ELSEVIER

Journal of Chromatography A, 938 (2001) 211–224

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Review

Sample treatment in chromatography-based speciation of organometallic pollutants

J.L. Gómez-Ariza*, E. Morales, I. Giráldez, D. Sánchez-Rodas, A. Velasco

Departamento de Química y Ciencia de los Materiales, Escuela Politécnica Superior, Universidad de Huelva, Campus de La Rábida, 21819 Palos de la Frontera (Huelva), Spain

Abstract

Speciation analysis is nowadays performed routinely in many laboratories to control the quality of the environment, food and health. Chemical speciation analyses generally include the study of different oxidation state of elements or individual organometallic compounds. The determination of the different chemical forms of elements is still an analytical challenge, since they are often unstable and concentrations in different matrices of interest are in the $\mu g\ l^{-1}$ or even in the $ng\ l^{-1}$ range (e.g., estuarine waters) or $ng\ g^{-1}$ in sediments and biological tissues. For this reason, sensitive and selective analytical atomic techniques are being used as available detectors for speciation, generally coupled with chromatography for the time-resolved introduction of analytes into the atomic spectrometer. The complexity of these instrumental couplings has a straightforward consequence on the duration of the analysis, but sample preparation to separate and transfer the chemical species present in the sample into a solution to be accepted readily by a chromatographic column is the more critical step of total analysis, and demands considerable operator skills and time cost. Traditionally, liquid–liquid extraction has been employed for sample treatment with serious disadvantages, such as consumption, disposal and long-term exposure to organic solvent. In addition, they are usually cumbersome and time-consuming. Therefore, the introduction of new reagents such as sodium tetraethylborate for the simultaneous derivatization of several elements has been proposed. Other possibilities are based in the implementation of techniques for efficient and accelerated isolation of species from the sample matrix. This is the case for microwave-assisted extraction, solid-phase extraction and microextraction, supercritical fluid extraction or pressurized liquid extraction, which offer new possibilities in species treatment, and the advantages of a drastic reduction of the extraction time and the embodiment into on-line flow analysis systems. This new generation of treatment techniques constitutes a good choice as fast extraction methods for feasible species-selective analysis of organometallic compounds under the picogram level, that can be used for national regulatory agencies, governmental and industrial quality control laboratories, and consequently, for manufacturers of analytical instrumentation.

Keywords: Reviews; Extraction methods; Organometallic compounds; Organotin compounds

Contents

*Corresponding author. Tel.: +34-959-017-403; fax: +34-959-017-414.
E-mail address: ariza@uhu.es (J.L. Gómez-Ariza).

0021-9673/01/$ – see front matter
PII: S0021-9673(01)01103-7

1. Introduction

Speciation has been defined as the occurrence of an element in separate identifiable forms (i.e., chemical, physical or morphological state) [1]. Chemical speciation analyses include the study of different state oxidation elements, or individual organometallic species. The major target species include well-known organometallic environmental pollutants which have created great environmental concern in the last few decades [2,3,5–7] (e.g., butyl- and phenyltin, alkyllead), products of transformation of toxic elements (e.g., methylmercury, organoarsenic) and complexes of essential and toxic metals and non-metals with biomolecules [4], such as selenomethionine and selenocystine.

The oxidation state assessment of some elements such as As(III) and (V), Se(IV) and (VI), or Cr(III) and (VI) is also of great interest, as they have different impact and behavior in relation to toxicity, mobility and bioavailability. Alkylation grade is another important cause of toxicity, as it is the case of trialkyltins compared to di- or monoalkyltin, or methylmercury (MHg) compared to Hg(II). Sometimes the introduction of a toxic single ion into a complex organic molecule produces a clear reduction of the element toxicity, such as As(III) against arsenobetaine (AsB), or the detoxification of inorganic selenium when converted into methylated forms, such as dimethylselenide (DMSe). Generally, metal alkylation helps transport across the biological membrane and therefore accumulation in the food chain [8–10]. In particular, the use of triorganotins (R_3SnX) in antifouling paints (R=butyl, phenyl) and pesticides (R=phenyl, cyclohexyl) has led to environmental problems, with these species suffering from different degradation processes that lead to a variety of di- and monoalkyltin compounds with differential toxicity. Other times, toxicity is caused by the volatility of organometallic species and easy absorption through the lungs, as is the case of mercury.

The determination of the chemical forms of elements is still an analytical challenge. Species are often unstable and the concentrations found in the different matrices of interest are often in the $\mu g\ l^{-1}$ level or in some cases (e.g., alkylated forms of metals such as Sn or Pb) even in the $ng\ l^{-1}$ (e.g., estuarine waters) or $ng\ g^{-1}$ (sediments and biological tissues) range, whereas inorganic forms can be simultaneously present at thousand-fold higher levels. For this reason sensitive and selective analytical atomic techniques are being used as available detectors for speciation, generally coupled with liquid or gas chromatography for the time-resolved introduction of analytes into the the atomic spectrometer [8]. The complexity involved in the coupling between several instruments has a straightforward consequence on the duration of the analysis as well as in the instrumentation costs. On the other hand, sample preparation has to transfer the elemental species present in the sample to a solution to be accepted readily by a chromatographic column. The preparation of such a solution

requires the extraction and derivatization of analytes present in the sample, which involves numerous steps and manipulations that increase species losses, and demand considerable operator skills and time cost. One of the most important trends to simplify the procedures is the improvement of sample preparation and treatment steps with the introduction of a new generation of simple, rapid and reliable procedures for species extraction and derivatization before their introduction into the tandem chromatograph/detector.

Moreover, the method development and setup requires the use of material of known composition (e.g., certified reference materials) which are not always available. Therefore, spiking experiments have to be performed for method quality control. In this case, emphasis has to be put on the spiking procedures, as they exert an influence on the recovery values. Even if the recoveries of spiked compounds equilibrated in a certain matrix are total, there is no evidence that the incurred compound will be extracted with the same efficiency. However, it can be concluded that although our present knowledge is not perfect, the use of spiking experiments helps to minimize errors.

Simultaneous speciation of several elements also constitutes an important task. Generally, problems arise from sample preparation (species extraction, enrichment and derivatization) due to the strongly different conditions needed for each element and this has led to the introduction of new reagents such as sodium tetraethylborate ($NaBEt_4$) for the simultaneous derivatization of several elements [11] (e.g., tin, lead, and mercury), as well as the implementation of techniques for efficient and accelerated isolation of the bulk of the analytes species from the sample matrix, such as microwave assisted extraction [30]. Finally, the integration and automation of all the steps between the sample and the detector significantly reduce the time of analysis increasing the reproducibility and accuracy. For this reason, the development of new single devices for the fully speciation of the samples is necessary [12,13].

