Anal Bioanal Chem (2002) 372 : 74–90
DOI 10.1007/s00216-001-1139-0

REVIEW

I. Rodriguez Pereiro · A. Carro Díaz

Speciation of mercury, tin, and lead compounds by gas chromatography with microwave-induced plasma and atomic-emission detection (GC–MIP–AED)

Received: 7 June 2001 / Revised: 10 September 2001 / Accepted: 20 September 2001 / Published online: 13 December 2001

Abstract Because of their high toxicity and widespread distribution, the reliable selective quantification of alkyl and aryl species containing mercury, tin, or lead has been one of the goals of speciation analysis in recent years. Since becoming commercially available, GC–MIP–AED has been one of the most-used tools in this work. In this paper, the value and limitations of GC–MIP–AED for the speciation of Hg, Sn, and Pb compounds in environmental samples are reviewed and compared with the analytical characteristics of other hyphenated GC-based techniques. Because quantification of Hg, Sn, and Pb species by GC techniques normally requires complex sample preparation involving several steps, the effect of sample-preparation methods on the accuracy and precision of the results is discussed. Finally, we describe the current status of a rapid, low-cost GC–MIP–PED system specifically designed for routine quantification of Hg, Sn, and Pb species in environmental control laboratories.

Keywords Speciation · Mercury · Tin · Lead · Gas chromatography–microwave-induced plasma–atomic emission

Introduction

Speciation analysis is the separation and quantification of identifiable chemical species containing a particular element [1]. Its aim is to determine the distribution of the element among the different chemical species in a sample. Few of the instrumental methods available for elemental analysis have sufficient selectivity for direct quantification of individual metal-containing species. Spectroscopic techniques are very sensitive but usually determine only the total amount of metal in the sample, and they must be combined with a separation technique before individual species can be quantified [2, 3]. Speciation analysis, therefore, normally relies on hyphenated techniques.

In this review we concentrate on what, with the exception of GC–MS, has probably been the most successful commercially marketed GC-based hyphenated technique, the combination of GC with detection of atomic emission stimulated by use of a microwave-induced helium plasma (GC–MIP–AED).

Because microwave-induced helium plasmas (MIP) are formed at lower temperatures than inductively coupled argon plasmas (ICP), liquid samples cannot be introduced into them, because they are extinguished by even small amounts of organic vapor. When MIP–AES is combined with GC it is, therefore, necessary to vent the GC solvent front before it arrives at the discharge tube. When this problem had been solved, GC–MIP–AED proved to have several advantages over GC–ICP–AED. The most important are, perhaps, the higher electron temperature and ionization energy of MIP, which enable quantification not only of metals but also of semi-metals, and even of other organic compounds containing elements with high ionization potentials (fluorine, chlorine, etc.) [4, 5, 6]. Other advantages of MIP are the small dead volume of the discharge tube, the compatibility of the plasma with the low carrier gas flows used in capillary GC columns, and the consumption of less gas than ICP. AES detection of elements excited by an MIP is, furthermore, both very selective and often (e.g. for selenium and for most elements with atomic masses lower than 40) less subject to interference than the more sensitive ICP–MS system [3, 7]. There is no doubt that these properties that were responsible for the worldwide commercial success of the GC–MIP–AED system marketed by Hewlett–Packard at the end of the nineteen-eighties.

One of the most important environmental applications of GC–MIP–AED is the quantification of alkylmetal species of low molecular-weight. These species are highly toxic at low concentrations and are easily bioaccumulated; some are regarded as endocrine system disrupters. In environ-

I.R. Pereiro (✉) · A.C. Díaz
Dpto. Química Analítica, Nutrición y Bromatología,
Facultad de Química, Universidad de Santiago de Compostela,
Santiago 15782, Spain
e-mail: qnisaac@usc.es

Table 1 Summary of GC–AES methods for the determination of inorganic mercury and organomercury species in various sample matrices

Species; sample matrix	Sample preparation	LOD	CRM used	Determination technique	Date	Ref.
MeHg; fish tissue	Alkaline digestion (KOH–MeOH)+derivatization ($HCl–CH_2Cl_2–NaBPh_4$)	0.4 pg MeHg as Hg	CRM 464, DORM-2	GC–MIP–AED	2000	[38]
MeHg, EtHg; standard aqueous solutions	(1) Ethylation ($NaBEt_4$)	(1) 0.04 pg MeHg as Hg	–	GC–MIP–AED	2000	[24]
	(2) Phenylation ($NaBPh_4$)	(2) 0.02 pg MeHg as Hg		GC–AFS		
		(2) 0.03 pg EtHg as Hg		GC–MS		
MeHg, Hg^{2+}; soil, sediment	(1) Derivatization (Grignard reagent) (2) CH_2Cl_2 extraction+ethylation ($NaBEt_4$)+Tenax collection	0.1 ng g^{-1} MeHg	IAEA 356, CRM 580, PACS-1	GC–MIP–AED	2000	[31]
MeHg, EtHg, Hg^{2+}; dogfish tissue	Derivatization (Grignard reagent)	0.2 pg MeHg and EtH, 0.3 pg Hg^{2+}	DORM-2, DOLT-2	GC–rf-HC–GD–AED	2000	[23]
MeHg; tuna fish, cockle, mussel, dogfish	MAE (HAc)+phenylation ($NaBPh_4$)	0.04 pg MeHg as Hg	CRM 463, CRM 464, DORM-2	GC–MIP–AED	2000	[43]
MeHg, Me_2Hg, Hg^{2+}; water, soil, sediment	(1) Ethylation ($NaBEt_4$) (2) Hydride generation ($NaBH_4$)+preconcentration on Chromosorb and thermal desorption	<1 ng L^{-1}	–	PTI–GC–MIP–AED	1999	[49]
Me_2Hg, Et_2Hg, Ph_2Hg; water, soil, sediment	(1) Direct SPME	(1) 144 pg mL^{-1} Me_2Hg as Hg, 30 pg mL^{-1} Et_2Hg as Hg	–	GC–MIP–AED	1999	[34]
	(2) HS-SPME	(2) 30 pg mL^{-1} Me_2Hg as Hg, 25 pg mL^{-1} Et_2Hg as Hg				
MeHg, EtHg, Hg^{2+}; fish tissue	Acid hydrolysis (HCl)+DDTC+derivatization (Grignard reagent)	1.3 ng mL^{-1} MeHg and EtHg, 3.0 ng mL^{-1} Hg^{2+}	DORM-2, DOLT-2	GC–rf-GD–AED, GC–dc-GD–AED	1998	[22]
MeHg, Me_2Hg, Hg^{2+}; natural gas condensate	Derivatization (Grignard reagent)	(1) 0.5 – (2) 2.1 pg Me_2Hg	–	(1) GC–FAPES	1998	[21]
		(1) 0.9 – (2) 4.1 pg MeHg		(2) GC–MIP–AED		
		(1) 1.7 – (2) 4.1 pg Hg^{2+}				
MeHg; grain, cereal products, fruit, vegetables	Acid hydrolysis (HCl)+Celite 545 column+CH_2Cl_2 elution+Kuderna Danish concentrator+stannic chloride–MeOH	0.24 pg as Hg	–	GC–AED	1998	[54]
MeHg; fish	Alkaline digestion (KOH–MeOH)+ethylation ($NaBEt_4$)+Carbotrap column	5 pg MeHg	–	PTI–GC–MIP–AED	1998	[39]
MeHg; fish	MAE (TMAH)+(1) ethylation ($NaBEt_4$)	(1) 3 pg g^{-1} MeHg	CRM 464	PTI–GC–MIP–AED	1997	[41]
	MAE (TMAH)+(2) hydride generation ($NaBH_4$)	(2) 12.5 pg g^{-1} MeHg				
MeHg, Hg^{2+}; fish tissues	TMAH digestion+ethylation ($NaBEt_4$)+Tenax-TA column+thermal desorption	7 pg MeHg, 1 pg Hg^{2+}	DOLT-2, TORT-2, DORM-2	PTI–GC–FAPES	1997	[44]

Table 1 (continued)

Species; sample matrix	Sample preparation	LOD	CRM used	Determination technique	Date	Ref.
MeHg, Hg^{2+}; water	Ethylation ($NaBEt_4$)	6 pg MeHg, 20 pg Hg^{2+}	–	PTI–GC–MIP–AED	1996	[71]
MeHg; sediment	(1) SFE (2) distillation (KCl–H_2SO_4)	0.1 ng g^{-1}	PACS-1	GC–MIP–AED	1996	[29]
MeHg; marine tissues	Extraction (Cu powder+$CuSO_4$)+ KBr+toluene	–	DORM-2, TORT-1, DOLT-2, IAEA 350	GC–MIP–AED	1996	[32]
MeHg, Me_2Hg, Hg^{2+}; natural gas condensate	(1) On-line amalgamation trap+derivatization (Grignard reagent)	(1) 0.24 µg L^{-1} Me_2Hg, 0.56 µg L^{-1} MeHg and Hg^{2+}	–	GC–MIP–AED	1996	[33]
	(2) HS-SPME+derivatization (Grignard reagent)	(2) 2 µg L^{-1} Me_2Hg, 3 µg L^{-1} MeHg, 2.3 µg L^{-1} Hg^{2+}				
MeHg, EtHg; marine tissues, sediment	Extraction (Cu powder+$CuSO_4$)+ KBr+toluene	0.8 pg MeHg as Hg	TORT-1, DOLT-2, IAEA 350, DORM-2....	GPC-GC–MIP–AED	1996	[30]
MeHg, EtHg, Hg^{2+}; sea water	SPE (DTC- resin)+acid thiourea elution+derivatization (Grignard reagent)	0.4 pg MeHg, EtHg and Hg^{2+}	–	GC–MIP–AED	1995	[47]
MeHg, Hg^{2+}; natural water rich in humic substances	SPE (DTC- resin)+acid thiourea elution+derivatization (Grignard reagent)	0.04 ng MeHg, 0.28 ng Hg^{2+}	–	GC–MIP–AED	1995	[46]
MeHg, EtHg, Hg^{2+}; water	Sulfhydryl cotton microcolumn+HCl elution+phenylation ($NaBPh_4$)	2 ng MeHg and EtHg, 3.2 ng Hg^{2+}	–	GC–MIP–AED	1995	[53]
MeHg, EtHg, PhHg, Hg^{2+}; biological tissues	Direct aqueous phase phenylation ($NaBPh_4$)	–	–	GC–MIP–AED	1995	[36]
MeHg; fish and other biological tissues	(1) Alkaline digestion (NaOH-NaCl) (2) Acid leaching (HCl-$NaCl_{sat}$)+ derivatization (Grignard reagent)	From low ng g^{-1} to µg g^{-1}	DOLT-2, TORT-2, CRM 464, CRM 463, IAEA-MA B3/TM	GC–MIP–AED	1994	[40]
MeHg; fish, biological tissues, sediment	Acid hydrolysis (HCl)+cysteine acetate aqueous solution+toluene	1.2 pg MeHg	DORM-1	GC–MIP–AED, GC–ECD	1994	[20]
MeHg, EtHg, Hg^{2+}; natural water	DTC-resin+elution with thiourea solution+derivatization (Grignard reagent)	0.025 ng MeHg and EtHg, 0.075 ng Hg^{2+}	–	Closed flow injection-GC–MIP–AED	1993	[45]
MeHg; atmospheric samples	Tenax column+thermal elution into benzene+concentration with a nitrogen gas flow	3 pg MeHg as Hg	–	GC–ICP–AED	1992	[19]
MeHg, EtHg; fish	Acid leaching (HCl–$NaCl_{sat}$)+derivatization (Grignard reagent)	0.8 pg MeHg as Hg, 1.3 pg EtHg as Hg	IAEA-MA B3/TM	GC–ECD, GC–MIP[a]	1991	[37]
MeHg; fish	(1) Acid hydrolysis (HCl)+cysteine acetate aqueous solution+Kuderna Danish concentrator (2) Extraction with diethyl ether–light petroleum+Kuderna Danish concentration	3 ng/8 µL MeHg	–	GC–ECD, GC-DCP AED	1987	[18]

