	
HG–CT–QFAAS	500 [120]	1000 [120]	3500 [120]				MMeT, DMeT TMeT: 500 as Sn [119]
	30–400 as Sn [119,125,136]	30–500 as Sn [119,125,136]	60–1000 as Sn [119,125,136]				
LC–ICP–AES	7000 as Sn [162]	7000 as Sn [162]	7000 as Sn [162]				
LC–ICP–MS			1.5–3.3 [79,85]			2.3–2.8 [79,85]	TMeT: 1.6 [79]
		20 as Sn [109]	40 as Sn [109]				
LC–MS		1300 [80]	1700 [80]				
LC–flame LEI			60 as Sn [157]				
LC–Fluorimetry		600 [46]	30000 [46]		600 [46]	1500 [46]	
			900 as Sn [160]			30 as Sn [160]	
LC–GFAAS	500 [153]	1100 [163]	800 [153]				

See List of abbreviations.

fortunately, a dramatic deterioration of the selectivity due to the sulfur emission at 390 nm was found in these operation modes [182]. On the other hand, oxidant flames can lead to poor sensitivity since the luminescence at 610 nm is attributed to tin hydride [53,57].

The sensitivity of the AES techniques is strongly dependent on the plasma source. In this regard, alternating current plasma (ACP)-AES [58] has detection limits at least two orders of magnitude higher than MIP-AES.

The GC–QFAAS techniques have LODs ca. two-orders of magnitude higher than former detection systems (i.e. ECD, FPD, MS, AED) coupled to GC techniques. Nevertheless, the suitable design of the interface and cGC columns can improve the sensitivity of the AAS by at least one-order of magnitude [34,72,180].

Among the LC methods, those using ICP-MS detection, either with ultrasonic or pneumatic nebulization, are the most sensitive for all the OTs, and are comparable to the most sensitive GC methods [59,79].

Although several fundamental articles have appeared about the ionisation mechanisms in different LC–MS interfaces, only thermospray has been applied to environmental studies [80]; it has moderate sensitivity, with detection limits about 2- or 3-orders of magnitude higher than ICP-MS. The outstanding improvements in sensitivity of the atmospheric pressure ionisation interfaces can raise the sensitivity in the LC–MS coupling.

On the other hand, the sensitivity attained with fluorometric detection depends both on the species and the fluorogenic reagent used, and in some cases very low detection limits are achieved [160], only improved by LC–ICP-MS by one order of magnitude.

3. Critical considerations

3.1. Storage and sample preparation

Sampling and transport are seldom discussed in the papers reviewed. When sediment or biological material is sampled and transported to the laboratory, it is rarely analysed as fresh sample, but usually stored, with or without pre-treatment. Aspects of storage and handling in sample pre-treatment (homogenisation, drying, freezing) are considered in some cases.

Freezing the wet material at −5 or −20°C is the procedure of choice to preserve OTs in biological samples during storage, but freeze-drying or rapid freezing in liquid nitrogen are also used. In the case of sediments, samples are also stored frozen or freeze-dried. Speciation changes or losses of OTs during storage are not well established, but the few available data on biological samples [126,183,184] indicate that good stability of butyl- and phenyltin compounds can be achieved (3–6 months) when samples are stored frozen, either wet or after lyophilization, whereas storage at room temperature should be avoided. On the other hand, studies on the effect of storage on sediment samples [185,186] showed that freezing or lyophilization and storage in refrigerator were both able to preserve butyltins for 12 months, whereas poorer results (3–4 months) were obtained with phenyltin species.

Sample preparation generally includes homogenisation of animal tissue previously removed from the shells (bivalves) or cleaned from skin and bones (fish). Although most of the papers (80%) point out that the sample was homogenised, various references (20–25%) give no information concerning the procedure. Some authors point out that frozen samples are homogenised after thawing, in order to overcome heterogeneity problems due to fractional freezing of constituents. For sediments, sieving steps are described in about 20% of the papers reviewed, although particle size has an important effect on the partition of OTs. In those cases in which sieving was performed, fractions below 100 μm were generally analysed. Some studies have pointed out that OTs are mainly associated with the finest fraction (silts and clays) and detritus fragments rather than sands [150,187,188]. Quevauviller et al. [188] reported a significant correlation between sediment organic carbon and butyltin content in sediments with high butyltin inputs, when only the finest fraction was considered. However, no correlation was found when the bulk sediment was considered [188,189].

Most analyses of biological matrices are undertaken on wet tissue (80%) rather than dried material and, in contrast, dry samples are analysed in about 60% of papers devoted to sediments. Lyophilization is the procedure generally used to dry biological samples before analysis [101,120,123,145,146, 156,158,161,185], but chemical- [33] or oven-drying [79] procedures are also reported. For sediment samples, procedures based on air-, freeze- and oven-drying (usually near 50°C) are used in a similar number.

The effects of drying on tin speciation are not well known, therefore, no indication as to whether samples should be dried can be given. There is some evidence that oven-drying at high temperatures produces changes in tin speciation [33,186] but results obtained using lyophilization are not conclusive, mainly for biological samples. Thus, whereas some authors [185] point out that lyophilization does not affect concentrations of OTs in oyster samples, important losses in TBT, as well as in methyl tin species, have been reported in some papers [33,122,126] when freeze-dried mussels and fish samples were used. According to Pannier et al. [126] direct analysis of dried mussel or salmon tissue resulted in low recoveries of TBT, but the problem was rehumidifying the sample before extraction. These results suggest that the low recoveries could be due to decrease in extractability of OTs from dried material rather than OT degradation on drying. On the other hand, differences in matrix composition may affect consequences of lyophilization, since, in contrast to biological material, no changes were described as a result of lyophilization of sediment samples [53,142]. In order to clarify this point, more detailed studies on the effects of drying on stability or extractability of OTs in different samples are necessary.

3.2. Spiking

In most papers reviewed, the information about spiking procedures and spiking levels is either non-existent or too scarce. Thus 70% reported the use of spiked samples, of which only about 25% described the spiking procedure with more or less detail and in 10% the spiking level is omitted.

Common steps of a spiking experiment are: (i) addition of a known amount of OT in solution, (ii) equilibration time to facilitate incorporation of the spike into the matrix and (iii) elimination of the solvent. Finally, the resultant material is subjected to the whole analytical procedure.

Spiking is generally carried out in each portion of sample to be analysed and only in a few cases an aliquot of a sample previously spiked and stored is analysed [126,135–137,160]. In the case of biological material, spiking is usually performed on wet samples, either in their original form or after rewetting them, whereas dry material is seldom spiked [120,145]. In contrast, spiking of sediment is usually performed on dried samples. In order 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 [190]. However, only few authors described this approach [130,159,166].

OTs are usually added as chloride, and rarely as oxide or acetate, dissolved in polar organic solvents (mainly methanol or ethanol) or in aqueous solutions [53,54,134]. Furthermore, the use of solutions in non-polar solvents is also reported [33,36,46,106] which is inadvisable in order to evaluate recovery rates since poor interaction between OTs and matrices occurs in these conditions.