2. Sample treatment

The use of high-performance liquid chromatography (HPLC) and especially gas chromatography (GC) as time-resolved species introduction techniques into the atomic spectrometer establishes some physico–chemical requirements for the analytes, which usually makes necessary a pre-treatment procedure using some type of reagent that conditions the matrix or leaches the species for the extraction step, in which the species are completely isolated from the matrix. Then the species are derivatized into suitable forms for analysis, generally volatile and thermally stables species for GC, which is a very frequent approach for speciation due to the good resolution and availability of sensitive detectors, despite the increasing popularity of HPLC–inductively coupled plasma (ICP) mass spectrometry (MS) coupling [14]. Finally, the extract is submitted to some clean-up step before its introduction into the chromatographic system. Sometimes separation of the species from the matrix is combined with a preconcentration step in order to improve the limit of detection. These major steps are completed by a series of minor operations such as drying of the organic phase, dilution, pH adjustment, change of solvent, transfer from one vessel to another or phase separation [12,14]. As a general rule, sample preparation strives to shorten the numbers of steps, their duration, sample handling and manipulation.

Many choices have been proposed for species pretreatment/extraction from environmental matrices: water, soils, sediments and biological materials, although they can be categorized [41] according to the solvent polarity, sample acidification to enhance the recoveries of the species, enzymatic hydrolysis for biotic samples, and use of chelating agents. Against these classical extraction techniques, other more recent approaches such as microwave-assisted extraction (MAE), supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), solid-phase extraction (SPE) or microextraction (SPME) offer new possibilities in species treatment, and advantages as a drastic reduction of the extraction time and an embodiment into on-line flow analysis systems can be highlighted. However, disadvantages of fast extraction methods (FEMs) should not be obviated, as the possible loss of chemical stability of the chemical forms of the elements during the extraction steps in those methods which employ high pressure and/or temperature (SFE, PLE

and MAE) [17]. Also, SFE procedures result in the extraction of multiply charged species, which are poorly soluble in supercritical fluids and have strong interactions with abiotic matrices, as is the case of sediments having varying sulfur or organic carbon [18,19]. In the case of MAE, the application of microwave energy to flammable organic compounds, such as solvents, can pose serious hazards in inexperienced hands [20]. Finally, extraction with SPME requires extreme precision during manufacturing of the coating and some level of degradation of the fiber occurs during repeated usage [21].

3. Solvent extraction procedures

3.1. Organotin and organolead species

Non-polar solvents such as hexane, benzene, toluene, chloroform, pentane or dichloromethane extract low polar species, e.g., tributhyltin (TBT), but highly polar mono- and dibutyltin (MBT, DBT) or mono- and dimethyltin (MMT, DMT) compounds need complexation or acidification of the sample. Some extraction conditions for organotin compounds are summarized in Table 1. There is no agreement about the solvent polarity required for extraction, medium polarity solvents are advisable to extract ionic organotin species, but also increase the number of substances that are co-extracted and impair the derivatization reactions [16] prior to GC analysis. Direct derivatization on sediment slurries or mussel tissues has been used by some workers to reduce the time of analysis. Sometimes the sample is homogenized with *n*-hexane for organotins pentylation by the Grignard reaction in diethyl ether [32]. However, Chau and Yang [43] suggest the direct contact of pentylmagnesium bromide with the sediment to drastically improve the recovery of MBT species. This latter method can be applied to the simultaneous speciation of organotin and alkyllead in sediments.

When the analytical methods for organotin com-

Table 1
Solvent extraction procedures for organotin species

Species	Extraction conditions	Ref.
Butyl- and phenyltin	HCl, pH 2–3 Extraction with 0.25% tropolone in diethyl ether	[31]
Butyl- and phenyltin	NaDDC complexation, toluene–HOAc (10:4) extraction	[26]
MBT, MPhT	Stirring with water–HCl (1:1), extraction with hexane	[27]
DBT, TBT, TPhT	Reflux, 80°C, 30 min with HCl–MeOH (5:95), extraction with benzene	[29]
Butyltin	Shaking overnight, sonication 30 min, extraction with pure HOAc	[34]
Butyltin	Sonication 30°C with 0.08% tropolone in MeOH, extraction with hexane	[35]
Butyl- and phenyltin	Stirring with water–HBr mixture, 30 min, extraction with 0.04% tropolone in Cl_2CH_2	[40]
Butyl- and phenyltin	Shaking with HBr, extraction with 0.07% troplone in pentane	[38]
Methyl- and butyltin	Sonication 2 h with 6 *M* HCl at 50°C	[45]
Butyltin	Extraction with 2 *M* HCl, 12 h	[46]
Butyltin	Conc. HCl+conc. HBr, extraction with 0.05% in pentane	[37]

Abbreviations: MBT, monobutyltin; MPhT, monophenyltin; DBT, dibutyltin; TBT, tributyltin; TPhT, triphenyltin.

pounds are based on the separation by liquid chromatography, the species are extracted from the sample (e.g., sea water) acidified with hydrochloridic acid using a tropolone solution in chloroform, then the extract is evaporated to dryness and re-dissolved in methanol for chromatographic separation [44].

The extraction with polar solvents such as aqueous hydrochloric acid [45–49], hydrochloric or acetic acids in polar solvents (methanol, acetone) [28,42,48–61] or polar solvents in basic medium [55], generally performed under sonication, has been used for organotins analysis from solid matrices [33,36,39]. Generally, this extraction is followed by a non-polar solvent extraction (benzene, cyclohexane, toluene) [35,52,53,60,62] to recover the species for derivatization. Salting out reagents and tropolone have also been used to increase the species recovery [22–25].

The extraction of lead compounds is very similar to that for organotins. Volatile non-polar tetralkylated compounds can be directly extracted from environmental samples with non-polar solvents such as benzene or hexane. Ionic alkyl compounds (R_2Pb^{2+} and R_3Pb^{+}) can be extracted and preconcentrated from water samples in the presence of NaCl and sodium diethyldithiocarbamate in hexane [63], benzene [64], and pentane [65].

3.2. Organomercury species

The extraction of $MeHg^{+}$ in sediments are based on protocols derived from the classic Westöö technique [66], involving the followings main steps: (i) organomercury compound liberation from the organic matrix (generally proteins) by displacing the mercapto group with halogen ion at low pH, (ii) selective extraction or organomercury species in toluene, (iii) purification of the organic extract by extraction with an aqueous solution of cysteine, (iv) redissociation of the organomercury–thiol complex in acid medium, and (v) re-extraction in an organic solvent and preconcentration by evaporation of the solvent. Other procedures are based on acidic leaching [67–72], alkaline digestion [74–77] or steam distillation [75–79], followed by one or two separation steps, e.g., solvent extraction, ion exchange, distillation or aqueous derivatization (hydride generation or ethylation).