Table 1 (continued)

Species; sample matrix	Sample preparation	LOD	CRM used	Determination technique	Date	Ref.
MeHg, Me_2Hg; water, fish	Acid hydrolysis (HBr–HI)+benzene	2 pg Me_2Hg, 0.5 pg MeHg	–	GC–ECD, GC-MIP[a]	1975	[28]
Organic Hg; salmon	Acid hydrolysis (HCl)+$HgCl_2$+Benzene+clean-up with thiosulphate	0.1 ng MeHgCl	–	GC-MIP[a]	1971	[27]

[a]Non-commercial microwave-induced plasma

mental samples they are normally present in polar species, making their conversion to compounds that are less polar and thermally stable a pre-requisite for gas chromatographic separation [7]. CG–MIP–AED is one of the best and most frequently used techniques for quantification of the resulting derivatives.

This paper reviews the application of CG–MIP–AED to the speciation of alkyl species containing mercury, tin, and lead in environmental samples – mainly water, sediments, and biological tissues. The scope and limitations of the technique are discussed, and its analytical performance is compared with that of other hyphenated techniques used in species analysis, including GC–AED systems with other plasma sources. Particular attention is given to sample preparation procedures and derivatization methods, because of their great influence on the precision and accuracy of the analytical results.

Speciation of mercury species

The biogeochemistry and the health effects of mercury (Hg) have received considerable attention because of the toxicity of methylmercury (MeHg) and dimethylmercury (Me_2Hg), the accumulation of Hg in biota, and its biomagnification in aquatic food chains [8, 9]. Knowledge of the concentration, transport, and dynamics of MeHg and other organomercury compounds in aquatic ecosystems is, therefore, needed to enable prediction of the potential impact on human and aquatic life [8, 10].

In the nineteen-eighties it became clear that GC with electron-capture detection (ECD) had poor selectivity for organomercury species and often required elaborate, time-consuming clean-up procedures before sample injection; a simpler, more specific technique was required [11, 12]. Although early GC–MIP–AED systems had many drawbacks (see below, Comparison of plasma sources and detection techniques), the commercial MIP–AED instrument has many advantages over these earlier designs, particularly with regard to venting of the solvent to protect the plasma, plasma stability, background correction, and convenience of data handling. The use of a high-performance monochromator with a photodiode-array spectrophotometer as detector also improves sensitivity [13] (atmospheric-pressure MIP are more sensitive and significantly more selective than low-pressure MIP for mercury; to obtain maximum sensitivity for mercury with a low-pressure MIP, hydrogen should be used as scavenger gas [14].) Table 1 lists studies of the application of GC–MIP–AED, and of some other GC methods, to the determination of Hg species in a variety of sample matrices. Note that in each example the table specifies the certified reference materials (CRM) used; in species analysis, as in other areas of analytical chemistry, the use of CRM is essential for good quality control and traceability [15, 16].

Although packed columns are sometimes useful, capillary columns are generally essential for complex environmental samples [17]. Because of its flexibility, ease of use, inertness, and ability to retain a variety of coatings, fused silica is the preferred material for capillary columns, its inertness being especially important in the determination of chemically active compounds such as organomercury compounds [14].

Plasma sources and detection systems

Early GC–MIP–AED systems had serious drawbacks – intolerance of large volumes of injected sample, plasma instability, poor reproducibility, poor precision, and inability to run unattended for long periods of time [18]. Because of this, at that time Panaro et al. developed a simple, inexpensive GC–AED method using a direct current plasma (DCP) [18]; an isothermal packed-column GC system dedicated to the DCP generator enabled routine qualitative and quantitative determination of organomercury species in complex food samples (when used to determine MeHg in fish, the sample was subjected to an extraction procedure based on the method of Hight and coworkers [11, 12] and included concentration by use of a Kuderna-Danish apparatus). Being element-selective, DCP–AED eliminated interferences and thus enabled more accurate determination of MeHg than ECD.

MIP–AED is very sensitive for volatile species containing metals but, as noted above, the introduction of solvent into the plasma quenches the discharge, making it necessary either to vent the solvent vapor before it enters the cavity or to ignite the plasma only after the solvent has passed through the cavity. An ICP can, on the other hand, be maintained in the presence of an organic solvent. Kato et al. combined GC with an axially viewed inductively coupled plasma (AXV-ICP) and AED [19]; air samples were collected in a Tenax column and eluted with benzene. AXV performed better than conventional side view-

ing – in particular, the LOD for alkylmercury compounds in the atmosphere was 20 times lower with the axial method.

After an acid-hydrolysis extraction procedure, CG–MIP–AED enables accurate quantification of MeHg in unclean marine samples and samples with a high fat content (e.g. mussels), which pose serious resolution problems for GC–ECD systems [20].

Frech et al. compared MIP–AED and furnace-atomization plasma-excitation spectrometry (FAPES) as detection systems for use with high-resolution GC [21]. The test analytes were the mercury species in a natural gas condensate, which had been derivatized by use of butylmagnesium chloride in tetrahydrofuran. Better LOD were achieved with FAPES, and MIP–AED measurement of Me_2Hg was, in fact, impossible, because the plasma could not withstand loading with hydrocarbon solvents. Although baseline disturbances occurred with both sources during sample elution, in FAPES they resulted from changes in background emission, a problem that could be ameliorated by means of a suitable background correction system, whereas in MIP–AED they were because the plasma lost excitation capability, a problem little can be done to solve.

Recently, the analytical potential of capillary GC with radiofrequency (rf) and direct current (dc) glow discharges (GD) and AED has been investigated for quantification of low levels of MeHg, ethylmercury (EtHg) and inorganic mercury (Hg^{2+}) in fish tissues [22]. Both dc-GD–AED and rf-GD–AED performed at a level similar to that of more common AED methods. GC–GD–AED enabled accurate determination of the Hg species without the need to resort to standard addition techniques. When a hollow-cathode was used to increase emission intensities, optimization of discharge conditions (pressure, He flow rate, rf power) afforded LOD that were 5–10 times better than those obtained by use of flat-cathode GD–AED and were also lower than those obtained with MIP–AED [23]. The hollow-cathode GD-AED system had a low construction cost and consumed 10–20 times less He than MIP–AED.

The performance indices of GC in combination with MIP–AES, mass spectrometry (MS), or atomic fluorescence spectrometry (AFS) have been evaluated for quantification of MeHg and EtHg after aqueous derivatization with sodium tetraethylborate and sodium tetraphenylborate [24]. Both GC–AFS and GC–MIP–AED had broad linear ranges, although the AFS sensitivity setting had to be adjusted for each particular sample on the basis of its Hg concentration. Phenylation seemed to be the better derivatization method, because it distinguished better between EtHg and Hg^{2+} and was less expensive than ethylation. It was concluded that although GC–MS is, perhaps, the most important technique for identification and confirmation, it is unlikely to provide the sensitivity required for determination of Hg in most environmental samples.

Sample pretreatment for mercury speciation with GC–MIP–AED

Extraction

The first extraction method developed specifically for quantification of mercury species involved the leaching of Hg compounds from the sample using hydrochloric acid [25, 26]. Since the nineteen-seventies this method has been used to prepare fish samples for the determination of several organic mercury salts by GC–MIP–AED [27, 28] (Talmi's paper [28] describes a procedure that makes the clean-up step of the Westöö method unnecessary.) The total analysis time for MeHg in fish is less than 15 min, and more than 30 benzene extracts can be analyzed per hour. As mentioned above, a modified acid hydrolysis procedure has also been applied to marine samples before quantification of MeHg by CG–MIP–AED [20].

Supercritical-fluid extraction (SFE) has been used to isolate MeHg from sediments before quantification by CG–MIP–AED [29]. SFE is fast and reliable, and is more sparing of solvents, labor and chemicals than other currently used methods such as steam distillation (the reference method in the study given in Ref. [29]).

Acid leaching procedures have been applied to both marine tissues and sediments [30, 31]. Interfering sulfur-containing species can be removed during sample extraction with copper powder, the extracts subsequently being themselves extracted with toluene after acidification with potassium bromide solution [30, 32]. High molecular-weight pigments and lipids can be removed from the extracts by preparative gel-permeation chromatography (GPC) before GC analysis [30].

Few studies have used solid-phase microextraction (SPME) to prepare samples for quantification of Hg species by GC–MIP–AED [33, 34]. SPME extracts volatile or semivolatile organic compounds directly from an aqueous or gaseous sample passed through a capillary or over a fused-silica fiber coated with an appropriate stationary phase. In combination with headspace sampling (HS), SPME has proved suitable for extraction of Me_2Hg and diethylmercury (Et_2Hg) in the analysis of aqueous and soil samples. It is also possible to use direct SPME for less volatile organomercury compounds in aqueous samples [34].

Derivatization

The derivatization of analytes before their determination by GC with low-pressure or atmospheric-pressure MIP–AED avoids capillary column passivation problems even if no prior extraction stage is used [35]. Direct ethylation or phenylation in an aqueous medium, and butylation with a Grignard reagent, have been compared with regard to their improvement of the multi-element determination of several organomethylates in biological tissue [36]. The addition of traces of a mixture of oxygen and hydrogen to the plasma improves the shape of the chromatogram peaks

by removing carbon deposits and preventing the formation of refractory oxides. For samples for which there is no information about the species present, derivatization by at least two procedures is recommended.