The equilibration step is carried out by shaking and/or leaving the sample to stand for times ranging from 15 min to 24 h: in 30% of the papers less than 1 h (mainly 15 or 30 min), in 30% from 1 h to 4 h and 40% between 12 and 24 h. In some papers equilibration time is not reported and hence analysis just after spiking is assumed. In relation to this step, an interlaboratory study of a TBT-spiked sediment revealed the need for spikes to equilibrate at least overnight to ensure a realistic assessment of extraction recoveries [194] but only nine papers reviewed follow this recommendation. On the other hand, a study of the effect of two equilibration times (15 min and 24 h) on the recovery efficiency of TBT and DBT revealed a decrease in DBT recovery (15%) at the longest time [25], which suggests that more studies are needed in order to determine the influence of this parameter.

The solvent elimination step is usually carried out by air-drying at room temperature for sediment samples, whereas this step is seldom performed for biological materials. In most cases evaporation is not described, although it is assumed since a low volume of solvent is added. It must be taken into account that if the solvent is not eliminated, its presence could modify the subsequent extraction.

In order to simulate the environmental conditions of incorporation of OTs in sediments, [135–137] used a significantly different spiking procedure: a large amount of sediment suspended in water is spiked with an aqueous solution of butyltin compounds, and left in darkness for 10 days at room temperature with shaking for periods of 10 min twice each day. Finally sediment is freeze-dried to eliminate the water.

The spiking levels range from 0.01 to 2 $\mu g\ g^{-1}$ and most of them between 0.1 and 1 $\mu g\ g^{-1}$, Tables 1–8. According to the classification of Cortez et al. [147] for TBT contamination in sediments, which is very similar to that of Dowson et al. [8], in half of the cases, sediments are spiked with "very high" level of OT, i.e., $>500\ ng\ g^{-1}$, the other half are spiked with "medium" or "high" level (20–500 ng g^{-1}) and only in two papers does the spiking concentration correspond to sediments from a "lightly contaminated area" (<20 ng g^{-1}). In the case of biological samples, 50% were spiked between 100 and 500 ng g^{-1}, 30% at higher levels and 20% at levels lower than 100 ng g^{-1}.

The most advisable option of spiking at two or more levels is reported by only about 30% of the papers reviewed. In some of these studies significantly differences in the extraction recoveries were observed at different levels [36,67,130].

3.3. Calibration

Calibration is an essential step in any analytical method. However, in some papers, specially in those devoted to environmental monitoring, little information, if any, is provided on this aspect.

In the methods based on GC, calibration is generally carried out with I.S. (63% of papers reviewed), however, external standards are also extensively used (34%). In contrast, the standard addition method is seldom used. In those methods that involve a CT of volatile species (hydrides or ethyl derivatives) calibration is performed by the method of standard addition (77%) or with matrix matched standards (23%). When the analytical technique applied is LC or GFAAS, quantitation is usually performed with external standards although the standard addition method is sometimes used.

When external standards are used, some authors point out that the standard solutions have been subjected to the entire extraction procedure [31,111,113]. In other cases [86,110,119,124], in order to account for matrix effects, matrix-matched standards are proposed. However, suitable analyte-free matrices to match sample matrices may not be available.

When using the I.S. method, several approaches are proposed. In the most common approach, the substance used as I.S. is added to the extracts before the derivatization step, usually as a trialkyltin, or just before the injection into the chromatograph as a tetraalkyltin. In the first case, the I.S. affords a compensation for the incompleteness of the derivatization reaction, for the possible losses occurring in the operations subsequent to derivatization (extractions, evaporations, clean-up) and for the instrumental variability. In the second case it only compensates for uncontrolled variations in the chromatographic measurements. A second approach [61,93,141,158,159] consists in the addition of the I.S. (in this case also called surrogate) at the beginning of the extraction process, providing a compensation for the losses taking place in the whole process, including the variability of the determination step. Finally, some authors [12,35,41,48,52] propose the use of both a surrogate and an I.S.. This allows the calculation of the recovery of the substance added as a surrogate and, on this basis, correction of the amounts of analytes recovered.

The substances most commonly used as I.S. and/or surrogates are tripropyltin (TPrT), tetrabutyltin (TeBT), tetrapehnyltin (TePeT) and triphenyltin (TPeT). Generally only one I.S. and/or surrogate is used but some alternative approaches have been proposed: (i) the use of different I.S.s [monophenyltriethyltin (MPhTEtT), diphenyldiethyltin (DPhDEtT), triphenylethyltin (TPhEtT), tributylmethyltin (TBMEtT)], depending on the nature of the OTs being determined, has been shown to be a more accurate way for correcting variations of the alkylation step [95], (ii) the use of several surrogates with different degrees of alkylation [tripropyltin (TPrT), monophenyltin (MPeT), diphenyltin (DPeT) and triphenyltin (TPeT)] in order to match the behaviour of the different OT moieties in the extraction step [92–94]. The need for such an approach can be illustrated by the data of Wade et al. [41]. The reported recovery of MBT, after being corrected on the basis of the surrogate (TPrT) recovery (70%) was 40%, which shows clearly that the behaviour of the surrogate and the analyte during the extraction procedure are not comparable.

Since standard alkylated OTs are not commercially available, they are prepared by the analysts, usually by means of Grignard reagents. It is generally assumed that the yield of the derivatization reaction is the same for both standards and sample extracts, but this is still controversial. On the other hand, parameters such as the storage period of OT solutions before alkylation and the type of agent used to destroy Grignard excess have been shown to significantly affect the derivatization efficiencies [95].

As stated before, the standard addition method is the calibration method usually performed with hydride generation. The influence of the sample matrix on the hydride formation, particularly in the case of TBT, is well documented [119,145,192]. Schebek et al. [142] found that the slopes of standard addition regression lines obtained from different extracts showed large variations. Standard additions are usually performed in the extracts or in the reactor vessel. They can also be carried out on the sample [75,108] at the beginning of the analysis, but this implies a considerably greater experimental effort, which can be performed during the method validation but not in routine analysis.

3.4. Accuracy

The accuracy of the analytical procedures is mostly evaluated through the analysis of either CRMs or spiked samples.

In the field of OTs in sediments, nowadays there are two CRMs available: the harbour sediment PACS-1 with certified values for MBT, DBT and TBT, and the coastal sediment CRM-462 with certified values for DBT and TBT (Table 10). There is also the Reference Material RM-424, with a reference value for TBT and indicative values for DBT and MBT. This situation points out that the analysis of CRM only allows the assessment of the accuracy for butyltin compounds, and thus the need of more CRM with certified values for other OTs of environmental relevance, such as phenyltin species becomes clear.

Although the analysis of CRM is preferable to that of spiked samples, only about 20% of the papers related with sediments reported in this review make use of this approach, and in most cases PACS-1 is the CRM analysed. This can be due to the fact that PACS-1 was the first CRM available for OTs, or because concentration levels of OTs are higher in PACS-1 than in CRM-462. In relation to the analysis of MBT in PACS-1 some problems have been reported. None of ten methods evaluated by Zhang et al. [32] could recover MBT from PACS-1 satisfactorily. On the other hand, a high scatter of results also prevented certification of MBT in CRM-462 [194]. Recently, some efforts have been focused on improving the extraction of MBT from sediments and some authors questioned the validity of the certified value for MBT in PACS-1, because new extraction methods lead to significantly higher concentration values for this analyte [50,72,118,153].