These sample preparation methods are not only laborious and time-consuming, but also lack sufficient efficiency and reliability [77,80,81]. HCl leaching at room temperature does not quantitatively release methylmercury compounds from sediment samples [75], and both alkaline digestion by 25% KOH in methanol and distillation quantitatively release $MeHg^{+}$ from sediments, but it takes 1 to 6 h for quantitative recoveries [73–79]. The diversity of leaching methods lead to necessary comparisons among them to help the choice of the optimum procedure. Huang [72] studied three procedures for sample preparation in the analysis of Me–Hg from environmental and biological matrices: (a) alkaline digestion of biologicals followed by acidification with hydrochloric acid, (b) distillation of Me–Hg from sediment, soil and water samples in the presence of an L-cysteine–ascorbic acid–phosphoric acid–potassium bromide mixture, and collection of the distillate in an $NH_2OH{\cdot}HCl$ solution, and (c) addition of EDTA to the sample solution and for masking the interfering metal cations.

3.3. Organoarsenic and organoantimony species

The more ubiquitous organoarsenic environmental molecules are monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine [$(CH_3)_3As^{+}CH_2COO^{-}$, AsB] and some arsenic ribosides (arsenosugars). Due to the stability of methylated arsenic species, they are leached together with total inorganic arsenic using warm [82,83] or cold [84,85] concentrated HCl from sediments and biological tissues. Crescelius et al. [86] recommend the use of acidic leaching (pH 2.3) for As(III) or basic leaching (pH 11.9) for As(V), MMA and DMA. Other weak leaching reagents such as acetate, citrate and oxalate buffers [87] selectively leach As(III), and phosphoric acid efficiently extracts total arsenic from soils [88] Other experimental approachs for arsenic evaluation in aquatic sediments involve the use of hydroxylammonium hydrochloride as extractant [90], as As is usually associated with iron oxides [89]. When biological tissues are considered (bivalves, fish, seaweed), the extraction procedures employ mainly water, methanol or water–methanol mixtures with the aid of sonication or Soxhlet extraction for their analysis by HPLC [91–94].

For antimony speciation in plants, Dodd et al. [95] homogenized frozen samples in a blender with acetic acid. Homogenates were sonicated for 1 h and left standing overnight, the extracts analyzed after filtration.

3.4. Organoselenium species

The organoselenium compounds leaching from environmental samples have not yet been completely solved [96]. A process largely used, consisting of a mixture of water–chloroform–methanol (2:3:5) and evaporation to dryness has been applied to selenium [97], this method has been lately modified by Potin-Gautier et al. [98] and Emteborg et al. [99]. The latter introducing an oscillating magnetic stirring for 5 h. Other methods use a methanol–water (1:1) mixture [100] or the same mixture with 0.28 mol l^{-1} HCl or 4% NH_3 [99], in all cases with two 30-min cycles of sonication. The samples are centrifuged to collect the supernatant, filtered through a 0.45 μm pore size filter and brought to pH 9.5 by adding 5 ml of a 1% ammonia solution to ionize the selenium species present in the sample extract. The extracts were then passed twice through end-capped C_{18} cartridges, and reduced in volume to 1–2 ml using rotatory evaporation.

Preconcentration until 2–40-fold of selenium (as organoselenium compounds) from wastewater, plant, and soil samples can be achieved by selective extraction of the element with 1-hexene from perchlorate–bromide medium [101]. Living bacterial cells (*Pseudomonas putida*) have been used to perform a separation preconcentration procedure for selenium cystamine (Se-Cystm) and determination of selenium slurry by electro-thermal atomic adsorption spectroscopy (ETAAS) after addition of Pd as chemical modifier [102]. The procedure makes possible the determination of Se-Cystm at low levels, detection limits of 0.01 ng l^{-1}, for 1000 ml sample volume and cell growth of 6 h. This correspond to an absolute limit of detection of 1 pg. The method was applied to the determination of Se-Cystm in natural waters spiked to 5 ng l^{-1} with this compound together with other selenium species.

Preparation of non-solid matrices such as urine is straightforward, and only precise dilution with water (1:4) prior to the analysis, although clean-up with C_{18} cartridges has been proposed for the determination of trimethylselenonium ion, selenomethionine, selenocysteine, selenite and selenate [103].

4. Basic and enzymatic hydrolysis

Basic and enzymatic digestions are usually restricted to biotic samples. Enzymes, even non-specific protease enzymes, are capable of breaking down a wide range of proteins into their amino acid components, this makes the embedded metallic species more available to the extracting agents. Basic hydrolysis with reagents such as tetramethylammonium (TMAH) is currently applied to organotin species under warm temperature conditions (60°C) for several hours [104–106]. Alternatively, ethanolic KOH at 60°C for 90 min [107,108] or NaOH at 40°C for 20 min [109] followed by pH adjustment have also been proposed. Basic treatment is followed by liquid–liquid extraction with hexane or other non-polar solvent to isolate the species. Acid protein hydrolysis with HCl at 110°C can also be used for selenium species leaching, but degradation of the selenium compounds has been observed during the treatment [110].

Enzymatic hydrolysis is becoming a promising approach in metal speciation, specially for organo-lead and organotin compounds [106–112]. This method has been studied by Gilon et al. [113] for selenium application using a protease that breaks the peptidic bonds of the proteins present in the material at pH 7.5 (phosphate citric buffer) and incubation at 37°C for 24 h. A similar procedure can be used for organotins [106–114] or organoselenium [115] compounds using a lipase–protease mixture under similar experimental conditions. Pannier et al. [111] also used a mixture of enzymes in aqueous phosphate buffer to release organotin compounds from marine biological samples, and pronase, a protease with a broad specificity, isolated from *Streptomyses griseus* has been used to monitor the levels of selenium in serum which is digested with the enzyme at 37°C overnight [115].

5. Fast extraction methods

5.1. Supercritical fluid extraction

The use of supercritical fluids is an attractive approach for sample preparation, due to the common effort to reduce the consumption, disposal and long-term exposure to organic solvents. Intrinsical characteristics of supercritical fluids are the low viscosity and diffusion coefficients, much lower than those of liquid, that contribute to a rapid mass transfer of solutes and faster extractions than those in liquid extractions. CO_2 is the most common supercritical fluid used for extractions, as it is non-toxic, non-flammable, relatively cheap and easily commercially obtained. However, it has low efficiency to extract polar compounds and precise addition of ''modifiers'' and/or complexing agents for complete recovery of polar and non-polar species, therefore few papers consider the use of supercritical fluids as sample preparation technique in metal speciation [116–125].