Extraction and derivatization

Fish and marine samples. Combining derivatization with extraction improves the chromatographic characteristics of the species to be separated. For MeHg and EtHg in fish, samples can be extracted with saturated sodium chloride solution and HCl; after the extracts have been shaken vigorously with sodium diethyldithiocarbamate (DDTC) and toluene, the toluene phase can be derivatized with butylmagnesium chloride in tetrahydrofuran (THF) [37]. Column efficiency, detection limits, and resolution of MeHg and EtHg are better in capillary GC–MIP–AED than packed column GC–ECD.

Alkaline digestion with KOH–methanol is an obvious alternative to acid treatment before extraction of Hg compounds with dichloromethane then phenylation [38] or ethylation [39]. When used to isolate MeHg from fish samples, alkaline digestion has been found to eliminate interferences with the derivatization reaction before GC–MIP–AED determination [38, 39]. International intercalibration studies of the simultaneous determination of MeHg and Hg^{2+} from reference and candidate reference materials by CG–MIP–AED after acid leaching or alkaline digestion and subsequent derivatization revealed very large differences between the extraction efficiencies of different sample work-up procedures. Artifact formation, detector selectivity, chromatographic performance, and the stability of Hg compounds are discussed on the basis of their results [40].

Microwave-assisted extraction (MAE) is a well accepted technique in elemental trace analysis and has also been used for quantification of organometallic compounds. Under the usual conditions (high applied energy, high pressures, and high temperatures) most compounds are destroyed and all speciation information is lost [41], but when performed under milder conditions in a closed system with sophisticated pressure and temperature control it achieves successful extraction of organomercury compounds [42]. Alternatively, an open system using focused microwaves has also been successfully applied to the digestion of fish samples before Hg species analysis by GC–MIP–AED [41]. Digestion of fish tissues with tetramethylammonium hydroxide (TMAH) is quick and simple, and losses of volatile analytes as a result of heating by the microwave field are reasonably low and reproducible. Two different derivatization and injection procedures have been examined (ethylation, extraction into hexane, and injection with a cooled injection system; and hydride generation with sodium tetrahydroborate then purge-and-trap injection (PTI)).

For determination of MeHg with the closed-vessel system the extraction and derivatization conditions have been optimized by use of a factorial experimental design [43]. Combination of MAE with a suitable derivatization procedure avoids the need for previous column treatment with inorganic salts before GC–MIP–AED, and also reduces solvent volume and analysis time.

PTI has also been used in other studies of the application of GC–MIP–AED [41] or GC–FAPES [44] to quantification of MeHg and Hg^{2+} in biological tissues. In the latter technique samples were solubilized with TMAH and the ionic species were purged from aqueous solution after ethylation; the species were then preconcentrated on Tenax-TA and thermally desorbed on to an isothermal GC column.

Water samples. In the quantification of Hg compounds in water samples, low concentration is without doubt the most serious problem; occasionally very large sample volumes must be processed. The method developed by Emteborg et al. [45] for simultaneous determination of mercury species in natural waters involves large sample volumes, preconcentration on a dithiocarbamate (DTC) resin-loaded microcolumn, extraction of the eluted species into toluene, and derivatization with a Grignard reagent; these derivatives are separated and quantified by GC–MIP–AED. One disadvantage of the method is that the preconcentration step fails in the presence of high concentrations of humic substances. To solve this problem a batch method has been developed [46] – Hg species enrichment is performed by adding purified DTC resin directly to the water sample. The accuracy of this method has been assessed, in part, by means of interlaboratory comparison with results from GC–AFS, and the ability of the columns to retain alkyl-Hg and Hg^{2+} compounds has been studied [47]. In a later variant, large volumes of the sample are injected in a packed-column GC system connected to a capillary GC system coupled to a MIP–AED device [48]. In this way the Hg species are focused before separation in the analytical column; this minimizes the risk of the plasma being extinguished by excess solvent. This variant has been applied to the determination of Hg species in river water.

In another study [49] Hg species were either ethylated or were converted to hydride with $NaBH_4$, stripped from solution with He, pre-concentrated on Chromosorb at room temperature or –160 °C, released from the adsorbent by thermal desorption, and quantified by PTI–GC–MIP–AED. Both these procedures were designed for analysis of soil and sediments and water.

Because of problems associated with the production of natural materials and the stability of Hg compounds in aqueous media, very few reliable reference materials are available for the quantification of mercury compounds in natural waters [50, 51]. Because of this the possibility of storage on a solid support has been studied [52]. The stability of Hg species from natural waters immobilized on sulfhydryl cotton fibers (SCF) was examined by elution into HCl solution, derivatization with $NaBPh_4$, and determination by GC–MIP–AED [53].

Gaseous samples. Hg species present in natural gas condensate have been extracted for determination by GC–

MIP–AED using an on-line amalgamation trap [33]. The Hg compounds can be collected from the column eluate within a specific time window and subsequently passed to the plasma as Hg vapor in a flow of pure helium. Use of the amalgamation trap improves the determination of mercury species in two ways. First, by separating analyte material from the matrix before detection it enables the introduction of samples containing large amounts of carbon compounds without any need to use split injectors or diluted or smaller sample masses to preserve chromatographic resolution and detector efficiency. Second, use of the trap enables the addition of standards directly after the gas chromatograph by injecting samples of air saturated with mercury vapor; this procedure enables independent calibration for standards separated by the chromatograph. Results obtained by use of the trap were compared with data obtained by HS-SPME and liquid sample injection followed by direct measurement of the column eluate. SPME might be a simple and useful alternative method for the determination of derivatized polar Hg species [33].

Soil samples. In addition to the method mentioned above in the section Water samples [49], extraction with dichloromethane then in situ ethylation and collection of the species on Tenax has been used for determination of MeHg in forest soils by GC–MIP–AED [31].

Food samples. Historically, Hg in food products other than seafood was not subjected to species analysis because of the lack of adequate methodology. The high specificity and selectivity of GC–MIP–AED, and the minimum analyte isolation required by this method (irrelevant matrix components being transparent to the detector) have, however, enabled its use for the determination of MeHg in thirty-two samples of grains, cereal products, fruits, and vegetables [54]. After acid hydrolysis with HCl the resulting chlorinated species were eluted from a Celite 545 sample homogenate column with dichloromethane, the eluate was treated with stannic chloride, and the analyte was isolated from co-extracted materials by use of a wide-bore capillary column for GC–MIP–AED.

Speciation of tin compounds

Organotin compounds found in environmental samples (water, sediments, particulate matter and living organisms) have both anthropogenic and natural origins. The most important anthropogenic compounds are butyl- and phenyltin species. Tributyltin (TBT), used mainly as an antifouling compound in paints, is highly toxic to both target and non-target marine organisms, and has recently been included in the list of endocrine system disrupters [55]. Dialkyltins with butyl and octyl groups are used as polymer stabilizers in, for example, PVC pipes, from which they can be released into water [56], or even into air, in fires or during processing of plastic materials at high temperature [57]. Dibutyltin (DBT) and monobutyltin (MBT) can also be generated in the environment by degradation of TBT. Triphenyltin (TPhT), although also used as an antifouling agent in paints, is mainly employed as a fungicide and biocide in agriculture [58]. Natural degradation of TPhT to diphenyltin (DPhT) and monophenyltin (MPhT) is well documented. Nowadays, use of all these compounds (especially TBT) is restricted, but they are still present in marine environments (mainly in sediments, from which they are slowly released into the aquatic environment). Naturally occurring organotin compounds are mainly biomethylated species generated from inorganic tin (Sn^{4+}) in sediments and estuarine environments. Natural methylation of butyltin compounds has also been reported [59].

The toxicity of organotin compounds depends on the number and kind of organic groups bound to the Sn atom. Species analysis is therefore essential for understanding the biological effects and environmental impact of these compounds. Accurate identification and quantification of tin species in environmental samples needs reliable analytical methods based on the combination of adequate sample preparation procedures with selective, sensitive analytical techniques. Most viable methods are based on a separation step followed by quantification, by use of an appropriate detector. Gas chromatographic separation is more widely used than HPLC because of the higher resolving power of GC columns, the smaller requirement for hazardous solvents, and the availability of detectors that are more sensitive and more selective. Among these techniques, GC–MIP–AED has been one of the most widely used in the past 10 years.

Experimental conditions and analytical features of GC–MIP–AED

Optimization of MIP–AED conditions for the analysis of organotin compounds was first performed by Lobinski et al. [60], and later by several others (Table 2). Although there are small differences among the measurement conditions used in these studies, there is general agreement that a helium make-up flow rate higher than 200 mL min^{-1} is necessary to prevent the interaction of tin compounds with the quartz discharge tube and to achieve maximum sensitivity. The presence of oxygen in the helium plasma was also found to be necessary to prevent deposition of carbon on the walls of the discharge tube, even though oxygen leads to the formation of refractory tin oxides and a consequent decrease in the emission signal. The negative effect of oxygen can be compensated by addition of hydrogen to the plasma gas; hydrogen probably produces very volatile hydrides that are easily atomized and excited, thereby reducing the detection limit of the technique [61, 62].

Although some authors claim absolute detection limits <0.2 pg of tin [60, 63, 64, 65], most authors have reported values between 0.5 and 5 pg. Slight variations in the helium make-up flow and reagent gas pressure are probably largely responsible for these small differences. With regard to the effect of the emission line selected, Tutschku

Table 2 Optimum MIP–AED conditions, and absolute detection limits (signal/noise=3) for organotin compounds

Emission line (nm)	He make-up (mL min^{-1})	H_2 pressure (Kpa)	O_2 pressure (Kpa)	ADL (pg Sn)	Ref.
270.651	220	448	207	1–5	[69, 145, 146]
303.419	240	400	160	ca 2–5	[61]
303.419	270	345	152	ca 2–3	[99]
270.651	240	414	138	0.5	[100]
326.23	240	200	200	0.8	[62]
–	150	450	150	2–4	[67]
303.419	200	–	–	5	[147]
303.419	240	345	138	0.05	[60]
303.419	240	345	138	0.15	[64, 65]

– Not available

et al. [62] obtained lower detection limits at 326.23 nm than with the more usual 270.651 and 303.419 nm lines. Table 2 summarizes MIP–AED conditions and detection limits for organotin compounds.