Table 10
Reference materials available for organotin speciation

Name of the material	Responsible organization	Type	Units	Compound			
				MBT	DBT	TBT	TPhT
PACS-1	National Research Council of Canada	Harbour sediment	ng g^{-1} as Sn	280±170	1160±180	1270±220	–
CRM-462	Institute for Reference Materials of the European Commission	Coastal sediment	ng g^{-1} as cation[b]	–	128±16 (63±8)	70±14 (24±6)	–
RM-424	Institute for Reference Materials of the European Commission	Industrial harbour sediment	ng g^{-1} as cation[b]	257[a]±54 (174±36)	53[a]±19 (27±10)	20±5 (8±2)	–
NIES-11	National Institute for Environmental studies of Japan	Fish (sea bass)	ng g^{-1} as chloride[b]	–	–	1300±100 (475±36)	6300[a] (1942)

[a] Indicative value.

[b] Values in parentheses correspond to the concentrations as Sn.

See List of abbreviations.

Although the efficiency of the extraction process depends not only on the particular species, but also on the kind of sediment, only very few authors [72,140,167,170] validate their method by analysing both CRMs.

In the field of biological materials, only one CRM for OTs has been available since 1991; it is a fish tissue with a certified value for TBT. Discrepancies in the procedures and in the results reported during the collaborative analysis meant that a certified value for TPhT is not available. However, only in 8% of the papers reviewed is the accuracy of the methods assessed by analysing this material. Nowadays, the Measurements and Testing Programme of the European Commission is carrying out a certification campaign for butyl- and phenyltin compounds in mussels and another is planned for sediments [191].

The second approach to the assessment of the accuracy of the analytical methods is based on the analysis of spiked samples, and the determination of the recoveries obtained for each analyte. The analysis of spiked samples is carried out in 70% of the papers reviewed. In this case the main problem lies in how the spiking has been performed because, as mentioned previously, this is one of the most critical points. In any case, experiments should be performed with several kinds of matrices, and at several concentration levels, always in the range of concentrations usually found in environmental samples. Moreover, it should be taken into account that the availability of spiked analytes in the extraction step can be higher than that of the same substances incorporated to the matrices in the environment. So, using spiked samples can lead to an overestimation of the extraction efficiency, and, therefore, quantitative recoveries from spiked materials do not ensure that the same result will be achieved with natural samples.

A different approach to determine the extraction efficiency, instead of spiking and re-extraction, was attempted by Schebeck et al. [142] and Cai et al. [136]. The method, which was suggested by Hellmann [193], is based on extracting sediment with various volumes of solvent in order to determine the true concentration of butyltin in the sediment. Nevertheless, this method is limited because it assumes a linear adsorption isotherm which is valid only for some compounds.

3.5. Precision

The precision of the analytical methods reviewed, presented in Tables 1–8, corresponds to the whole analytical procedure, that is to say: the extraction, the derivatization and the determination technique.

A first consideration is that there are few data concerning precision. Furthermore, they have often been calculated from only three experiments which, taking into account the complexity of these analytical procedures, limits their representativity. In spite of that, an attempt has been made to point out some trends about the precision of the reviewed methods. Two groups including the methods most commonly applied have been considered: those based on GC–FPD as determination technique and those based on CT-QFAAS. Independently of the analytical method used, the analysis of OTs in biological materials gives more precise results than in sediments. For instance, in the case of TBT, relative standard deviations (R.S.D.s) calculated as the mean of the different methods and concentrations are 12% and 8.5% for sediments and biological materials, respectively (Table 11). The precision of methods using GC–FPD seems to be somewhat better than those using CT-QFAAS: 10.5 vs. 13 for sediments and 7 vs. 10 for biological materials. This trend is also noticeable in the results of the certification campaign of a coastal sediment (CRM-462) of the European Commission [194]. One of the reasons for the higher precision of CG-FPD may be the fact that I.S.s are used in the calibration step of this technique whereas in the case of CT-QFAAS the standard addition method is usually applied. Taking into account that the extraction techniques commonly used in CT-QFAAS methods are simpler that those used in GC–FPD methods, it can be concluded that in these methods the main source of variability is the determination technique. This conclusion is supported by the results of Pannier et al. [125] and Tolosa et al. [91]. In the former work, using CT-QFAAS, similar precisions are obtained in the analysis of different tissue extracts and in the replicate analysis of the same extract. In the second work, the standard deviations obtained for standard solutions by means of cGC–FPD are comparable to those obtained by other authors with real samples. Despite few data for phenyls have been reported, it has been observed that

Table 11
Precision for phenyl- and butyltin compounds using GC–FPD, CT-QFAAS, GC–AED and GC–MS techniques

	Sediments								Biota							
	GC–FPD		CT-QFAAS		GC–AED		GC–MS		GC–FPD		CT-QFAAS		GC–AED		GC–MS	
	RSD (%)	Ref.[a]	RSD (%)	Ref.[a]	RSD (%)	Ref.[a]	RSD (%)	Ref.[a]	RSD (%)	Ref.[a]	RSD (%)	Ref.[a]	RSD (%)	Ref.[a]	RSD (%)	Ref.[a]
MBT	9.5 (29)	1	14 (17)	7	8 (17)	9	52 (18) 14 (10)	14	8 (28)	18	10 (16)	23	6 (16)	25	24 (22)	29
DBT	10 (39)	2	14 (17)	7	6 (18)	10	17 (28)	14	9 (42)	19	8 (16)	23	5 (16)	26	19 (22)	29
TBT	12 (58)	3	11 (22)	8	7 (21)	11	10 (28) 45 (3)	15	5 (67)	20	11 (21)	24	7 (16)	26	19 (22)	29
MPhT	6, 18, 85	4	no data		no data		18 (10)	16	7 (24)	21	no data		no data		20 (18)	30
DPhT	12 (19)	5	no data		83 (6), 1 (3)	12	12 (10)	16	6 (24)	21	no data		3 (3)	27	20 (18)	30
TPhT	9 (27)	6	no data		1 (3)	13	7 (10)	17	7 (47)	22	no data		15 (11)	28	16 (18)	30

Values were calculated as mean of R.S.D. (%) reported in the literature. The total number of determinations is shown in parentheses. Some values extremely different from the others were not considered.

See List of abbreviations.

[a] References: (1) [36,83,108,138,140,159]; (2) [32,36,83,99,108,138,140,159,170]; (3) [33,36,44,83,99,108,130,138,159,166,170]; (4) [83,159,170]; (5) [83,59,70]; (6) [83,99,159,170]; (7) [121,135,142,146,154]; (8) [121,135,137,142,152,154]; (9) [47,50,164]; (10) [47,50,55,164]; (11) [47,50,55,58,164]; (12) [50,70]; (13) [50]; (14) [43,159]; (15) [43,45,159]; (16) [159]; (17) [45,159]; (18) [57,82–84,159]; (19) [41,57,82–84,111,113,127,159,174]; (20) [57,64,82–84,111–113,127,159,173,174]; (21) [81–83,159]; (22) [81–83,113,159,173,174]; (23) [119,120,122,125]; (24) [119,120,122]; (25) [97,125,164,172]; (26) [97,164,172]; (27) [97]; (28) [97,172]; (29) [43,96,141]; (30) [96,141].

precisions for phenyl- and butyltins are not significantly different using GC–FPD.

The MIP-AED was introduced in the nineties in the field of GC. It has not been widely applied to the analysis of OTs. However, some trends in the precision of this technique can be pointed out. An inter-laboratory study carried out in USA among ten laboratories [168], which analysed fourteen OTs compounds in three pentylated extracts of soils and sediments gave intra-laboratory R.S.D.s between 2 and 4% for most compounds. This affords an estimation of the precision of the detection technique. On the other hand, when the precision of the whole analytical method is evaluated, including extraction and derivatization (Table 11) the R.S.D. values are obviously higher but slightly lower than those obtained with GC–FPD and CT-QFAAS. No significant differences are noticed between the precisions obtained with sediments and organisms.