SFE has been specially focused on organotin compounds extraction. Several CO_2 modifiers have been tested such as formic acid [118] and methanol [121]. Low recoveries are obtained in the extraction of di- and monoderivatives, and two approaches have been used to improve the efficiency of the extractions: (i) the addition of complexing agents such as sodium diethyldithiocarbamate (NaDDC) and diethylammonium diethyldithiocarbamate (DEA-DDC) [121,122,126,127], and (ii) alkylation in the extraction cell prior to the extraction [128]. SFE has been applied to different environmental matrices: sediments [120], soils [121,122], potato and almond matrices [118], biological samples [123,125] and sea-water [119] using a combination of liquid–solid extraction on a disc followed by in situ Grignard ethylation and SFE.

In addition, SFE with CO_2 as solvent has been reported for the determination of $MeHg^+$ in sediments [using GC–microwave induced plasma-atomic emission spectroscopy (MIP-AES) detection] with an extraction efficiency of $49 \pm 5\%$ for a 37.5 dynamic extraction. Butyl magnesium chloride was used to derivatize this species to butylmethylmercury which is amenable to GC [18]. Other approaches for $MeHg^+$ use CO_2 [129] or methanol modified CO_2 [130] instead of a derivatization agent.

5.2. Pressurized liquid extraction

Few automated extraction systems are currently available for efficiently processing organic and organometallic compounds in solid matrices. Several versions of automated Soxhlet extractors are offered, but all have limited capacity, long extraction times, and require large solvent volumes. Supercritical fluid extractors have intended to overcome these problems, but present the drawbacks outlined in the previous section: matrix dependence of the extraction, time-consuming and incomplete recovery for polar organometallic species. PLE now constitutes an emerging and promising alternative based on the use of organic solvents at high temperatures under pressure. Extraction time for PLE averages 11 min per soil samples. PLE has been studied for organic compound extraction but only a few papers focus on metal speciation, considering the extraction of organotin compounds from sediments [127,128]. The extraction of organotin compounds in sediments can be achieved by treating 2.5 g of freeze–dried sample with 1 *M* sodium acetate and 1 *M* acetic acid in MeOH. The extraction cells filled with solvent have to be heated within 5 min to 100°C, using three to five static cycles of 5 min. Between each static extraction cycle, 4 ml of solvent is renewed. The recovery average is ca. 99%.

PLE has also been used for the extraction of organoarsenic species from ribbon kelp [131], using a 3 ml cell, MeOH–water (30:70, w/w) mixture at a pressure of 3500 KPa. The extraction program had three cycles, and each one included a 1-min heat step, a 1-min static step, a 90% volume flush and a 120 s purge. A total of three cycles were performed. Analyses are performed by ion chromatography–electrospray ionization-tandem mass spectrometry (IC–ESI-MS–MS). The extraction efficiencies were close to 73%.

5.3. Solid-phase extraction

The use of liquid–solid extraction in organometallic preconcentration presents undoubted advantages,

especially when the solid phase is housed in cartridges or disks that make possible its integration into online flow analysis systems. In addition, SPE has other advantages: (i) it requires less volume of solvent than traditional liquid–liquid extraction, (ii) it involves simple manipulations which are not time-consuming and makes possible in field treatment of samples, (iii) the cartridges can be used for storage of the species, and (iv) it provides high enhancement factors if great volume of water is passed through the cartridge without breakthrough.

Cationic organometallic species can be preconcentrated on reversed-phase columns or cartridges. Adsorption of methyl- butyl- or phenyltin compounds present in water samples can be achieved in a silica-gel C_{18} disposable column [132], and the species eluted later with a tetrahydrofuran–acetic acid mixture containing 0.5% (w/v) tropolone. This method pre-concentrates organotin species with a concentration factor of 1000 (1 l to 1 ml), and the time required for water sample extraction is about 100 min. With simultaneous extractions, more than 20 samples could be analyzed in a day. Organotin SPE can also be developed in other shaped housings, disks and cartridges with different types of solid phases: Carbopack, C_{18}, C_8, C_2. The eluents employed are acid ethyl acetate, methanol, 1% (v/v) HBr solution in methanol, and 1.0% (v/v) HBr and 0.1% (w/v) tropolone solution in methanol. With a C_{18} column or disks only TBT and TPT are eluted, presenting SPE discs advantages over SPE columns [133] due to the remarkable reduction of the background signal of the GC–electron-capture detection chromatograms. Selective separation of the organotins from the C_{18} cartridge can be achieved by successive elution with solvents of different strength [134]: methanol for TBT and TPT, 0.4% (v/v) HBr solution in methanol for DBT and DPT, and 0.4% (v/v) HBr and 0.1% (w/v) tropolone solution in methanol for MBT and MPT.

Anionic organometallic species can be preconcentrated on anionic cartridges which also avoid their interference and signal overlapping with cationic species in complex mixtures analyzed by online hyphenated instrumental systems. This is the case of overlapping peaks of As(III) and AsB in the determination of As(III), As(V), MMA, DMA, AsB and AsCh by HPLC–atomic detection that can be prevented placing an anionic cartridge before of the HPLC column [135,136]. Yalcin and Le [137] have studied the use of both anion-exchange and reversed-phase cartridges to separate As(III) and As(V) from water with a very low time of operation, 1.5 min, and detection limits of 0.2 and 0.4 ng ml^{-1}, respectively, using hydride generation and atomic absorption or atomic fluorescence spectroscopy (HG-AAS or HG-AFS).

Simultaneous preconcentration of inorganic and volatile organic selenium species is a more difficult task, but an SPE procedure has been proposed [138] based on the use of two different sorbent phases, octadecyl (C_{18}) and quaternary ammonium (strong anion-exchange, SAX), in separate cartridges stacked together for the simultaneous preconcentration of Se(IV), Se(VI), dimethylselenium (DMSe), dimethyldiselenium (DMDSe), diethylselenium (DESe) and diethyl diselenide (DEDSe) in water. Both cartridges have to be conditioned before the separation, the SAX cartridge is stacked on top of the C_{18} cartridge and 1000 ml of water (at pH 7–8) is passed through at 8 ml min^{-1}. The cartridges are then separated. Inorganic selenium species are eluted from the SAX cartridge: Se(IV) with formic acid and Se(VI) with hydrochloric acid. The C_{18} cartridge is dried under a stream of nitrogen and the organic selenium species are eluted with CS_2.

The preconcentration of Hg species ($MeHg^+$, $PhHg^+$ and Hg^{2+}) with SPE requires the use of some reagents, so the Hg species can be retained in the solid surface, such as sulfydryl cotton microcolumn [139], crown-ethers [140] and chelating agents such as ditizone [141], carbamates (ammonium 1-pyrrolidine carbodithioc acid (APDC), DDC) [142] or 2-mercaptoethanol [143].