Table 3 lists the detection limits achieved by GC-based systems other than GC–MIP–AED for quantification of organotin compounds. Those achieved by GC–MIP–AED are similar to those of the best GC-FPD instruments and of GC–MS systems with a quadrupole mass analyzer operating in SIM mode (ion-trap mass analyzers are a valuable alternative to high-sensitivity scanning, and have detection limits similar to those of quadrupole instruments in SIM mode) [66]. In GC–MIP–AED, however, all organotin compounds are quantified under identical conditions, whereas with quadrupole SIM MS detection several different masses must be monitored [67]. The combination of gas chromatography with AAS is less sensitive for tin compounds than GC–MIP–AED, because of the high atomization temperatures of tin and the possible formation of refractory oxides [63]. Detection limits one or two orders of magnitude lower than those of CG–MIP–AED have only been achieved with customer developed combinations of gas chromatography with ICP–MS detection.

Table 3 Absolute detection limits (S/N=3) for organotin compounds achieved by gas chromatography systems other than GC–MIP–AED

System	Instrumental detection limits (pg tin)	Ref.
GC-FPD	3	[148]
	0.2	[149]
	2–4	[150]
	0.2–0.5	[151]
	0.3–18	[152]
GC-QF AAS	33–71	[63]
	10–100	[153]
GC–MS	1–10	[66, 67]
	1.5–8	[154]
GC–ICP–MS	0.050	[155]
	0.015–0.034	[156]
	0.052–0.17	[112]
	0.05–0.08	[157]

With regard to the linearity of response, several papers have reported GC–MIP–AED calibration curves that are linear over the range 10 to 2500 ng tin mL^{-1}, with correlation coefficients >0.999 [68, 69]. The detection limits noted above and the elemental selectivity of CG–MIP–AED have made this technique the workhorse for quantification of organotin compounds in environmental samples.

In the discussion below the possibilities and limitations of GC–MIP–AED for the speciation of organotin compounds in a variety of different matrices are discussed. Some comments on sample-preparation and derivatization strategies are also made.

Water samples

The levels of organotin compounds in polluted waters (rivers, estuaries, harbors, shipyard areas, and tap water in contact with certain polymeric materials) are below the detection limits of GC–MIP–AED or any other gas chromatography-based technique used in organotin species analysis. A concentration step is therefore necessary before analytical determination. In general, concentration strategies are very similar for all gas chromatographic techniques used in the speciation of tin, Table 4.

Classical approaches are based on the extraction of organotin compounds (mainly butyl and phenyl compounds) using a complexing agent (tropolone or sodium diethyldithiocarbamate) in combination with a volatile organic solvent, followed by derivatization with a Grignard reagent [60, 67]. A faster option is the use of $NaBEt_4$, and more recently $NaBPr_4$, as derivatization agent (the latter enables the investigation of ethyltin compounds in water samples) [61, 64, 70]; in both reactions alkyl derivatives are formed in the aqueous medium and extracted simultaneously into an organic solvent. $NaBEt_4$ has also been used to derivatize polar organotin species previously retained on a solid extraction cartridge [65].

Methyltin compounds can be ethylated in aqueous samples using $NaBEt_4$, and simultaneously extracted and concentrated with a purge-and-trap device; these injectors can use cryogenically cooled capillary traps [71] or solid adsorbents operating at room temperature [49]. Polar butyltin species can be converted by treatment with $NaBH_4$ into

Table 4 Summary of GC–MIP–AED procedures for the quantification of organotin compounds in water samples

Compounds	Sample volume (mL)	Extraction technique	Derivatization reagent	Detection limits (ng L^{-1})	Ref.
Butyl and phenyltin	50	LLE (hexane)	$NaBEt_4$	0.1[b]	[64]
Butyl and phenyltin	50	SPE, C18[a]	$NaBEt_4$	0.1[b]	[65]
Butyl, methyl and diphenyltin	100–250	LLE (hexane–tropolone)	EtMgBr	10–15	[147]
Butyl and methyltin	1500	LLE (pentane–NaDDTC)	PeMgBr	–	[60]
Butyl and phenyltin	100	LLE (hexane)	$NaBEt_4$	17–33	[61]
Butyl and phenyltin	100	LLE (hexane)	$NaBPr_4$	3–12	[70]
Methyltin	10	P&T	$NaBEt_4$	0.15	[71]
Butyltin	4	Direct SPME (PDMS fibers)	$NaBEt_4$	ca. 20	[73]

[a]Derivatization of polar compounds on the stationary phase of the adsorbent cartridge

[b]Calculated for an injection volume of 25 μL, using a PTV injector

– Not available

volatile compounds that can be purged from water samples, an option that has normally involved the use of a packed column coupled to a QF-AAS instrument [72]; as far as we are aware, analysis of butyltin compounds as hydrides by GC–MIP–AED has not been reported in the literature.

The possibility of direct derivatization in aqueous samples enables the use of solid-phase microextraction (SPME) as a concentration technique [73, 74, 75, 76]. Non-polar fibers are normally used (mainly with polydimethylsiloxane as stationary phase). The sampling step can be performed directly in the aqueous phase or in the headspace over the sample. The latter procedure enables faster equilibration between sample and fiber for volatile and semivolatile compounds, and also more selective extraction. Although methyl- and butyltin species are normally sampled at room temperature [77, 78], for less volatile species such as phenyltin compounds better sensitivity is achieved at high temperature [79].

Despite the high concentration factors achieved with these techniques, and their low or at best medium selectivity, GC–MIP–AED suffers from no interferences at tin emission lines (271, 303 and 326 nm). Some problems with blanks have, however, been reported. Szpunar et al. [80], who used Grignard derivatization with pentylmagnesium bromide, observed organotin signals in blanks when several microliters of the organic phase were introduced into the chromatography column by use of a PTV injector. Blanks with organotin signals have also been detected when $NaBEt_4$ was used as derivatization agent; possible sources of this contamination are plastic holders, the polypropylene body of SPE cartridges [65], and reagents used in sample preparation, including the $NaBEt_4$ [81]. Szpunar et al. also reported that the use of sodium diethyldithiocarbamate (NaDDTC) as a complexing agent and then Grignard derivatization of the organic extract led to noisy baselines, probably because of reaction of the Grignard reagent with decomposition products of NaDDTC [80]. Stäb et al. [67] using GC–MS have identified MBT and DBT, at levels of 5–12 ng L^{-1}, in blank chromatograms corresponding to the analysis of water. Finally, Rosenberg et al. have reported variations of 30–40% in the analysis of butyltin compounds at low concentrations when using HS SPME with GC–MIP–AED [82]. Apart from problems described by the authors in relation to the SPME fiber surface, it is also possible that blank signals are also responsible for this lack of repeatability when organotin compounds are analyzed at concentrations below the μg L^{-1} level.

Solid matrices

Sample preparation procedures for determination of organotin compounds in solid matrices by gas chromatography comprise several steps, the precise number of which depends on the derivatization technique (Grignard reaction, direct alkylation with sodium tetraalkylborates in aqueous solution, or hydride generation) [83] and on whether a clean-up step is needed, which in turn depends on the derivatization technique (alkylborates normally lead to cleaner extracts than Grignard reactions, which require the use of complexing reagents such as tropolone [84]), on the kind of sample, and above all on the selectivity of the GC detector. For GC–MIP–AED systems, concentration of the final extracts from solid matrices is not normally necessary, because instrument sensitivity matches target detection limits for environmental samples (approx. 1 ng g^{-1}) [85].

Sediment samples

Because organotin compounds are not involved in mineralogical processes and bind only to the surface of sediments, complete dissolution of the matrix is not considered necessary. Acid leaching combined with mechanical shaking [86] or sonication [77], and microwave-assisted leaching [87, 88], are, therefore, the basic approaches used to release organotin compounds from sediments. Leaching can be achieved by use of dilute acids with complexing agents (tropolone or sodium diethyldithiocarbamate) dissolved in an organic solvent [84, 89], or using only aqueous or methanolic solutions of acetic or hydrochloric

acids [88]; normally the former choice is followed by Grignard derivatization and the latter by direct alkylation with $NaBEt_4$ or $NaBPr_4$. Methods based on hydride generation have been shown to be poorly efficient for extracts with high sulfur, hydrocarbon, or inorganic metal content, and are therefore not advisable for sediment analysis [72].

The element selectivity of GC–MIP–AED makes it unnecessary to perform the time-consuming desulfuration procedures described in the literature for the determination of organotin species in sediments by GC-FPD [90, 91]. In general, no clean-up procedures are necessary with GC–MIP–AED, although Ceulemans et al. [89] have recommended that if tropolone is used as complexing reagent the final organic extract should be passed over basic alumina, or excess tropolone can contaminate the head of the column.

The analytical characteristics (sensitivity and selectivity) of GC–MIP–AED are, in principle, good enough to solve the detection step in the analysis of tin compounds in sediments. Problems mainly arise in sample preparation [92] and in the limited number of reference materials (currently only reference sediment material PACS-2, with certified concentrations of MBT, DBT, and TBT, is commercially available). As a consequence, validation of analytical procedures for phenyltin species is a difficult task. Some of the problems related with the analysis of organotin compounds (mainly MBT and phenyltin species) in sediments are well known and clearly described in the literature. Few sample extraction procedures for MBT claim quantitative yields, and recoveries are sometimes estimated by use of spiked samples [84, 93]. In real polluted sediments interaction of MBT with the matrix, which is directly related to sample sulfur and organic carbon content [84], is probably even stronger than in the spiked samples, and the extraction yield accordingly lower. Because of its structure and polarity, similar behavior is expected of MPhT. Another problem is encountered in the extraction of phenyltin compounds – these species are partially degraded by some leaching procedures designed for butyltin compounds. Degradation is of special significance when acid conditions are combined with high temperatures. Despite their lability during sample preparation, however, surveys of phenyltin compounds, especially TPhT, in sediments are of environmental interest, because of their toxicity and their persistence under the anaerobic conditions obtaining in sediments [67].

Both problems (non-quantitative extraction and degradation) could be compensated by use of isotope-labeled organotin compounds as internal standards. If the label is introduced in the tin atom [94] the excellent sensitivity and multielemental capabilities of ICP–MS might justify marketing an interface between GC and ICP–MS as a complementary technique to GC–MIP–AED for organotin speciation (and for volatile organometallic speciation in general) [3]. A similar effect could be achieved with ^{13}C or deuterated organotin standards; with these, determination can be achieved by use of conventional quadrupole GC–MS [95], a technique available in most analytical chemistry laboratories which is sufficiently sensitive for the analysis of organotin compounds in solid matrices.

Some authors have found that GC–MIP–AED chromatograms for some sediment samples show not only methyl-, butyl-, and phenyltin compounds but also peaks corresponding to minor organotin species [96]. Identification of these species is the first step towards understanding their origin and environmental behavior. GC–MS is currently the only hyphenated technique capable of providing information about their structures. Because the detection limits of quadrupole mass analyzers, working in scan mode, are still far above those achieved with MIP–AED, the use of ion-trap MS instruments is advisable [66].