About seven groups of researchers have applied GC–MS to OT analysis. However, only few papers report data about precision of the results (Table 11). These data indicate that GC–MS gives R.S.D. values higher than the techniques previously commented, both for sediments and biota. This trend was also noticed by Tolosa et al. [91], when they compared the precision of different detection techniques applied to OT standard solutions.

3.6. Environmental acceptance and analytical cost

From the point of view of environmental acceptance, methods using SFE, acid extraction, basic or enzymatic hydrolysis are the best choice. Nevertheless, most of the published methods are based on extraction with organic solvents. Hexane, DCM, toluene and diethyl ether are commonly proposed. Benzene, which was used in some early methods [7,36,132] is still utilised today [58,83,85], especially in extraction of biological materials [48,52,81–84,86,87]. However, the nature of the chemical is not the only issue when assessing the environmental acceptance, and the volume of solvent or acid should also be considered. Volumes of organic solvent can range between few ml [32] to some hundreds [12,33,112], whereas in some cases large volumes (more than 50 ml) of concentrated acids, mainly HCl, are used [7,57,60,90]. Therefore, in order to provide information about this subject, the volumes of solvent used in extraction steps have been included in the Tables 1–8.

When the analytical cost of the procedure is to be estimated, there are several points to consider: reagents, instrumentation, and personnel requirements. Usually reagents are the least important contribution to the cost, unless large amounts of solvents or very expensive reagents are used. In relation with instrumentation the differences mostly lie in the kind of detector used and whether instrumentation is used in the extraction step. For instance, methods using detectors such as ICP-MS or MIP-AES requires very expensive instrumentation, and there is also a high contribution to the cost due to gas consumption and maintenance. In the case of methods based on SFE there is a similar situation; besides the cost of the equipment, the maintenance is also expensive. Finally the personnel requirements must be considered. This is usually an important contribution to the final cost of the analysis, and it is strongly related to the analysis time. At present in most of the methods the extraction of OTs from the sample, their derivatization and the clean-up step requires a lot of manipulation. In an attempt to reflect the complexity of methods, an equation has been introduced in Tables 1–8 that considers all the operations previous to the chromatographic analysis. Unfortunately, because the operations of the analytical procedure are not equally detailed in all the papers considered, the drawing of conclusions from the equation has some limitations. However, the main trends are next pointed up. Methodologies based on an extraction with a polar solvent, followed by an on-line HG-CT, are the most simple. However, since calibration must be carried out by standard addition in these methods, this simplicity is partially balanced by the lengthy calibration procedure. Among the methods using GC, those that obtain the volatile derivative by means of a Grignard reagent, as has been repeatedly mentioned in the literature, are the most laborious while those using $NaBEt_4$ look simpler. Recently, several attempts have been made to integrate extraction and derivatization steps. The addition of a Grignard reagent in the extraction cell of SFE [170] and ethylation by means of $NaBEt_4$ simultaneously with MAE [195] can be mentioned as promising strategies. LC methods avoid the derivatization step and usually even the clean-up, a fact that make them less complex than GC methods.

4. Conclusions

Important advances in the field of OT speciation have taken place over the last decade. Most of them have been related to the improvement of chromatographic separation and detection techniques. However, similar developments were not achieved in the previous steps to determination and most of the established methodologies rely on labour intensive protocols.

Extraction of OTs from solid matrices is one of the most troublesome step, due to the limited stability of analytes and the strong interactions between analytes and matrices. To date, a comprehensive evaluation of the extraction variables of conventional extraction techniques has not been carried out. Microwave assisted extraction (MAE) and SFE are emerging extraction techniques which deserve interest for the OTs extraction from solid matrices in terms of solvent consumption and analysis time reduction. Instrumentation cost reduction and reliability improvements are still needed to involve MAE and SFE in routine analysis.

CRMs with certified contents of all the OTs of major concern in both biotic and abiotic samples are required. Moreover, mid-term stability of OT content in CRMs under different storage conditions need to be investigated. The lack of appropriate CRMs has led to the practice of spiking experiments in order to validate the proposed methodologies. The main objection to these experiments is the uncertainty about the representativity of the behaviour of the added analytes. Moreover, in spite of the great variety of spiking procedures used, their influence on the recovery values has not been systematically studied. Composition of the spiking solutions and contact time with the sample can affect the results.

Nowadays OT speciation based on cGC is a well established technique, which has an unsurpassed resolution. Moreover, multiple surrogates and/or internal standards can be introduced in different steps of the analytical procedure to trace them. The main drawback of GC techniques, that is to say the need of derivatization before determination, can be overcome by the simultaneous extraction–derivatization methods. However this approach need to be improved in case of complex matrices.

In the field of LC, in spite of the great number of methods proposed, only a few of them have been applied to complex samples. Ion-exchange seems the most successful LC mode. ICP-MS is the only detection technique with a LOD at the subpicogram level. Atmospheric pressure interfaces appear to be of interest due to their sensitivity in the LC–MS coupling. Fluorogenic post-column derivatization allows high sensitivity for determination of TPhT. However, further improvements in the separation and the detection are required.

In some of the papers reviewed, there is not sufficient information on how the quality parameters of the method were determined. This mainly refers to the precision (concentration level, number of replicates) and the detection limit. In some cases, uncertainties arise about whether the results were corrected in relation to the recoveries of the surrogates. In addition, there is also ambiguity on the species to which the results were referred (e.g., Sn, TBT, TBTCl,...). In a few cases, even the type of calibration carried out is not specified.

Further developments: (i) studies on the stability of OTs throughout the analytical process including sample storage; (ii) study of products and intermediates in abiotic/biotic transformation processes; (iii) development of fast screening low cost analytical techniques for environmental monitoring; (iv) development of analytical procedures for OT determination in wastes (i.e., sewage, industrial waste, leaches, dumping sites) and gas-phase emission during industrial processes.

The state of the art in the field of OT analysis points out that OTs determination tends to be routine, but depending on the analytes (e.g., MBT or phenyltins) and the complexity of the matrix there are still some issues to solve, especially those related to OTs extraction. Therefore a concerted effort between the scientific community and the research funding agencies is still necessary to improve the existing analytical procedures.