5.4. Microwave-assisted extraction

The efficiency of MAE for sample preparation in environmental applications has been proved for different solid matrices (e.g., soils, sediments, and biological tissues) and constitutes an appropriate tool for a rapid treatment of solid samples in organometallic speciation analysis [144]. Essential parameters, such as the extraction medium, power applied and exposure time have to be optimized [59]. This approach has been successfully adapted to organotin

[14,58,145], organomercury [146,147] and organoarsenic [148] compounds speciation. MAE is considerably faster than other sample preparation and extraction procedures, a typical sample treatment can take only 3 min.

The more important drawback of MAE is that analytes in the polar leachate have to be later derivatized and transferred to a non-polar solvent to produce a solution suitable for GC analysis, which increases the number of steps in the analytical procedure. This obstacle can be eliminated by integrating sample preparation for speciation analysis in only one step: (i) combining leaching, derivatization and liquid–liquid solvent extraction to directly produce a solution of the analytes to be analyzed by GC (microwave-assisted derivatization solvent extraction, MADSE); and (ii) integrating leaching, derivatization and liquid–gas extraction (purge), this constitutes an alternative for more volatile derivatives, which can be recovered in a cryotrapping device to avoid losses (microwave-assisted purge-and-trap, MAPT).

MAE has been used to perform the extraction of tin [149,150], mercury [146,147,151,152,172] and arsenic species [148] from biological material (fish, mussels, tuna tissues, urine), soils and sediments, under the extraction conditions described in Table 2. Simultaneous extraction of organotins and mercury species present in sediments and biological tissues can be rapid and simple achieved following a protocol also based in an open focused microwave system [153]. More frequently the approach is applied for two-step (leaching plus derivatization/extraction) or one-step (MADSE) biological sample complete treatment [154]. For organotin speciation in sediments [14] leaching is performed with acetic acid in 3 min followed by extraction/derivatization (ethylation) in 5 min, the extract can be analyzed by capillary GC with MIP detection, which limited the sample throughput due to the duration of the GC run (10 min), although this drawback can be overcome using the faster multicapillary gas chromatography [155] (3 min per chromatographic run). This approach can also be used for HPLC organotin analysis [156] with microwave-assisted leaching of the species from sediments with acetic acid (during 3 min) in the presence of sodium 1-pentanesulfonate as ion pair agent, for later direct injection into the HPLC system.

5.5. Solid-phase microextraction

This experimental approach constitutes a good choice for fast organometallic species pretreatment on the basis of simultaneous aqueous ethylation ($NaBEt_4$) and SPME prior to analysis by GC. Therefore, microextraction has been applied to metal speciation for organotin, -mercury and -lead compounds [157–162], this topic has been recently reviewed in detail by Mester et al. [21]. On the other hand, the use of SPME technique in combination with multielemental detection hyphenated techniques such as GC–ICP-MS makes possible the simultaneous speciation of mercury, tin, and lead organometallic compounds in aqueous samples by sorption of ethylated derivatives on a poly(dimethylsiloxane)-coated fused-silica fiber [163]. Ethylation–SPME has also been used for the speciation of mercury [164],

Table 2
Microwave-assisted extraction (MAE) conditions for organometallic species

Species	Extraction conditions	Ref.
Organotin, $MeHg^+$	TMAH or KOH in MeOH, 40–60 W, 2–4 min	[147,149–151]
Organotin	0.5 *M* HOAc in MeOH, 70 W, 3 min	[171]
Butyltin	HOAc–water (1:1), 60 W, 3 min	[173]
Butyltin	25% TMAH, 60 W, 3 min	[173]
$MeHg^+$	1% $NaPhB_4$+17 *M* HOAc+toluene, 100°C, 690 kPa, 6 min	[174]
$MeHg^+$	2 *M* HNO_3, 40–60 W, 2–4 min	[146]
$MeHg^+$	6 *M* HCl, toluene, 120°C, 950 W, 10 min	[161]
Organoarsenic	Methanol, 10 min, 150 W	[175]
Organoarsenic	Methanol–water (1:1), 50 W, 5 min	[148]

alkylated Hg, Pb, and Sn species [165] in urine using GC–MS for analysis. Limits of detection (DLs) are improved with the second procedure due to the use of the ion-trap GC–MS–MS that makes possible DLs between 7 and 22 ng l^{-1} for all the species studied. An alternative alkylation procedure based on methylation of mercury species with methylpentacyanocobaltate(III) or methyl-bis(dimethylglioximato)pyridinecobalt(III) can also be used for SPME of this element from water and water–soil slurries [166].

Organoarsenic compounds can be determined in waters by SPME after dithio derivatization to form stable five-membered ring structures, calibration curves are linear over three orders of magnitude and limits of detection are less than $6 \cdot 10^{-9}$ *M*, which represent an improvement over 400-fold compared to conventional solvent extraction [167]. Triphenylarsine and triethylarsine can be determined in water by SPME using poly(dimethylsiloxane)-modified fused-silica fibers [168]. Finally, direct extraction of monomethylarsonic acid in dimethylarsinic acid has been performed by SPME after thioglycol methylated derivatization, and method has been applied to human urine samples using GC–MS for analysis [169].

5.6. Fully automated systems for speciation

Manual handling of samples for organometallic speciation leads to long analysis time, low efficiency, poor reproducibility, multiplication of analytical errors and changes in the conditions of the analysis. Automation of the hyphenation should be the innovating approach to overcome problems arising from manual operation. The resulting computer-assisted hyphenated technique for automatic on-line routine analysis should be, however, fully optimized to satisfy the demand of environmental analysis in terms of simplicity, reproducibility, accuracy, sample throughput and economic cost [13]. Tseng et al. [15] have proposed a fully automated online hyphenated system for Hg speciation in environmental samples, both solid (sediments, biotissues, and suspended matter) and liquid (sea, and fresh water) samples. The samples are derivatized by hydride generation or ethylation, preconcentrated by cryotrapping and determined by GC–quartz furnace (QF)-AAS. Automation of the hyphenation results in improved reproducibility of the analysis. Although the system was specifically optimized for the analysis of mercury compounds, it is also potentially operative for other hydride or ethylated derivative forming elements. Detection limits of the method are of 0.5, 3, 0.1 ng l^{-1} for both mercury species in dry sediments, biological tissues and aqueous samples, respectively. A sample throughout of 6 or 3 samples h^{-1} is achieved for hydride generation and ethylation, respectively. Metal ions or any other inorganic compounds from sediments and large organic molecules from biological tissues may interfere in the detection step. Sodium chloride or other minor components in sea-water samples also strongly affect the sensitivity, reproducibility and selectivity of the analysis. The presence of metal ions strongly decreases the sensitivity in the determination of both Hg^{2+} and $MeHg^{+}$ hydride generation, but has no effect if ethylation is used as derivatization technique [170]. EDTA partially eliminates the interfering effect of metals in the determination of $MeHg^{+}$ by hydride generation and avoid the decomposition of $MeHg^{+}$ to HgO, promoted by NaCl.