Biological tissues

Speciation of tin compounds in fish and other seafood tissue has been studied for the past 15 years, since their negative effects on the reproduction of marine organisms such as oysters and other mollusks were discovered [97, 98]. Nowadays, two reference materials are available – NIES-11 (fish tissue from the National Institute for Environment Studies, Japan) and BCR-477 (mussel tissue prepared by the former BCR). The concentration of TBT in the former is certified and an approximate level is also indicated for TPhT; the latter contains MBT, DBT, TBT, MPhT, and TPhT, at least, although only the concentrations of MBT, DBT, and TBT are certified.

As for sediments, sample preparation is usually performed in several steps, the first of which is sample digestion. Because organotin compounds can be incorporated in tissues, complete sample decomposition is a prerequisite for quantitative extraction. Acid solutions (mainly acetic acid and dilute hydrochloric acid), modified supercritical CO_2, and mixtures of lipase and protease have all been used to release organotin compounds from biological tissues, but highest yields seem to be achieved with aqueous TMAH solutions [99, 100, 101, 102, 103]. The second step is derivatization and extraction of the organotin derivatives into an organic solvent (except for hydride-generation techniques, when cryogenic purge-and-trap devices are used). Fast, integrated sample-preparation procedures have been described in which tissue digestion, derivatization (ethylation), and extraction of the ethylated derivatives into an organic solvent occur simultaneously in only 3 min under the action of a microwave field [83].

The problems encountered in the sample preparation step are similar to those reported for sediment samples: sub-quantitative recovery and the degradation of phenyltin compounds [101, 104]. TPhT seems to be more stable at basic pH [79, 99] than in acid media [101], however, which is another reason for preferring solubilization with TMAH to acid leaching.

Irrespective of the digestion and derivatization agents used, the final extracts from biological samples are colored solutions containing large amounts of lipids. Clean-up of the organic extract containing the derivatized organotin species has therefore been recommended, to prevent column deterioration and to eliminate baseline drift with

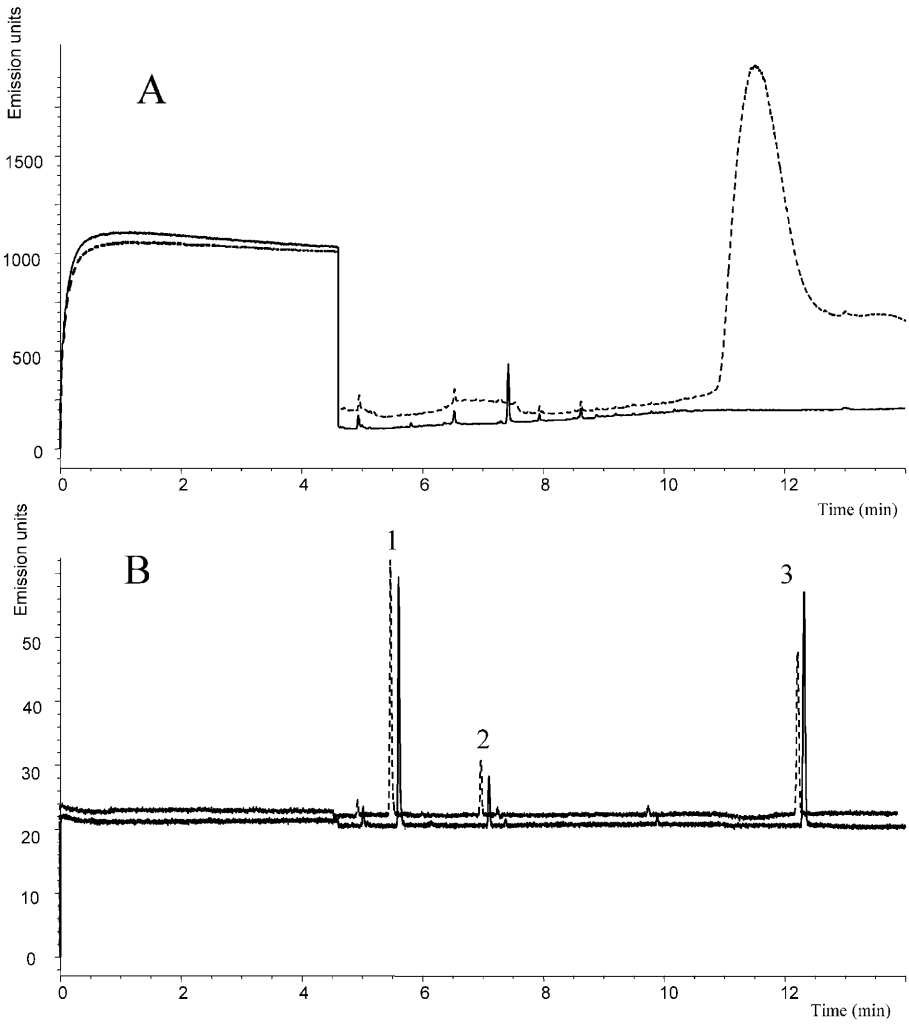

Fig. 1 GC–MIP–AED chromatograms obtained from a mussel-tissue extract, with clean-up over alumina (*solid line*) and without clean-up (*dotted line*). Extraction was performed as described elsewhere [99]. *1*. TPT (IS), *2*. MPhT, *3*. TPhT. **A**. 248 nm carbon emission line. **B**. 271 nm tin emission line

increasing oven temperature when relatively poorly selective detectors such as scan-mode MS or FPD are used. Polar adsorbents such as silica [100], alumina [80, 99] and Florisil [105, 106] are used for this purpose. Szpunar et al. have shown that with CG–MIP–AED a stable, flat baseline is obtained even without clean-up, although they also noted that the response to ethylated TPhT depended on whether or not clean-up had been performed [80]. In our laboratory we have had the same problem with the determination of TPhT in biological materials; the 248 nm carbon channel, monitored simultaneously with the 271 nm tin line, shows a large, broad signal at the retention time of TPhT (Fig. 1). The species responsible for this non-specific signal (probably lipids) might temporarily modify the internal wall of the quartz discharge tube, causing loss of sensitivity in tin emission signals.

Speciation of lead compounds

Organolead compounds are ubiquitous pollutants in air, atmospheric aerosols, water, and sediments. Tetraalkyllead species (TAL; mainly Et_4Pb, Me_4Pb, and $Me_nEt_{4-n}Pb$), still used in some countries as anti-knocking additives in gasoline [107], can penetrate the skin and biological membranes and are readily absorbed via the lungs. The toxicity of organolead compounds depends on the organic groups bound to the lead atom – methylated species are less toxic than the corresponding ethylated compounds, but are more stable and volatile [108].

TAL enter the atmosphere via vehicle exhaust pipes and as a result of accidental spillage. There they are decomposed to inorganic lead (Pb^{2+}) via tri- and dialkyl compounds. Photolysis and radical reactions are responsible for the fast decomposition of Me_4Pb and Et_4Pb ($t_{1/2}$=41 and 8 h, respectively). Ionic organolead species (Me_3Pb^+, Et_3Pb^+, Et_2Pb^{2+}, and Me_2Pb^{2+}) are less toxic than tetraalkylated species but have longer half-lives, enabling them to be transported considerable distances from their anthropogenic sources [109].

The combination of gas chromatography with spectroscopic techniques (AAS, MIP–AED, MS or ICP–MS) is common in the speciation of lead compounds. As for tin, the separation of lead compounds by gas chromatography requires prior derivatization of ionic alkylated species to thermally stable volatile compounds. This reaction can be

performed with Grignard reagents after chelation of these species and extraction into an organic solvent such as hexane or pentane. Another option is to use borate reagents. Although sodium tetraethylborate is only useful for methylated lead compounds (both inorganic and ethylated lead species yield Et_4Pb [110]), Pawliszyn et al. have recently overcome this problem by using deuterium-labeled $NaBEt_4$ [111]; because the isotope-labeled ethyl group is not present in environmental samples, it can be used to distinguish between ethylated inorganic lead and native ethyllead species. Lower-cost alternative derivatization reagents are sodium tetrapropylborate [10, 112] and tetrabutylammonium tetrabutylborate [113, 114], both of which enable simultaneous determination of most of the ionic alkyllead (IAL) species commonly found in environmental samples (Me_3Pb^+, Et_3Pb^+, and $Me_nEt_mPb^{(4-n-m)+}$) [115].

Table 5 Absolute detection limits (S/N=3) for organolead compounds achieved by GC-based hyphenated techniques

Hyphenated technique	Absolute detection limits (pg as lead)	Ref.
GC–MIP–AED	0.03–1	[107, 116]
	0.01	[123]
	0.04–0.08	[114]
GC–ICP–MS	0.01–0.016	[122]
	0.7	[158]
	0.04–0.09	[112]
GC–AAS	40–95 (Flame)	[125]
	30–45 (Quartz furnace)	[47]
	1–2 (Quartz furnace)	[159]
GC–MS	2	[110]
	4	[130]
	7–8	[131]

Analytical features of GC–MIP–AED

Detection limits obtained in the speciation of lead compounds by use of a variety of different GC-based hyphenated techniques are compared in Table 5. The detection limits of GC–MIP–AED are similar to those reported for GC–ICP–MS, and between two and three orders of magnitude better than those obtained using GC–MS systems or custom-made combinations of GC with AAS.

The GC–MIP–AED system enables measurement of lead emission at 261.418 nm and 405.783 nm. The latter line is preferred because of its higher sensitivity, which is maximum with a helium make-up flow of approximately 300–330 mL min^{-1} [114, 116, 117, 118]. Oxygen and hydrogen are also necessary as reagent gases; oxygen prevents carbon from being deposited on the walls of the discharge tube (oxygen pressure is normally adjusted to 138 kPa (20 psig)) and, as for tin, the presence of hydrogen improves sensitivity (pressures of 550–650 kPa are reported as optimum [116, 119, 120]).

With the 405.783 nm emission line, good linearity has been obtained for injected amounts of organolead species between 0.1–100 pg, as Pb. If very high levels of organolead species reach the plasma, lead can condense on the wall of the discharge tube, causing peak tailing and reduced sensitivity [116]. Because more than 99.9% of the lead in most samples is Pb^{2+} [121], and part of this inorganic lead can be derivatized and extracted with the native organolead species, it is advisable to vent the chromatographic peak corresponding to native Pb^{2+}, to prevent contamination of the discharge tube [120].