5. List of abbreviations

AAS	Atomic absorption spectrometry
ACP	Alternating current plasma
AED	Atomic emission detection
AES	Atomic emission spectrometry
BMgCl	Butylmagnesium chloride
BTPeT	Butyltripentyltin
C	Centrifugation
cGC	Capillary gas chromatography
CT	Cold trapping
CU	Clean-up
D	Derivatization
DBDMeT	Dibutyldimethyltin
DBHeT	Dibutylhexyltin
DBT	Dibutyltin
DCM	Dichloromethane
DCP	Direct current plasma
DCyHeT	Dicyclohexylhexyltin
DCyT	Dicyclohexyltin
DDC	Diethyldithiocarbamate
DEA	Diethylammonium
DMeBT	Dimethylbutyltin
DMeDPeT	Dimethyldipentyltin
DMeT	Dimethyltin
DOcT	Dioctyltin
DPeT	Dipentyltin
DPhDEtT	Diphenyldiethyltin
DPhT	Diphenyltin
DPrDPeT	Dipropyldipentyltin
ECD	Electron-capture detection
EtMgBr	Ethylmagnesium bromide
Ev	Evaporation
Ex	Extraction
F	Filtration
FBTO	Fenbutatin oxide
FIA	Flow-injection analysis
FID	Flame ionization detection
FPD	Flame photometric detection
GFAAS	Graphite furnace atomic absorption spectrometry
GPC	Gel permeation chromatography
HOAc	Acetic acid
HeMgBr	Hexylmagnesium bromide
HeTBT	Hexyltributyltin
HG	Hydride generation
ICP	Inductively coupled plasma
I.S.	Internal standard
ISMS	Ion spray mass spectrometry
LEI	Laser enhanced ionization
LLE	Liquid–liquid extraction

LOD	Limit of detection
MAE	Microwave assisted extraction
MBT	Monobutyltin
MeDBT	Methyldibutyltin
MeMgBr	Methylmagnesium bromide
MeMgCl	Methylmagnesium chloride
MeMgI	Methylmagnesium iodide
MeOH	Methanol
MIP	Microwave induced plasma
MMeT	Monomethyltin
MOcT	Monooctyltin
MPeT	Monopentyltin
MPhT	Monophenyltin
MPhTEtT	Monophenyltriethyltin
MS	Mass spectrometry
MS-SIM	Mass spectrometry selective ion monitoring
$NaBEt_4$	Sodium tetraethylborate
NH_4OAc	Ammonium acetate
nr	Not reported
OAc	Acetate
P	Pre-treatment
PeMgBr	Pentylmagnesium bromide
QFAAS	Quartz furnace atomic absorption spectrometry
R.S.D.	Relative standard deviation
SFC	Supercritcal fluid chromatography
SFE	Supercritical fluid extraction
TBEtT	Tributylethyltin
TBMeT	Tributylmethyltin
TBT	Tributyltin
TCyHeT	Tricyclohexylhexyltin
TCyT	Tricyclohexyltin
TeBT	Tetrabutyltin
TeEtT	Tetraethyltin
TeMeT	Tetramethyltin
TePeT	Tetrapentyltin
TePrT	Tetrapropyltin
TEtT	Triethyltin
THF	Tetrahydrofurane
TMAH	Tetramethylammonium hydroxide
TMeT	Trimethyltin
TOcT	Trioctyltin
TPeBT	Tripentylbutyltin
TPeEtT	Tripentylethyltin
TPeT	Tripentyltin
TPhEtT	Triphenylethyltin
TPhT	Triphenyltin
TPrPeT	Tripropylpentyltin
TPrT	Tripropyltin
UV	Ultraviolet radiation

Acknowledgements

The financial support of the CIRIT is gratefully acknowledged. M.A. and C.L. thank the Spanish Ministry of Education and Science for FPI grants.

References

[1] S.J. Blunden and C.J. Evans, in O. Hutzinger (Editor), Anthropogenic Compounds, Springer-Verlag, Berlin, 1990, Ch. 3, p. 2.

[2] K. Fent, Crit. Rev. Toxicol. 26 (1996) 1.

[3] R.J. Maguire, Appl. Organomet. Chem. 1 (1987) 475.

[4] R.J. Huggett, M.A. Unger, P.F. Seligman, A.O. Valkirs, Environ. Sci. Technol. 26 (1992) 232.

[5] T.P. Traas, J.A. Stäb, P.R.G. Kramer, W.P. Cofino, T. Aldenberg, Environ. Sci. Technol. 30 (1996) 1227.

[6] J.M. Ruiz, G. Bachelet, P. Caumette, O.F.X. Donard, Environ. Pollut. 93 (1996) 195.

[7] R.J. Maguire, R.J. Tkacz, Y.K. Chau, G.A. Bengert, P.T.S. Wong, Chemosphere 15 (1986) 253.

[8] P.H. Dowson, J.M. Bubb, J.N. Lester, Mar. Pollut. Bull. 26 (1993) 487.

[9] R. Ritsema, Appl. Organomet. Chem. 8 (1994) 5.

[10] F.A. Espourteille, J. Greaves, R.J. Huggett, Environ. Toxicol. Chem. 12 (1993) 305.

[11] C.A. Krone, J.E. Stein, U. Varanasi, Environ. Monit. Assess. 40 (1996) 75.

[12] T.L. Wade, B. Garcia-Romero, J.M. Brooks, Chemosphere 20 (1990) 647.

[13] B. Garcia-Romero, T.L. Wade, G.G. Salata, J.M. Brooks, Environ. Pollut. 81 (1993) 103.

[14] P.F. Seligman, J.G. Grovhoug, A.O. Valkirs, P.M. Stang, R. Fransham, M.O. Stallard, B. Davidson, R.F. Lee, Appl. Organomet. Chem. 3 (1989) 31.

[15] E.A. Clark, R.M. Sterritt, J.N. Lester, Environ. Sci. Technol. 22 (1988) 600.

[16] M.D. Müller, L. Renberg, G. Rippen, Chemosphere 18 (1989) 2015.

[17] S.J. Blunden and A. Chapman, in P.J. Craig (Editor), Organometallic Compounds in the Environment, Longman, Harlow, 1986, Ch. 3, p. 111.

[18] J.J. Zuckerman, R.P. Reisdorf, H.V. Ellis, III and R.R. Wilkinson, in F.E. Brickman and J.M. Bellama (Editors), Organometals and Organometalloids: Occurrence and Fate in the Environment, (ACS Symp. Ser. No. 82), American Chemical Society, Washington DC, 1978, p. 388.

[19] J.M. Bayona, in Ph. Quevauviller (Editor), Quality Assurance for Environmental Analysis, Elsevier, Amsterdam, 1995, Ch. 15, p. 465.

[20] J.M. Bayona, Y. Cai, Trends Anal. Chem. 13 (1994) 327.

[21] G. Lespes, Analusis 23 (1995) 382.

[22] S.J. Hill, A. Brown, C.Rivas, S. Sparkes and L. Ebdon, in Ph. Quevauviller (Editor), Quality Assurance for Environmental Analysis, Elsevier, Amsterdam, 1995, Ch. 16, p. 411.

[23] R. Morabito, S. Chiavarini and C. Cremisini, in Ph. Quevauviller (Editor), Quality Assurance for Environmental Analysis, Elsevier, Amsterdam, 1995, Ch. 17, p. 435.

[24] R. Ritsema, F.M. Martin and Ph. Quevauviller, in Ph. Quevauviller (Editor), Quality Assurance for Environmental Analysis, Elsevier, Amsterdam, 1995, Ch. 19, p. 489.

[25] W.M.R. Dirkx, R. Lobinski, F.C. Adams, Anal. Chim. Acta 286 (1994) 309.

[26] W.M.R. Dirkx, R. Lobinski and F.C. Adams, in Ph. Quevauviller (Editor), Quality Assurance for Environmental Analysis, Elsevier, Amsterdam, 1995, Ch. 15, p. 357.

[27] X. Dauchy, A. Astruc, M. Borsier, M. Astruc, Analusis 20 (1992) 41.

[28] C.F. Harrington, G.K. Eigendorf, W.R. Cullen, Appl. Organomet. Chem. 10 (1996) 339.

[29] J. Ashby, S. Clark, P.J. Craig, J. Anal. Atom. Spectrom. 3 (1988) 735.