6. Conclusions

The use of FEMs versus the classical liquid–liquid extraction represents an improvement for sample treatment, on the basis of time reduction, sample and reagents consumption and reduction of the steps involved in the procedure. Efforts have been made in recent years to apply FEMs for speciation of organometallic compounds (Sn, As, Se, Hg, Pb), with positive or promising results. However, some drawbacks should be considered, as the potential instability of species under extreme conditions (e.g., temperature, and/or pressure) used during the extraction, the difficult extraction of polar or charged species in SFE, the hazards derived of high energy sources on flammable solvents, such as MAE, and the critical performance of SPME. Therefore, further work will have to be undertaken to overcome these problems

and to cover the wide range of possible sample matrices usually found in the environment.

Acknowledgements

The authors thank the DGICYT (Dirección General de Investigación Científica y Técnica) for financial support under grant No. PB98-0947-C02-01.

References

[1] E. Nieboer, Y. Thomassen, Analyst 120 (1995) 583.
[2] P.J. Craig, Organometallic Compounds in the Environment – Principles and Reactions, Longman, Essex, 1986.
[3] O.F.X. Donard, P. Michel, Analusis 20 (1992) M45.
[4] R. Lobinski, Appl. Spectrosc. 51 (1997) 260A.
[5] M. Berlin, in: L. Friberg, G.F. Norberg, V.B. Vouk (Eds.), Handbook on the Toxicology of Metals, Vol. II, Elsevier, Amsterdam, 1986, p. 387.
[6] FAO–WHO, Technical Report Series, No. 505, 1972.
[7] T. Kjellström, P. Kennedy, S. Wallis, C. Mantell, Nat. Swedish Environ. Protect. Board, (Report) PM 3642, 1989.
[8] O.F.X. Donard, R. Ritsema, in: D. Barceló (Ed.), Environmental Analysis (Techniques, Application and Quality Assurance), 2nd ed., Elsevier, Amsterdam, 1993, p. 549.
[9] M. Ceulemans, F.C. Adams, J. Anal. Atom. Spectrom. 11 (1996) 201.
[10] Ph. Quevauviller, E.A. Maier, in: European Comisión Report, Report 16000 EN, 1994, p. 57.
[11] Ph. Quevauviller, O.X.F. Donard, E.A. Maier, B. Griepink, Mikrochim. Acta 169 (1992) 109.
[12] R. Lobinski, I.R. Pereiro, H. Chassaigne, A. Wasik, J. Szpunar, J. Anal. Atom. Spectrom. 13 (1998) 859.
[13] A. de Diego, C. Pecheyran, C.M. Tseng, O.F.X. Donard, in: A. Sanz Medel (Ed.), Flow Analysis with Atomic Spectrometric Detectors, Elsevier, Amsterdam, 1999.
[14] J. Szpunar, V.O. Schmitt, R. Lobinski, J.L. Monod, J. Anal. Atom. Spectrom. 11 (1996) 193.
[15] C.M. Tseng, A. de Diego, H. Pinnaly, D. Amouroux, O.F.X. Donard, J. Anal. Atom. Spectrom. 13 (1998) 755.
[16] M. Abalos, J.M. Bayona, R. Compañó, M. Granados, C. Leal, M.D. Prat, J. Chromatogr. A 788 (1997) 1.
[17] C. Gerbersmann, M. Hesiterkemp, F.C. Adms, J. Broekaert, Anal. Chim. Acta 350 (1997) 273.
[18] H. Emteborg, E. Björklund, F. Ödman, L. Karsson, L. Mathiasson, W. Frexh, D.C. Baxter, Analyst 121 (1996) 19.
[19] J.M. Bayona, Trends Anal. Chem. 19 (2000) 107.
[20] M.J. Vázquez, A.M. Carro, R.A. Lorenzo, R. Cela, Anal. Chem. 69 (1997) 221.
[21] Z. Mester, R. Sturgeon, J. Pawliszyn, Spectrochim. Acta Part B 56 (2001) 233.
[22] Y.K. Chau, P.T.S. Wong, G.A. Bengert, Anal. Chem. 54 (1982) 246.
[23] Y.K. Chau, F. Yang, R.J. Maguire, Anal. Chim. Acta 320 (1996) 165.
[24] M.D. Müller, Anal. Chem. 59 (1987) 617.
[25] R.J. Maguire, H. Huneault, J. Chromatogr. 209 (1981) 458.
[26] M. Abalos, J.M. Bayona, Ph. Quevauviller, Appl. Organomet. Chem. 12 (1998) 541.
[27] T. Tsuda, H. Nakanishi, T. Morita, J. Takebayashi, J. Assoc. Off. Anal. Chem. 69 (1986) 981.
[28] M.D. Muller, Fresenius J. Anal. Chem. 317 (1986) 32.
[29] Y. Hattori, A. Kobayashi, S. Takemoto, K. Takami, Y. Kuge, A. Sigimae, M. Nakamoto, J. Chromatogr. 315 (1984) 341.
[30] J.R. Ashby, P.J. Craig, Sci. Total Environ. 78 (1989) 219.
[31] I. Tolosa, J.M. Bayona, J. Albaigés, L.F. Alencastro, J. Tarradellas, Fresenius J. Anal. Chem. 339 (1991) 646.
[32] M. Astruc, R. Levigne, V. Desauziers, A. Astruc, R. Pinel, O.F.X. Donard, in: Proc. Int. Conf. Heavy Metals in the Hydrocycle, Lisbon, September 6–8, 1988, p. 447.
[33] Ph. Quevauviller, O.X.F. Donard, Fresenius J. Anal. Chem. 339 (1991) 6.
[34] Ph. Quevauviller, O.X.F. Donard, Appl. Organomet. Chem. 4 (1990) 353.
[35] J.L. Gómez-Ariza, E. Morales, R. Beltran, I. Giraldez, M. Ruiz-Benitez, Analyst 120 (1995) 1171.
[36] H.A. Meinema, T. Burger-Wiersma, G. Versluis-de Haan, E.C. Gevers, Environ. Sci. Technol. 12 (1978) 288.
[37] I. Martin-Landa, F. Pablos, I.L. Marr, Appl. Organomet. Chem. 5 (1991) 399.
[38] J.L. Gómez-Ariza, M. Morales, M. Ruiz-Benitez, Analyst 117 (1992) 641.
[39] J.L. Gómez-Ariza, M. Morales, M. Ruiz-Benitez, Appl. Organomet. Chem. 6 (1992) 279.
[40] J.L. Gómez-Ariza, E. Morales, I. Giraldez, R. Beltran, Int. J. Environ. Anal. Chem. 66 (1997) 1.
[41] J.L. Gómez-Ariza, E. Morales, I. Giraldez, R. Beltran, J.A. Pozas-Escobar, Fresenius J. Anal. Chem. 357 (1997) 1007.
[42] G. Bressa, F. Cima, P. Fonti, E. Sisti, Fresenius Environ. Bull. 6 (1997) 16.
[43] Y.K. Chau, F. Yang, Appl. Organomet. Chem. 11 (1997) 851.
[44] P. Bermejo-Barrera, M. Tubio-Franco, J.M. Aguiar-Paz, R.N. Soto-Ferreiro, A. Bermejo-Barrera, Microchem. J. 53 (1996) 395.
[45] R. Francois, J.H. Weber, Mar. Chem. 25 (1988) 279.
[46] S. Rapsomanikis, R.M. Harrison, Appl. Organomet. Chem. 2 (1988) 151.
[47] L. Randall, J.S. Han, J.H. Weber, Environ. Technol. Lett. 7 (1986) 571.
[48] S. Shawky, H. Emons, H.W. Dürbeck, Anal. Commun. 33 (1996) 107.
[49] V. Dezauziers, F. Leguille, R. Lavigne, M. Astruc, R. Pinel, Appl. Organomet. Chem. 3 (1989) 469.
[50] L.S. Krull, K.W. Panaro, J. Noonam, D. Erickson, Appl. Organomet. Chem. 3 (1989) 295.