Water and other aqueous samples

Because of their short half-lives and low solubility in water, the presence of TAL compounds in aqueous samples is not common [107]. The levels of IAL species in rain, surface, and tap water (mainly dimethyl-, trimethyl-, di-

Table 6 Speciation of organolead compounds in water and other aqueous samples

Sample volume (mL)	Extraction procedure	Derivatization reagent	Detection technique	Detection limits (ng L^{-1})	Ref.
100–150	LLE hexane	PrMgCl	PTV GC–MIP–AED	0.1	[120]
75–120 g (snow)	LLE hexane	PrMgCl	PTV GC–MIP–AED	10 fg g^{-1}	[123]
60–80 (wine)	LLE hexane	PrMgCl	GC–MIP–AED	1–3	[119]
20	LLE hexane	Bu_4N^+ Bu_4B^-	PTV GC–MIP–AED	0.04–0.08	[114]
100	LLE hexane	PrMgCl	GC–MIP–AED	0.5–0.9	[117]
25	SPME	$NaBEt_4$	GC–ICP–MS	0.1	[74]
10 (urine)	SPME	$NaBEt_4$	GC–MS–MS	7	[126]
100	LLE hexane	$NaBEt_4$	GC–MS	2.5	[110]
20	SPME	$NaBEt_4$	GC–MS	83–130	[111]
500	LLE pentane	BuMgCl	GC–QF AAS	1–2.2	[128]
1000	LLE pentane	Bu_4N^+ Bu_4B^-	GC–QF AAS	10–30	[113]
25	SPE	PrMgCl	GC–MS	1–4	[115]
50	Purge and trap	$NaBEt_4$	GC–QF AAS	–	[121]
50	LLE hexane	PrMgCl	GC–ICP–MS	0.05–0.08	[122]

PTV: programmed temperature vaporization
– Not available

ethyl-, and triethyllead) are at most a few ng L^{-1} [47, 117, 118, 121, 122]. The concentration of organolead compounds in polar snow is even lower, although it is indicative of the atmospheric distribution of these pollutants and of the world production of leaded petrol [120, 123, 124]. Because of these low concentrations, the first step in the quantification of organolead compounds in aqueous samples is enrichment. Table 6 lists reported sample preparation procedures. The earliest concentration techniques were based on liquid–liquid extraction of IAL species with hexane or pentane after complexation with sodium diethyldithiocarbamate at pH 8–9; this was followed by derivatization with Grignard reagents such as propyl- or butylmagnesium chloride [117, 120, 122, 123, 124]. Simultaneous alkylation and extraction of IAL into organic solvents can be performed by use of $NaBEt_4$ [110, 111], $NaBPr_4$ [10, 112] or Bu_4NBBu_4 [113, 114], for all of which the highest yield is achieved at pH 4. Irrespective of whether a Grignard reagent or a borate is used, inorganic lead present in the sample is co-extracted and derivatized; to prevent large quantities of alkylated inorganic lead from contaminating the MIP discharge tube (or the ion source of GC–MS systems), inorganic lead is normally masked with EDTA before extraction of IAL compounds.

With initial sample volumes of 100–200 mL and the injection of 25–50 μL of the final organic extract into the chromatographic column, GC–MIP–AED achieves detection limits of the order of 0.1 ng L^{-1} (Table 6). At these low concentrations, however, the accuracy and precision of the analysis can easily be disturbed by blank signals and the presence of artifacts. In fact, organolead compounds are very often detected in blanks because of contamination and transalkylation reactions. Steps can be taken to prevent this:

- For samples with concentrations below 0.1 pg g^{-1}, sample preparation should be performed in clean cabinets to avoid contamination with airborne IAL [123].
- Concentrated standards should be prepared and stored in a different room from the sample [107].
- Impurities in reagents (buffer solutions and complexing and masking agents) can be removed by pre-extraction with hexane [116, 117, 119, 123].
- Derivatization reagents are another possible source of problems. Purification of Grignard reagents is very difficult because of their low stability. PrMgCl is normally preferred to BuMgCl and PeMgCl for quantification of organolead compounds by GC–MIP–AED because it causes less baseline disturbance [120].

If Grignard derivatization is used, Pb^{2+} must be masked before extraction of organolead compounds because otherwise it will react with the Grignard reagent, giving not only the main product (e.g. Pr_4Pb, if PrMgCl is used) but also minor compounds such as $MePr_3Pb$ and $EtPr_3Pb$, which are formed by transalkylation reactions [80]. For the alkylborate derivatization reagents $NaBEt_4$, $NaBPr_4$, and Bu_4NBBu_4, which also react quantitatively with both IAL and inorganic lead [111, 112, 121], we know of no reports of transalkylation reactions; Pb^{2+} is, nevertheless, usually masked with EDTA to reduce consumption of borate [110, 114]. The presence of EDTA does not affect the derivatization of IAL because only inorganic lead forms stable chelates [113].

Solid-phase procedures can be used as an alternative to liquid–liquid extraction for the quantification of lead species in water samples [47, 115, 125]; adsorbents containing dithizone or dithiocarbamate groups are usually used. Purge-and-trap and SPME are also alternatives that can be used after in-situ derivatization with borate reagents [74, 111, 112, 121, 126, 127]; both techniques require smaller volumes of sample than LLE (Table 6) and airborne contamination is also avoided, because samples are processed in closed vessels; contamination problems arising from derivatization reagents cannot, however, be circumvented by use of these approaches.

Air samples

Determination of IAL and TAL compounds in the atmosphere, in which they are found at levels below 1 ng m^{-3}, requires the concentration of large volumes of air. Filters, solid adsorbents such as Tenax, Porapak Q, and Amberlites, water-filled gas bubblers, and cryogenic traps have all been used to extract organolead compounds from atmospheric aerosol and gas phases [108, 109, 128, 129]. Because of the possibility of decomposition of TAL compounds in the presence of ozone, a layer of ferrous sulphate is normally placed before to the trap [129].

Solid samples

In addition to water and air, organolead compounds have been found in soil, sediments, road dust, grass, and tree leaves. Wet atmospheric deposition, direct contamination (in the vicinity of emission sources) and absorption from contaminated waters through plant roots are the mechanisms responsible for the presence of alkyllead species in these samples. The excellent sensitivity and selectivity of GC–MIP–AED for lead compounds enables quantification of levels in these samples without any need for high concentration factors or extensive clean-up procedures. Because organolead species are labile, however, care must be taken to extract them without modifying their chemical structure.

The extraction of lead compounds from sediments and particulate matter can be performed under mild conditions by use of organic solvents in the presence of complexing agents [107, 130], supercritical CO_2 modified with methanol [131], buffer solutions of pH 4, or direct dissolution in water containing NaCl [121]. Most of these procedures give satisfactory yields for Me_3Pb^+ and Et_3Pb^+, but not for dialkyllead species. Validation of the extraction procedure is, moreover, only possible for Me_3Pb^+, for which there is a road dust reference material (BCR 605, containing 7.9±1.2 μg kg^{-1} of Me_3Pb^+).

With regard to biological samples, TMAH has been used as a tissue solubilizer for the speciation of lead compounds in grass and tree leaves. The digestion step takes several hours, and unless performed at low temperature affords very low yields of dialkyllead compounds, presumably because of their transformation into inorganic lead [132]. Enzymatic hydrolysis of biological tissues has also been used – samples are treated with a mixture of lipase and protease at 37 °C for 24–48 h [107]. SPME has been described as a promising technique for the analysis of Pb^{2+} and organolead compounds in urine and blood – after precipitation of erythrocytes (from blood), samples are diluted with water and adjusted to pH 4, after which lead compounds are derivatized in-situ and adsorbed on to a 100 μm polydimethylsiloxane-coated fused-silica SPME fiber [126, 133].

Simultaneous analysis of organometallic compounds by GC–MIP–AED

Although GC–MIP–AED is not really a multielemental technique, it nevertheless enables simultaneous monitoring of several emission lines, corresponding to one or several elements, as long as they all fall within the spectral region covered by the photodiode-array spectrophotometer, which has a breadth of ca. 40 nm. Volatile lead, mercury and tin compounds can therefore be analyzed in a single chromatographic run by using the emission lines at 261.418, 253.652, and 270.651 nm, and because similar sample preparation procedures are used for organometallic compounds of these three elements (especially for water samples), their simultaneous determination by GC–MIP–AED is possible. It should, nevertheless, be emphasized that the multielemental detection mode is less sensitive than the individual determination of each group of compounds. The first reason for this is that the 261 nm lead line is less sensitive than the 406 nm line. Secondly, and more importantly, optimum make-up flows are different for mercury, tin, and lead (ca. 50, 250, and 300 mL min^{-1}, respectively) [36]. Tin and lead compounds interact with the walls of the plasma discharge tube, making high flows desirable to minimize this interaction; for mercury species, for which no such interaction has been described, high flows simply increase dilution and so reduce sensitivity. There are similar differences among optimum hydrogen pressures, which are higher for tin and lead than for mercury [36].

Despite these problems, applications of GC–MIP–AED to simultaneous determination of Hg, Sn, and Pb species have been described in the literature. Ceulemans et al. [71] found that methyl species of mercury, lead, and tin can be derivatized and purged from water samples under similar conditions (ethylation with $NaBEt_4$ at pH 5, purge time 10 min), and proceeded to perform simultaneous quantification of tin, lead, and mercury methyl derivatives in water samples by use of a cryogenic purge-and-trap device. The MIP–AED working conditions (helium make-up flow and hydrogen pressure) were those previously found to be optimum for tin, and detection limits lower than 1 ng L^{-1} of metal were achieved for all compounds with a sample intake of 10 mL. Schubert et al. [70] have described the use of $NaBEt_4$ and $NaBPr_4$, then liquid–liquid extraction with hexane, for the simultaneous determination of organotin (butyl and phenyl compounds) and organolead (Et_3Pb^+ and Me_3Pb^+) in water samples; the two groups of compounds were analyzed at 270.651 and 261.418 nm, and the 247.857 nm carbon line was also monitored to obtain information about possible interferences from organic compounds. Finally, Minganti et al. [36] have shown that lead, tin, and mercury speciation in water and biological tissues is possible after extraction and simultaneous derivatization with *n*-pentylmagnesium bromide.

A low-cost GC–MIP–PED system for rapid species analysis

The first commercial GC–MIP–AED instrument, marketed by Hewlett–Packard in 1989, has enjoyed great success in the speciation of volatile compounds. For some years, an improved version of the same system has also been available. This hyphenated technique is, however, still beyond the financial means of most environmental control laboratories, which need cheap, fast, reliable instrumentation for daily monitoring of volatile organometallic species included in international lists of priority pollutants. Accordingly, with the financial support of the European Union, efforts have been made to develop a low-cost instrument designed specifically for species analysis of volatile compounds. The proposed system, the automated speciation analyser (ASA), is based on a combination of a multicapillary (MC) column (made of a bundle of approximately nine hundred 1 m×40 μm i.d. capillaries housed in an isothermal oven) with a helium MIP and a photoemission detector (PED) [134]. The analytical performances of each component of this system, as described in earlier papers, are described briefly below.