[30] K.M. Attar, Appl. Organomet. Chem. 10 (1996) 317.

[31] P.T.S. Wong, Y.K. Chau, M. Brown, D.M. Whittle, Appl. Organomet. Chem. 8 (1994) 385.

[32] S. Zhang, Y.K. Chau, W.C. Li, A.S.Y. Chau, Appl. Organomet. Chem. 5 (1991) 431.

[33] C.D. Rice, F.A. Espourteille, R.J. Huggett, Appl. Organomet. Chem. 1 (1987) 541.

[34] W.M.R. Dirkx, F.C. Adams, Mikrochim. Acta 109 (1992) 79.

[35] A.D. Uhler, G.S. Durell, W.G. Steinhauer, A.M. Spellacy, Environ. Toxicol. Chem. 12 (1993) 139.

[36] R.J. Maguire, Environ. Sci. Technol. 18 (1984) 291.

[37] A. Astruc, R. Lavigne, V. Desauziers, R. Pinel, M. Astruc, Appl. Organomet. Chem. 3 (1989) 267.

[38] A. Astruc, M. Astruc, R. Pinel, M. Potin-Gautier, Appl. Organomet. Chem. 6 (1992) 39.

[39] G.B. Jiang, P.S. Maxwell, K.W.M. Siu, V.T. Luong, S.S. Berman, Anal. Chem. 63 (1991) 1506.

[40] M. Astruc, A. Astruc, R. Pinel, Mikrochim. Acta 109 (1992) 83.

[41] T.L. Wade, B. Garcia-Romero, J.M. Brooks, Environ. Sci. Technol. 22 (1988) 1488.

[42] C. Stewart, S.J. De Mora, M.R.L. Jones, M.C. Miller, Mar. Pollut. Bull. 24 (1992) 204.

[43] C.A. Krone, D.W. Brown, D.G. Burrows, R.G. Bogar, S.L. Chan, U. Varanasi, Mar. Environ. Res. 27 (1989) 1.

[44] D.S. Page, C.C. Ozbal, M.E. Lanphear, Environ. Pollut. 91 (1996) 237.

[45] J.A. Stäb, W.P. Cofino, B. van Hattum, U.A.Th. Brinkman, Fresenius J. Anal. Chem. 347 (1993) 247.

[46] J.A. Stäb, M.J.M. Rozing, B. van Hattum, W.P. Cofino, U.A.Th. Brinkman, J. Chromatogr. A 609 (1992) 195.

[47] M. Ceulemans, F.C. Adams, Anal. Chim. Acta 317 (1995) 161.

[48] T. Higashiyama, H. Shiraishi, A. Otsuki, S. Hashimoto, Mar. Pollut. Bull. 22 (1991) 585.

[49] A.D. Uhler, G.S. Durell, A.M. Spellacy, Bull. Environ. Contam. Toxicol. 47 (1991) 217.

[50] Y.K. Chau, F. Yang, R.J. Maguire, Anal. Chim. Acta 320 (1996) 165.

[51] X. Dauchy, R. Cottier, A. Batel, M. Borsier, A. Astruc, M. Astruc, Environ. Technol. 15 (1994) 569.

[52] H. Shiraishi, M. Soma, Chemosphere 24 (1992) 1103.

[53] J.L. Gómez-Ariza, R. Beltrán, E. Morales, I. Giráldez, M. Ruiz-Benítez, Appl. Organomet. Chem. 9 (1995) 51.

[54] W.M.R. Dirkx, M.B. de la Calle, M. Ceulemans, F.C. Adams, J. Chromatogr. A 683 (1994) 51.

[55] R. Lobinski, W.M.R. Dirkx, M. Ceulemans, F. Adams, Anal. Chem. 64 (1992) 159.

[56] S.L. Tong, F.Y. Pang, S.M. Phang, H.C. Lai, Environ. Pollut. 91 (1996) 209.

[57] I. Martin-Landa, F. Pablos, I.L. Marr, Appl. Organomet. Chem. 5 (1991) 399.

[58] J.M. Ombaba, E.F. Barry, J. Chromatogr. 598 (1992) 97.

[59] F.Y. Pang, Y.L. Ng, S.M. Phang, S.L. Tong, Int. J. Environ. Anal. Chem. 53 (1993) 53.

[60] J.W. Short, Bull. Environ. Contam. Toxicol. 39 (1987) 412.

[61] Y. Arakawa, O. Wada, T.H. Yu, H. Iwai, J. Chromatogr. 207 (1981) 237.

[62] L. Ebdon, K. Evans, S. Hill, Sci. Total Environ. 83 (1989) 63.

[63] J.L. Kacprzak, Int. J. Environ. Anal. Chem. 38 (1990) 561.

[64] J.M. Hungerford, K.D. Walker, J.D. Torkelson, K. Steinbrecher, M.M. Wekell, Talanta 37 (1990) 975.

[65] C. Stewart, S.J. de Mora, Appl. Organomet. Chem. 6 (1992) 507.

[66] S.J. de Mora, C. Stewart, D. Phillips, Mar. Pollut. Bull. 30 (1995) 50.

[67] T. Tsuda, H. Nakanishi, T. Morita, J. Takebayashi, J. Assoc. Off. Anal. Chem. 69 (1986) 981.

[68] J.C. Mckie, Anal. Chim. Acta 197 (1987) 303.

[69] S. Clark, J. Ashby, P.J. Craig, Analyst 112 (1987) 1781.

[70] T.J. Gremm, F.H. Frimmel, Water Res. 26 (1992) 1163.

[71] R.D. Wilken, J. Kuballa, E. Jantzen, Fresenius J. Anal. Chem. 350 (1994) 77.

[72] J. Kuballa, R.D. Wilken, E. Jantzen, K.K. Kwan, Y.K. Chau, Analyst 120 (1995) 667.

[73] G. Pritzl, F. Stuer-Lauridsen, L. Carlsen, A.K. Jensen, T.K. Thorsen, Int. J. Environ. Anal. Chem. 62 (1996) 147.

[74] J.W. Short, J.L. Sharp, Environ. Sci. Technol. 23 (1989) 740.

[75] K.W.M. Siu, G.J. Gardner, S.S. Berman, Anal. Chem. 61 (1989) 2320.

[76] Y. Arakawa, O. Wada, T.H. Yu, H. Iwai, J. Chromatogr. 216 (1981) 209.

[77] T.H. Yu, Y. Arakawa, J. Chromatogr. 258 (1983) 189.

[78] T. Tsuda, H. Nakanishi, S. Aoki, J. Takebayashi, J. Chromatogr. 387 (1987) 361.

[79] U.T. Kumar, J.G. Dorsey, J.A. Caruso, E.H. Evans, J. Chromatogr. A 654 (1993) 261.