[51] F. Pannier, A. Astruc, M. Astruc, Appl. Organomet. Chem. 8 (1994) 595.
[52] K. Sasaki, T. Ishizaka, T. Siziki, Y. Saito, J. Assoc. Off. Anal. Chem. 71 (1988) 360.
[53] C.L. Matthias, S.J. Bushong, L.W. Hall, J.M. Bellama, F.E. Brickman, Appl. Organomet. Chem. 2 (1988) 547.
[54] Y. Cai, S. Rapsomanikis, M.O. Andreae, Talanta 41 (1994) 589.
[55] Y. Cai, S. Rapsomanikis, M.O. Andreae, J. Anal. Atom. Spectrom. 8 (1993) 119.
[56] Y. Cai, S. Rapsomanikis, M.O. Andreae, Anal. Chim. Acta 274 (1993) 243.
[57] Y. Cai, S. Rapsomanikis, M.O. Andreae, Mikrochim. Acta 109 (1992) 67.
[58] O.F.X. Donard, B. Lalère, F. Martin, R. Lobinski, Anal. Chem. 67 (1995) 4250.
[59] B. Lalère, J. Szpunar, H. Budzinski, Ph. Garrigues, O.F.X. Donard, Analyst 120 (1995) 2665.
[60] Ph. Quevauviller, S. Chiavarini, C. Cremisini, R. Morabito, M. Bianchi, H. Muntau, Mikrochim. Acta 120 (1995) 281.
[61] D. Milde, Z. Plzak, M. Suchanek, Collect. Czech. Chem. Commun. 62 (1997) 1403.
[62] C. Rivas, L. Ebdon, E.H. Evans, S.J. Hill, Appl. Organomet. Chem. 10 (1996) 61.
[63] M. Heisterkamp, T. De Smaele, J.P. Candelone, L. Noens, R. Dams, F.C. Adams, J. Anal. Atom. Spectrom. 12 (1997) 1077.
[64] S.A. Estes, P.C. Uden, R. Barnes, Anal. Chem. 53 (1981) 1336.
[65] D. Chakraborti, W.R.A. De Jonghe, W.E. Van Mol, R.J.A. Van Cleuvenbergen, F.C. Adams, Anal. Chem. 56 (1984) 2692.
[66] G. Westöö, Acta Chem. Scand. 20 (1967) 1790;
G. Westöö, Acta Chem. Scand. 22 (1968) 2277.
[67] K. May, M. Stoeppler, K. Reisinger, Toxicol. Environ. Chem. 13 (1987) 153.
[68] M. Hempel, H. Hintelmann, R.D. Wilken, Analyst 117 (1992) 669.
[69] H. Hintelmann, R.D. Wilken, Appl. Organomet. Chem. 7 (1993) 173.
[70] Ph. Quevauviller, O.F.X. Donard, J.C. Wasserman, F.M. Martin, J. Schenider, Appl. Organomet. Chem. 6 (1992) 221.
[71] Y. Cai, G. Tang, R. Jaffe, R. Jones, Int. J. Environ. Anal. Chem. 68 (1998) 331.
[72] Z. Huang, Fenxi Ceshi Xuebao 17 (1998) 22.
[73] N.S. Bloom, Can. J. Fish. Aquat. Sci. 46 (1989) 1131.
[74] L. Liang, M. Horvat, E. Cernichiari, B. Gelein, S. Balogh, Talanta 1996 (1883) 43.
[75] M. Horvat, N.S. Bloom, L. Liang, Anal. Chim. Acta 281 (1993) 135.
[76] Y.H. Lee, J. Munthe, A. Iverfeldt, Appl. Organomet. Chem. 8 (1994) 659.
[77] M. Horvat, V. Mandic, L. Liang, N.S. Bloom, S. Padberg, L.H. Lee, H. Hintelmann, J. Benoit, Appl. Organomet. Chem. 8 (1994) 533.
[78] M. Floyd, L.E. Sommer, Anal. Lett. 8 (1975) 525.
[79] M. Horvat, K. May, M. Stoeppler, A.R. Byrne, Appl. Organomet. Chem. 2 (1988) 515.
[80] C.J. Cappon, J.C. Smith, Anal. Chem. 49 (1977) 365.
[81] R. Cela, R.A. Lorenzo, M.C. Mejuto, M.H. Bollain, M.C. Casais, A. Botana, E. Rubi, M.L. Medina, Mikrochim. Acta 109 (1992) 111.
[82] M.H. Arbab-Zavar, Ph.D. Thesis, University of Southampton, 1982.
[83] W. Fitchett, E.H. Daughtrey, P. Mushak, Anal. Chim. Acta 79 (1975) 93.
[84] A. Yatsui, C. Tsutsumi, S. Toda, Agric. Biol. Chem. 42 (1978) 2139.
[85] A. Shinagawa, K. Shiomi, H. Yamanaka, T. Kikuchi, Bull. Jpn. Soc. Sci. Fish. 49 (1983) 75.
[86] E.A. Crescelius, N.S. Bloom, C.E. Cowan, E.A. Jenne, in: Arsenic Speciation, Vol. 2, EPRI, Batelle Northwest Laboratories, Washington, DC, 1986, p. 18.
[87] J. Dedina, D.L. Tsalev, in: J.D. Winefordner (Ed.), Hydride Generation Atomic Absorption Spectrometry, Wiley, Chichester, 1995, p. 213.
[88] B. Amran, F. Lagarde, M.J.F. Leroy, A. Lamotte, C. Desmeney, M. Ollé, M. Albert, G. Rauret, J.F. Lopez-Sanchez, in: Ph. Quevauviller, E.A. Mayer, B. Griepink (Eds.), Quality Assurance for Environmental Analysis, Vol. 17, Elsevier, Amsterdam, 1995, p. 285.
[89] W. Maher, E. Butler, Appl. Organomet. Chem. 2 (1988) 191.
[90] J.L. Gómez-Ariza, D. Sánchez-Rodas, I. Giráldez, J. Anal. Atom. Spectrom. 13 (1998) 1375.
[91] D. Madsen, W. Goessler, S.N. Pedersen, K.A. Francesconi, J. Anal. Atom. Spectrom. 15 (2000) 657.
[92] J.L. Gómez-Ariza, D. Sánchez-Rodas, I. Giráldez, E. Morales, Talanta 51 (2000) 257.
[93] J.L. Gómez-Ariza, D. Sánchez-Rodas, I. Giráldez, E. Morales, Analyst 125 (2000) 401.
[94] G. Raber, K.A. Francesconi, K.J. Irgolic, W. Goessler, Fresenius J. Anal. Chem. 367 (2000) 181.
[95] M. Dodd, S.A. Pergantis, W.R. Cullen, H. Li, G.R. Eigendorf, K.J. Reimer, J. Anal. Atom. Spectrom. 121 (1996) 223.
[96] R. Muñoz-Olivas, O.F.X. Donard, N. Gilon, M. Potin-Gautier, J. Anal. Atom. Spectrom. 11 (1996) 1171.
[97] J.L. Martin, M.L. Gerlach, Anal. Biochem. 29 (1969) 257.
[98] M. Potin-Gautier, C. Boucharat, A. Astruc, M. Astruc, Appl. Organomet. Chem. 7 (1993) 593.
[99] H. Emteborg, G. Bordin, A.R. Rodriguez, Analyst 123 (1998) 245.
[100] J. Alberti, R. Rubio, G. Rauret, Fresenius J. Anal. Chem. 351 (1995) 420.
[101] V.G. Torgov, M.G. Demidova, A.D. Kosolapov, J. Anal. Chem. 53 (1998) 846.
[102] A.J. Aller, C. Robles, J. Anal. Atom. Spectrom. 13 (1998) 469.
[103] M.M. Gómez, T. Gasparic, M.A. Palacios, C. Camara, Anal. Chim. Acta 374 (1998) 241.
[104] S. Zhang, Y.K. Chau, W.C. Li, A.S.Y. Chau, Appl. Organomet. Chem. 5 (1991) 431.
[105] J. Kuballa, R.D. Wilken, E. Jantzen, K.K. Kwan, Y.K. Chau, Analyst 120, 667.
[106] M. Ceulemans, C. Witte, R. Lobinski, F.C. Adams, Appl. Organomet. Chem. 8 (1994) 451.