With regard to the separation step, the potential of MC columns for speciation analysis has been demonstrated by Lobinski et al. [135]. Theoretically, the efficiency of such columns is a function of the internal diameter of each single capillary, and sample capacity is determined by the number of capillaries. For the MC column described above maximum efficiency was achieved at flow rates between 50 and 150 mL min^{-1}, so the use MC columns with a length of only one meter (rendering a large number of theoretical plates per unit length), in combination with high carrier gas flows, produced fast chromatographic separations. The use of an isothermally operated MC column with the Hewlett–Packard MIP AES detector enabled quantification of tin, lead, and mercury species in less than 1 min with detection limits equal to or better than those achieved with a conventional 30 m×0.32 mm i.d. capillary column [136, 137]. Volatile organometallic species are introduced at the head of the MC column as a narrow band using a split injector or a custom-developed

cryogenic purge-and-trap injector [138, 139]. These procedures have been validated by analysis of reference materials (sediments, biological tissues, urine, and petrol) with certified levels of tin, lead, and mercury compounds. Other papers have reported the possibility of using isothermal columns as short as 5–22 cm combined with ICP–MS for analysis of mercury and tin species [140, 141].

When the chromatographic separation stage had been simplified and accelerated, attention was focused on the selection of an inexpensive but reliable detector. The choice made was an MIP–PED. The helium MIP device consists basically of a surfactron cavity, a rectangular wave-guide in which waves can propagate only in the transverse electronic mode (whereas the Hewlett–Packard MIP–AED system uses a Beenakker TM_{010} cavity), and a ceramic discharge tube needing no cooling [142]. Discrimination between plasma radiation and emission by an analyte element is achieved by use of an oscillating narrow-band interference filter followed by a photomultiplier tube [143]. This MIP–PED assemblage is much cheaper than the polychromator and photodiode-array spectrometer used in the commercial MIP–AED system. In combination with conventional GC columns the MIP–PED system had already been used for quantification of mercury compounds [144]. In combination with MC columns, it has achieved absolute detection limits of 3–4 pg Hg in the determination of $MeHg^+$ and Hg^{2+} in reference material TORT-2 [134]. Further applications and the commercial success of this low cost, dedicated, speciation system depends on many factors, among them the development of a range of interference filters for such elements as tin, lead, and selenium which offer adequate flexibility, in particular with regard to maximum transmission wavelength and bandwidth [134].

Conclusions

For quantification of volatile Hg, Sn, and Pb species in environmental samples the performance of GC–MIP–AED is currently unmatched, and only for water samples is pre-concentration of the analytes necessary before quantification. Nowadays, only GC–ICP–MS gives similar or better detection limits than GC–MIP–AED in the speciation of these three elements.

The ASA, a low-cost instrument designed for daily monitoring of organometallic Hg, Sn, and Pb species in control laboratories, and based on combination of a multicapillary column with a photoemission detector, has achieved performance similar to that of the commercial GC–MIP–AED system for Hg, but has yet to be validated for Sn and Pb by use of certified reference materials corresponding to environmental samples.

The precision and accuracy of species-selective analysis, especially for phenyltin and organolead species, is limited by degradation problems and the formation of artifacts during sample preparation. The easiest way to overcome these problems is to use isotope-labeled standards and MS detection. We regard this as the main advantage of GC–ICP–MS over GC–MIP–AED and other atomic emission detection systems for quantification of mercury, tin, and lead species.

Acknowledgements Financial support from the Spanish DGICT (project REN 2000–0984HIP) is acknowledged.

References

1. Guevremont R, Sturgeon RE (2000) J Anal At Spectrom 15: 37–42
2. Adams F, Slaets S (2000) Trends Anal Chem 69:2411–2417
3. Lobinski R (1998) Spectrochim Acta Part B 53:177–185
4. Gurka DF, Pyle S, Titus R (1997) Anal Chem 69:2411–2417
5. Sullivan JJ (1991) Trends Anal Chem 10:23–26
6. Sullivan JJ, Quimby D (1992) In: Uden PC (ed) ACS Symposium Series, Element-specific chromatographic detection by atomic emission spectroscopy. American Chemical Society, Washington, DC, p 62
7. Lobinski R, Adams FC (1997) Spectrochim Acta Part B 52: 1865–1903
8. Horvat M, Wilken RD (2000) Fresenius J Anal Chem 366: 415–416
9. EPA-452/R-97–007 Mercury study report to congress. Vol V: Health effects of mercury and mercury compounds. Office of Air Quality Planning and Standards and Office of Research and Development. US EPA. December 1997
10. Hempel M, Kuballa J, Jantzen E (2000) Fresenius J Anal Chem 366:470–475
11. Hight SC, Capar SG (1983) J Assoc Off Anal Chem 66:1121–1128
12. Hight SC, Corcoran MT (1987) J Assoc Off Anal Chem 70: 24–30
13. Ceulemans M, Adams FC (1994) LC–GC Int 7:694–697
14. Olsen KB, Sklarew DS, Evans JC (1985) Spectrochim Acta Part B 40:357–365
15. Quevauviller P (1996) J Chromatogr A 750:25–33
16. Horvat M (1999) Chemosphere 39:1167–1179
17. Rubí E, Lorenzo RA, Casais C, Carro AM, Cela R (1992) J Chromatogr 605:69–80
18. Panaro KW, Erickson D, Krull IS (1987) Analyst 112:1097–1105
19. Kato T, Uheiro T, Yasuhara A, Morita M (1992) J Anal At Spectrom 7:15–18
20. Carro-Díaz AM, Lorenzo-Ferreira RA, Cela-Torrijos R (1994) J Chromatogr A 683:245–252
21. Frech W, Snell JP, Sturgeon RE (1998) J Anal At Spectrom 13:1347–1353
22. Orellana-Velado NG, Pereiro R, Sanz-Medel A (1998) J Anal At Spectrom 13:905–909
23. Orellana-Velado NG, Pereiro R, Sanz-Medel A (2000) J Anal At Spectrom 15:49–53
24. Cai Y, Monsalud S, Jaffe R, Jones RD (2000) J Chromatogr A 876:147–155
25. Westöö G (1966) Acta Chem Scand 20:2131–2137
26. Westöö G (1967) Acta Chem Scand 21:1790–1800
27. Bache CA, Lisk DJ (1971) Anal Chem 43:950–952
28. Talmi Y (1975) Anal Chim Acta 74:107–117
29. Emteborg H, Björklund E, Ödman F, Karlsson L, Mathiasson L, Frech W, Baxter DC (1996) Analyst 121:19–29
30. Donais MK, Uden PC, Schantz MM, Wise SA (1996) Anal Chem 68:3859–3866
31. Qian J, Skyllberg U, Tu Q, Bleam WF, Frech W (2000) Fresenius J Anal Chem 367:467–473
32. Behlke MK, Uden PC, Schantz MM (1996) Anal Commun 33:91–92
33. Snell JP, Frech W, Thomassen Y (1996) Analyst 121:1055–1060