[80] W. Nigge, U. Marggraf, M. Linscheid, Fresenius J. Anal. Chem. 350 (1994) 533.
[81] S. Ohhira, H. Matsui, Bull. Environ. Contam. Toxicol. 44 (1990) 294.
[82] S. Ohhira, H. Matsui, J. Chromatogr. 525 (1990) 105.
[83] H. Harino, M. Fukushima, M. Tanaka, Anal. Chim. Acta 264 (1992) 91.
[84] H. Iwata, S. Tanabe, T. Mizuno, R. Tatsukawa, Environ. Sci. Technol. 29 (1995) 2959.
[85] H.J. Yang, S.J. Jiang, Y.J. Yang, C.J. Hwang, Anal. Chim. Acta 312 (1995) 141.
[86] K. Kannan, S. Tanabe, R. Tatsukawa, Chemosphere 30 (1995) 925.
[87] H. Iwata, S. Tanabe, N. Miyazaki, R. Tatsukawa, Mar. Pollut. Bull. 28 (1994) 607.
[88] Y.K. Chau, S. Zhang, R.J. Maguire, Analyst 117 (1992) 1161.
[89] Y.K. Chau, S. Zhang, R.J. Maguire, Sci. Total Environ. 121 (1992) 271.
[90] W.R. Cullen, G.K. Eigendorf, B.U. Nwata, A. Takatsu, Appl. Organomet. Chem. 4 (1990) 581.
[91] I. Tolosa, J.M. Bayona, J. Albaigés, L.F. Alencastro, J. Tarradellas, Fresenius J. Anal. Chem. 339 (1991) 646.
[92] K. Fent, J. Hunn, Environ. Sci. Technol. 25 (1991) 956.
[93] K. Fent, J. Hunn, Environ. Toxicol. Chem. 14 (1995) 1123.
[94] K. Fent, M.D. Müller, Environ. Sci. Technol. 25 (1991) 489.
[95] J.A. Stäb, U.A.Th. Brinkman, W.P. Cofino, Appl. Organomet. Chem. 8 (1994) 577.
[96] J.A. Stäb, M. Frenay, I.V. Freriks, U.A.Th. Brinkman, W.P. Cofino, Environ. Toxicol. Chem. 14 (1995) 2023.
[97] T. Suzuki, R. Matsuda, Y. Saito, J. Agric. Food Chem. 40 (1992) 1437.
[98] T. Suzuki, R. Matsuda, Y. Saito, H. Yamada, J. Agric. Food Chem. 42 (1994) 216.
[99] K. Becker-van Slooten, J. Tarradellas, Arch. Environ. Contam. Toxicol. 29 (1995) 384.
[100] M.D. Müller, Anal. Chem. 59 (1987) 617.
[101] M.D. Stephenson, D.R. Smith, Anal. Chem. 60 (1988) 696.
[102] J.R. Ashby, P.J. Craig, Sci. Total Environ. 78 (1989) 219.
[103] M.O. Stallard, S.Y. Cola, C.A. Dooley, Appl. Organomet. Chem. 3 (1989) 105.
[104] C.A. Dooley and G. Vafa, Proceedings of the Organotin Symposium of the Oceans '86 Conference, Washington DC, September 1986, IEEE, New York, 1986, p. 1171.
[105] D.S. Page, Mar. Pollut. Bull. 20 (1989) 129.
[106] D.J. Hannah, T.L. Page, L. Pickston, J.A. Taucher, Bull. Environ. Contam. Toxicol. 43 (1989) 22.
[107] G.B. Jiang, M. Ceulemans, F.C. Adams, J. Chromatogr. A 727 (1996) 119.
[108] K.W.M. Siu, P.S. Maxwell, S.S. Berman, J. Chromatogr. 475 (1989) 373.
[109] J.W. McLaren, K.W.M. Siu, J.W. Lam, S.N. Willie, P.S. Maxwell, A. Palepu, M. Koether, S.S. Berman, Fresenius J. Anal. Chem. 337 (1990) 721.
[110] D.K. Orren, W.M. Braswell, P. Mushak, J. Anal. Toxicol. 10 (1986) 93.
[111] K. Sasaki, T. Suzuki, Y. Saito, Bull. Environ. Contam. Toxicol. 41 (1988) 888.
[112] I.S. Krull, K.W. Panaro, J. Noonan, D. Erickson, Appl. Organomet. Chem. 3 (1989) 295.
[113] T. Ishizaka, S. Nemoto, K. Sasaki, T. Suzuki, Y. Saito, J. Agric. Food Chem. 37 (1989) 1523.
[114] A.M.A. Abd-Allah, Chemosphere 30 (1995) 707.
[115] K. Becker-van Slooten, J. Tarradellas, Environ. Toxicol. Chem. 13 (1994) 755.
[116] I.S. Krull, K.W. Panaro, Appl. Spectrosc. 39 (1985) 960.
[117] M. Abalos, manuscript in preparation.
[118] Y.K. Chau, F. Yang, M. Brown, Anal. Chim. Acta 304 (1995) 85.
[119] R. Francois, J.H. Weber, Mar. Chem. 25 (1988) 279.
[120] S. Rapsomanikis, R.M. Harrison, Appl. Organomet. Chem. 2 (1988) 151.
[121] L. Randall, J.S. Han, J.H. Weber, Environ. Technol. Lett. 7 (1986) 571.
[122] S. Shawky, H. Emons, H.W. Dürbeck, Anal. Commun. 33 (1996) 107.
[123] V. Desauziers, F. Leguille, R. Lavigne, M. Astruc, R. Pinel, Appl. Organomet. Chem. 3 (1989) 469.
[124] J.S. Han, J.H. Weber, Anal. Chem. 60 (1988) 316.
[125] F. Pannier, A. Astruc, M. Astruc, Anal. Chim. Acta 287 (1994) 17.
[126] F. Pannier, A. Astruc, M. Astruc, Appl. Organomet. Chem. 8 (1994) 595.
[127] K. Sasaki, T. Ishizaka, T. Suzuki, Y. Saito, J. Assoc. Off. Anal. Chem. 71 (1988) 360.
[128] J.J. Sullivan, J.D. Torkelson, M.M. Wekell, R.A. Hollingworth, W.L. Saxton, G.A. Miller, K.W. Panaro, A.D. Uhler, Anal. Chem. 60 (1988) 626.
[129] C.L. Matthias, S.J. Bushong, L.W. Hall, J.M. Bellama, F.E. Brinckman, Appl. Organomet. Chem. 2 (1988) 547.
[130] C.L. Matthias, J.M. Bellama, G.J. Olson, F.E. Brinckman, Int. J. Environ. Anal. Chem. 35 (1989) 61.
[131] J.J. Cooney, A.T. Kronick, G.J. Olson, W.R. Blair, F.E. Brinckman, Chemosphere 17 (1988) 1795.
[132] Y. Hattori, A. Kobayashi, S. Takemoto, K. Takami, Y. Kuge, A. Sugimae, M. Nakamoto, J. Chromatogr. 315 (1984) 341.
[133] S. Wuertz, M.E. Miller, M.M. Doolittle, J.F. Brennan, J.J. Cooney, Chemosphere 22 (1991) 1113.
[134] Y. Cai, S. Rapsomanikis, M.O. Andreae, Talanta 41 (1994) 589.
[135] Y. Cai, S. Rapsomanikis, M.O. Andreae, J. Anal. Atom. Spectrom. 8 (1993) 119.
[136] Y. Cai, S. Rapsomanikis, M.O. Andreae, Anal. Chim. Acta 274 (1993) 243.
[137] Y. Cai, S. Rapsomanikis, M.O. Andreae, Mikrochim. Acta 109 (1992) 67.
[138] Y. Yonezawa, K. Nakata, Y. Miyakozawa, A. Ochi, T. Kowata, H. Fukawa, Y. Sato, S. Masunaga, Y. Urushigawa, Environ. Toxicol. Chem. 12 (1993) 1175.
[139] O.F.X. Donard, B. Lalère, F. Martin, R. Lobinski, Anal. Chem. 67 (1995) 4250.
[140] B. Lalère, J. Szpunar, H. Budzinski, Ph. Garrigues, O.F.X. Donard, Analyst 120 (1995) 2665.
[141] Ph. Quevauviller, S. Chiavarini, C. Cremisini, R. Morabito, M. Bianchi, H. Muntau, Mikrochim. Acta 120 (1995) 281.