34. Mothes S, Wennrich R (1999) J High Resol Chromatogr 22: 181–182
35. O'Reilly JE (1982) J Chromatogr 238:433–444
36. Minganti V, Capelli R, De Pellegrini R (1995) Fresenius J Anal Chem 351:471–477
37. Bulska E, Baxter DC, Frech W (1991) Anal Chim Acta 249: 545–554
38. Palmieri HEL, Leonel LV (2000) Fresenius J Anal Chem 366: 466–469
39. Swan HB (1998) Bull Environ Contam Toxicol 60:511–518
40. Emteborg H, Hadgu N, Baxter DC (1994) J Anal At Spectrom 9:297–302
41. Gerbersmann C, Heisterkamp M, Adams FC, Broekaert JAC (1997) Anal Chim Acta 350:273–285
42. Vázquez MJ, Carro AM, Lorenzo RA, Cela R (1997) Anal Chem 69:221–225
43. Abuín M, Carro AM, Lorenzo RA (2000) J Chromatogr A 889:185–193
44. Jiménez MS, Sturgeon RE (1997) J Anal At Spectrom 12:597–601
45. Emteborg H, Baxter DC, Frech W (1993) Analyst 118:1007–1013
46. Emteborg H, Baxter DC, Sharp M, Frech W (1995) Analyst 120:69–77
47. Johansson M, Emteborg H, Glad B, Reinholdsson F, Baxter DC (1995) Fresenius J Anal Chem 351:461–466
48. Hänström S, Briche C, Emteborg H, Baxter DC (1996) Analyst 121:1657–1663
49. Reuther R, Jaeger L, Allard B (1999) Anal Chim Acta 394: 259–269
50. Carro AM, Mejuto MC (2000) J Chromatogr A 882:283–307
51. Snell J, Qian J, Johansson M, Smit K, Frech W (1998) Analyst 123:905–909
52. Mena ML, McLeod CW (1996) Mikrochim Acta 123:103–108
53. Mena ML, McLeod CW, Jones P, Withers A, Minganti V, Capelli R, Quevauviller P (1995) Fresenius J Anal Chem 351: 456–460
54. Madson MR, Thompson RD (1998) J Assoc Off Anal Chem Int 81:808–816
55. Takeuchi M, Mizuishi K, Hobo T (2000) Anal Sci 16:349–359
56. Becker G, Janak K, Colmsjö A, Östman C (1997) J Chromatogr A 775:295–306
57. Vainiotalo S, Häyri L (1990) J Chromatogr 523:273–280
58. Attar KM (1996) Appl Organomet Chem 10:317–327
59. Rapsomanikis S, Harrison RM (1988) Appl Organomet Chem 2:151–157
60. Lobinski R, Dirkx W, Ceulemans M, Adams FC (1992) Anal Chem 64:159–165
61. Girousi S, Rosenberg E, Voulgaropoulos A, Grasserbauer M (1997) Fresenius J Anal Chem 358:828–832
62. Tuschku S, Mothes S, Dittrich K (1994) J Chromatogr A 683:269–276
63. Dirkx W, Lobinski R, Adams FC (1993) Anal Sci 9:273–278
64. Ceulemans M, Lobinski R, Dirkx W, Adams FC (1993) Fresenius J Anal Chem 347:256–262
65. Szpunar J, Ceulemans M, Lobinski R, Adams FC (1993) Anal Chim Acta 278:99–113
66. Stab JA, Brinckman UAT, Cofino WP (1994) Appl Organomet Chem 8:577–585
67. Stäb JA, Cofino WP, van Hattum B, Brinkman UAT (1993) Fresenius J Anal Chem 347:247–255
68. David F, Sandra P (1992) Analusis 20:53–54
69. Liu Y, Lopez-Avila V, Alcaraz M, Beckert WF (1993) J High Resol Chromatogr 16:106–112
70. Schubert P, Rosenberg E, Grasserbauer M (2000) Fresenius J Anal Chem 366:356–360
71. Ceulemans M, Adams FC (1996) J Anal At Spectrom 11:201–206
72. Leroy MJF, Quevauviller P, Donard OFX, Astruc M (1998) Pure Appl Chem 70:2051–2064
73. Tutschku S, Mothes S, Wennrich R (1996) Fresenius J Anal Chem 354:587–591
74. Moens L, De Smaele T, Dams R, Van Den Broeck P, Sandra P (1997) Anal Chem 69:1604–1611
75. Lespes G, Desauziers V, Montigny C, Potin-Gautier M (1998) J Chromatogr A 826:67–76
76. Aguerre S, Montigny C, Lespes G, Potin-Gautier M (2000) Analyst 125:263–268
77. Millan E, Pawliszyn J (2000) J Chromatogr A 873:63–71
78. Morcillo Y, Cai Y, Bayona JM (1995) J High Resol Chromatogr 18:767–770
79. Vercauteren J, De Meester A, De Smaele T, Vanhaecke F, Moens L, Dams R, Sandra P (2000) J Anal At Spectrom 15: 651–656
80. Szpunar J, Ceulemans M, Dirkx W, Witte C, Lobinski R, Adams FC (1994) Mikrochim Acta 113:287–298
81. Tao H, Rajendram RB, Quetel CR, Nakazato T, Tominaga M, Miyazaki A (1999) Anal Chem 71:4208–4215
82. Haberhauer-Troyer C, Crnoja M, Rosenberg E, Grasserbauer M (2000) Fresenius J Anal Chem 366:329–331
83. Rodriguez Pereiro I, Schmitt VO, Szpunar J, Donard OFX, Lobinski R (1996) Anal Chem 68:4135–4140
84. Ceulemans M, Adams FC (1995) Anal Chim Acta 317:161–170
85. Dirkx W, Lobinski R, Adams FC (1994) Anal Chim Acta 286:309–318
86. Dauchy X, Cottier R, Batel A, Borsier M, Astruc A, Astruc M (1994) Environ Technol 15:569–576
87. Rodríguez Pereiro I, Wasik A, Lobinski R (1999) Fresenius J Anal Chem 363:460–465
88. Szpunar J, Schmitt VO, Donard OFX, Lobinski R (1996) Trends Anal Chem 15:181–187
89. Ceulemans M, Slaets S, Adams F (1998) Talanta 46:395–405
90. Schubert P, Fernández-Escobar I, Rosenberg E, Bayona JM (1998) J Chromatogr A 810:245–251
91. Fernández-Escobar I, Gibert M, Messeguer A, Bayona JM (1998) Anal Chem 70:3703–3707
92. Abalos M, Bayona JM, Compañó R, Granados M, Leal C, Prat MD (1997) J Chromatogr A 788:1–49
93. Chau YK, Yang F, Maguire RJ (1996) Anal Chim Acta 320: 165–169
94. Ruiz-Encinar J, García-Alonso JI, Sánz-Medel A (2000) J Anal At Spectrom 15:1233–1239
95. Arnold CG, Berg M, Müller SR, Domman U, Schwarzenbach RP (1998) Anal Chem 70:3094–3101
96. Suzuki T, Kondo K, Uchiyama M, Murayama M (1999) J Agric Food Chem 47:3886–3894
97. Alzieu C, Sanjuan J, Deltreil JP, Borel M (1986) Mar Pollut Bull 17:494–498
98. Morcillo Y, Porte C (1998) Trends Anal Chem 17:109–116
99. Rodríguez I, Santamarina M, Bollaín MH, Mejuto MC, Cela R (1997) J Chromatogr A 774:379–387
100. Chau YK, Yang F, Brown M (1997) Anal Chim Acta 338: 51–55
101. Ceulemans M, Witte C, Lobinski R, Adams FC (1994) Appl Organomet Chem 8:451–461
102. Quevauviller P, Astruc M, Morabito R, Ariese F, Ebdon L (2000) Trends Anal Chem 19:180–188
103. Quevauviller P, Morabito R (2000) Trends Anal Chem 19: 86–96
104. Szpunar J, Schmitt VO, Lobinski R, Monod JL (1996) J Anal At Spectrom 11:193–196
105. Gomez-Ariza JL, Morales E, Beltran R, Giráldez I, Benitez MR (1995) Analyst 120:1171–1174
106. Pellegrino C, Massanisso P, Morabito R (2000) Trends Anal Chem 19:97–106
107. Lobinski R, Dirkx WMR, Szpunar- Lobinska J, Adams FC (1994) Anal Chim Acta 286:381–390
108. Pyrzynska K (1996) Mikrochim Acta 122:279–293
109. Metcalfe PJ (1989) Anal Proc 26:134–136
110. Zufiaurre R, Pons B, Nerín C (1997) J Chromatogr A 779: 299–306

111. Yu X, Pawliszyn J (2000) Anal Chem 72:1788–1792
112. De Smaele T, Moens L, Dams R, Sandra P (1996) Fresenius J Anal Chem 355:778–782
113. Bergmann K, Neidhart B (1996) Fresenius J Anal Chem 356: 57–61
114. Heisterkamp M, Adams FC (1998) Fresenius J Anal Chem 362:489–493
115. Baena JR, Cárdenas S, Gallego M, Valcárcel M (2000) Anal Chem 72:1510–1517
116. Lobinski R, Adams FC (1992) Anal Chim Acta 262:285–297
117. Paneli M, Rosenberg E, Grasserbauer M, Ceulemans M, Adams FC (1997) Fresenius J Anal Chem 357:756–762
118. Sadiki A, Williams DT (1996) Chemosphere 32:1983–1992
119. Lobinski R, Szpunar-Lobisnka J, Adams FC, Teissedre PL, Cabanis JC (1993) J Assoc Off Anal Chem Int 76:1262–1267
120. Lobinski R, Adams FC (1992) J Anal At Spectrom 7:987–992
121. Craig PJ, Dewick RJ, Elteren JT (1995) Fresenius J Anal Chem 351:467–470
122. Heisterkamp M, De Smaele T, Candelone JP, Moens L, Dams R, Adamas FC (1997) J Anal At Spectrom 12:1077–1081
123. Lobinski R, Boutron CF, Candelone JP, Hong S, Szpunar-Lobinska J, Adams FC (1993) Anal Chem 65:2510–2515
124. Lobinski R, Szpunar-Lobinska J, Adams FC (1994) Analusis 22:M54-M57
125. Salih B (2000) Spectrochim Acta Part B 55:1117–1127
126. Dunemann L, Hajimiragha H, Begerow J (1999) Fresenius J Anal Chem 363:466–468
127. Gorecki T, Pawliszyn J (1996) Anal Chem 68:3008–3014
128. Dirkx WM, Van Cleuvenbergen R, Adams FC (1992) Mikrochim Acta 109:133–135
129. Allen AG, Radojevic M, Harrison RM (1988) Environ Sci Technol 22:517–522
130. Nerín C, Pons B, Zufiaurre R (1995) Analyst 120:751–754
131. Johansson M, Berglöf T, Baxter DC, Frech W (1995) Analyst 120:755–759
132. Van Cleuvenbergen R, Chakraborti D, Adams F (1990) Anal Chim Acta 228:77–84
133. Yu X, Yuan H, Górecki T, Pawliszyn J (1999) Anal Chem 71: 2998–3002
134. Rosenkranz B, Quevauviller P, Bettmer J (1999) Am Lab 31: 17–24
135. Rodriguez-Pereiro I, Schmitt VO, Lobinski R (1997) Anal Chem 69:4799–4807
136. Rodriguez-Pereiro I, Wasik, Lobinski R (1998) J Chromatogr A 795:359–370
137. Rodriguez-Pereiro I, Lobinski R (1997) J Anal At Spectrom 12:1381–1385
138. Wasik A, Rodriguez-Pereiro I, Lobinski R (1998) Spectrochim Acta Part B 53:867–879
139. Wasik A, Rodriguez-Pereiro I, Dietz C, Szpunar J, Lobinski R (1998) Anal Commun 35:331–335
140. Slaets S, Adams F, Rodriguez-Pereiro I, Lobinski R (1999) J Anal At Spectrom 14:851–857
141. Rodriguez I, Mounicou S, Lobinski R, Sidelnikov, Patrushev Y, Yamanaka M (1999) Anal Chem 71:4534–4543
142. Rosenkranz B, Bettmer J (2000) Trends Anal Chem 19:138–156
143. Müller H, Cammann K (1988) J Anal At Spectrom 3:907–913
144. Bettmer J, Bradter M, Buscher W, Erber D, Rieping D, Cammann K (1995) Appl Organomet Chem 8:541–545
145. Lopez-Avila V, Liu Y, Beckert WF (1997) J Chromatogr A 785:279–288
146. Liu Y, Lopez-Avila V, Alcaraz M, Beckert WF (1994) Anal Chem 66:3788–3796
147. Gremm TJ, Frimmel FH (1992) Water Res 26:1163–1169
148. Müller M (1987) Anal Chem 59:617–623
149. Michel P, Averty B (1991) Appl Organomet Chem 5:393–397
150. M. Nagase, M. Toba, H. Kondo, K. Hasebe (1998) Analyst 123:1091–1094
151. Gómez-Ariza JL, Morales E, Giráldez I, Beltrán R (1997) Intern J Environ Anal Chem 66:1–13
152. Jiang GB, Xu FZ (1996) Appl Organomet Chem 10:77–82
153. Wilken RD, Kuballa J, Jantzen E (1994) Fresenius J Anal Chem 350:77–84
154. Quevauviller P, Maier EA, Griepink B (1995) Quality assurance for environmental analysis. Elsevier, Amsterdam
155. Prange A, Jantzen E (1995) J Anal At Spectrom 10:105–109
156. De Smaele T, Moens L, Dams R, Sandra P, Van der Eycken J, Vandyck (1998) J Chromatogr A 793:99–106
157. Aguerre S, Lespes G, Desauziers V, Potin-Gautier M (2001) J Anal At Spectrom 16:263–269
158. Kim AW, Foulkes ME, Ebdon L, Hill SJ, Patience RL, Barwise AG, Rowland SJ (1992) J Anal At Spectrom 7:1147–1149
159. Forsyth DS, Hayward S (1995) Fresenius J Anal Chem 351: 403–409