[142] L. Schebek, M.O. Andreae, H.J. Tobschall, Int. J. Environ. Anal. Chem. 45 (1991) 257.

[143] L. Schebek, M.O. Andreae, H.J. Tobschall, Environ. Sci. Technol. 25 (1991) 871.

[144] Ph. Quevauviller, R. Lavigne, R. Pinel, M. Astruc, Environ. Pollut. 57 (1989) 149.

[145] Ph. Quevauviller, F. Martin, C. Belin, O.F.X. Donard, Appl. Organomet. Chem. 7 (1993) 149.

[146] Ph. Quevauviller, O.F.X. Donard, Appl. Organomet. Chem. 4 (1990) 353.

[147] L. Cortez, Ph. Quevauviller, F. Martin, O.F.X. Donard, Environ. Pollut. 82 (1993) 57.

[148] P.H. Dowson, J.M. Bubb, J.N. Lester, Mar. Pollut. Bull. 24 (1992) 492.

[149] P.H. Dowson, P. Pershke, J.M. Bubb, J.N. Lester, Environ. Pollut. 76 (1992) 259.

[150] P.H. Dowson, J.M. Bubb, J.N. Lester, Appl. Organomet. Chem. 7 (1993) 623.

[151] P.H. Dowson, J.M. Bubb, J.N. Lester, Chemosphere 28 (1994) 905.

[152] M. Astruc, R. Pinel, A. Astruc, Mikrochim. Acta 109 (1992) 73.

[153] F. Pannier, X. Dauchy, M. Potin-Gautier, A. Astruc, M. Astruc, Appl. Organomet. Chem. 7 (1993) 213.

[154] P.M. Sarradin, A. Astruc, R. Sabrier, M. Astruc, Mar. Pollut. Bull. 28 (1994) 621.

[155] C. Rivas, L. Ebdon, E.H. Evans, S.J. Hill, Appl. Organomet. Chem. 10 (1996) 61.

[156] J.L. Gómez-Ariza, E. Morales, R. Beltrán, I. Giráldez, M. Ruiz-Benítez, Analyst 120 (1995) 1171.

[157] K.S. Epler, T.C. O'Haver, G.C. Turk, W.A. MacCrehan, Anal. Chem. 60 (1988) 2062.

[158] A.M. Caricchia, S. Chiavarini, C. Cremisini, R. Morabito, R. Scerbo, Anal. Sci. 7 (1991) 1193.

[159] A.M. Caricchia, S. Chiavarini, C. Cremisini, R. Morabito, C. Ubaldi, Int. J. Environ. Anal. Chem. 53 (1993) 37.

[160] R. Compañó, M. Granados, C. Leal, M.D. Prat, Anal. Chim. Acta 314 (1995) 175.

[161] K. Okamoto, Biological Trace Element Research, (ACS Symp. Ser. No. 445), American Chemical Society, Washington DC, 1991, p. 257.

[162] P. Rivaro, L. Zaratin, R. Frache, A. Mazzucotelli, Analyst 120 (1995) 1937.

[163] M.J. Waldock, M.E. Waite, Appl. Organomet. Chem. 8 (1994) 649.

[164] J. Szpunar, V.O. Schmitt, R. Lobinski, J.-L. Monod, J. Anal. Atom. Spectrom. 11 (1996) 193.

[165] J. Dachs, J.M. Bayona, J. Chromatogr. 636 (1993) 277.

[166] J. Dachs, R. Alzaga, J.M. Bayona, Ph. Quevauviller, Anal. Chim. Acta 286 (1994) 319.

[167] Y. Liu, V. López-Avila, M. Alcaraz, W.F. Beckert, Anal. Chem. 66 (1994) 3788.

[168] Y. Liu, V. López-Avila, M. Alcaraz, W.F. Beckert, J. Assoc. Off. Anal. Chem. 78 (1995) 1275.

[169] Y. Liu, V. López-Avila, M. Alcaraz, W.F. Beckert, J. High Resolut. Chromatogr. 16 (1993) 106.

[170] Y. Cai, R. Alzaga, J.M. Bayona, Anal. Chem. 66 (1994) 1161.

[171] K. Li, S.F.Y. Li, J. Chromatogr. Sci. 33 (1995) 309.

[172] M. Ceulemans, C. Witte, R. Lobinski, F.C. Adams, Appl. Organomet. Chem. 8 (1994) 451.

[173] M. Nagase, H. Kondo, K. Hasebe, Analyst 120 (1995) 1923.

[174] M. Nagase, K. Hasebe, Anal. Sci. 9 (1993) 517.

[175] D.S. Forsyth, C. Cleroux, Talanta 38 (1991) 951.

[176] I. Fernández, personnal communication.

[177] R. Morabito, Appl. Organomet. Chem., (1997) in press.

[178] Y. Cai, J.M. Bayona, J. Chromatogr. Sci. 33 (1995) 89.

[179] C. Stewart, J.A.J. Thompson, Mar. Pollut. Bull. 28 (1994) 601.

[180] W.M.R. Dirkx, R. Lobinski, F.C. Adams, Anal. Sci. 9 (1993) 273.

[181] S.C.K. Shum, R. Neddersen, R.S. Houk, Analyst 117 (1992) 577.

[182] J.M. Bayona, personnal communication.

[183] A.M. Caricchia, S. Chiavarini, C. Cremisini, R. Morabito, R. Scerbo, Anal. Chim. Acta 286 (1994) 329.

[184] E. Morales, Thesis, University of Sevilla (1993).

[185] J.L. Gómez-Ariza, E. Morales, R. Beltrán, I. Giráldez, M. Ruiz-Benítez, Quím. Anal. 13 (1994) S76.

[186] Ph. Quevauviller, O.F.X. Donard, Fresenius J. Anal. Chem. 339 (1991) 6.

[187] W.J. Langston, N.P. Pope, Mar. Pollut. Bull. 31 (1995) 32.

[188] Ph. Quevauviller, H. Etcheber, C. Raoux, O.F.X. Donard, Oceanologica Acta 11 (1991) 247.

[189] I. Tolosa, L. Merlini, N. De Bertrand, J.M. Bayona, J. Albaigés, Environ. Toxicol. Chem. 11 (1992) 145.

[190] R. Morabito, Fresenius J. Anal. Chem. 351 (1995) 378.

[191] Ph. Quevauviller, M. Astruc, L. Ebdon, H. Muntau, W. Cofino, R. Morabito, B. Griepink, Mikrochim. Acta 123 (1996) 163.

[192] F.M. Martin, O.F.X. Donard, J. Anal. Atom. Spectrom. 9 (1994) 1143.

[193] H. Hellman, Fresenius' Z. Anal. Chem. 319 (1984) 267.

[194] Ph. Quevauviller, M. Astruc, L. Ebdon, V. Desauziers, P.M. Sarradin, Appl. Organomet. Chem. 8 (1994) 629.

[195] I. Rodriguez-Pereiro, V.O. Schmitt, J. Szpunar, O.F.X. Donard, R. Lobinski, Anal. Chem. 68 (1996) 4136.