[107] M. Nagase, K. Hasebe, Anal. Sci. 9 (1993) 517.
[108] M. Nagase, H. Kondo, K. Hasebe, Analyst 1995 (1923) 120.
[109] J.A. Stäb, U.A.Th. Brinkman, W.P. Cofino, Appl. Organomet. Chem. 8 (1994) 577.
[110] L.N. Mackey, T.A. Beck, J. Chromatogr. 240 (1982) 455.
[111] F. Pannier, A. Astruc, M. Astruc, Anal. Chim. Acta 327 (1996) 287.
[112] D.S. Forsyth, R. Iyengar, J. Organomet. Chem. 3 (1998) 211.
[113] N. Gilon, A. Astruc, M. Astruc, M. Potin-Gautier, Appl. Organomet. Chem. 9 (1995) 633.
[114] D.S. Forsyth, C. Clerous, Talanta 38 (1991) 951.
[115] Y. Tan, W.D. Marshall, Analyst 122 (1997) 13.
[116] S.L. Cleland, L.K. Olson, J.A. Caruso, J.M. Carey, J. Anal. Atom. Spectrom. 9 (1994) 975.
[117] K. Li, S.F.Y. Li, J. Chromatogr. Sci. 33 (1995) 309.
[118] J.W. Oudsema, C.F. Poole, Fresenius J. Anal. Chem. 344 (1992) 426.
[119] R. Alzaga, J.M. Bayona, J. Chromatogr. A 655 (1993) 5.
[120] J. Dachs, R. Alzaga, J.M. Bayona, P. Quevauviller, Anal. Chim. Acta 286 (1994) 319.
[121] Y. Liu, V. Lopez-Avila, M. Alcaraz, W.F. Beckert, J. High Resolut. Chromatogr. 16 (1993) 106.
[122] Y. Liu, V. Lopez-Avila, M. Alcaraz, W.F. Beckert, Anal. Chem. 66 (1994) 3788.
[123] U. Kumar, N.P. Vela, J.G. Dorsey, J.A. Caruso, J. Chromatogr. A 655 (1993) 340.
[124] J.M. Bayona, Y. Cai, Trends Anal. Chem. 13 (1994) 327.
[125] N.P. Vela, J.A. Caruso, J. Anal. Atom. Spectrom. 11 (1996) 1129.
[126] Y.K. Chau, F. Yang, M. Brown, Anal. Chim. Acta 304 (1995) 85.
[127] C.G. Arnold, M. Berg, S.R. Mueller, U. Dommann, R.P. Schwarzenbach, Anal. Chem. 70 (1998) 309.
[128] C. Maldonado, R. Alzaga, P. Bou, J.M. Bayona, presented at the 8th Symposium of Environmental and Biological Samples in Chromatography, Almeria, October 1997.
[129] C.M. Wai, Y. Lin, R. Brauer, S. Wang, W.F. Beckert, Talanta 40 (1993) 1325.
[130] M. Ashraf-Khorassani, L.T. Taylor, Anal. Chim. Acta (1999) 379.
[131] P.A. Gallagher, J.A. Shoemaker, X. Wei, C.A. Brockhoff-Schwegel, J.T. Creed, Fresenius J. Anal. Chem. 369 (2001) 71.
[132] K. Kadokami, T. Uehiro, M. Morita, K. Fuwa, J. Anal. Atom. Spectrom. 3 (1998) 1887.
[133] O. Evans, B.J. Jacobs, A.L. Cohen, Analyst 116 (1991) 15.
[134] J.L. Gómez-Ariza, R. Beltran, E. Morales, I. Giráldez, M. Ruiz-Benitez, Appl. Organomet. Chem. 8 (1994) 553.
[135] A. Lopez, M. Gomez, C. Camara, M.A. Palacios, J. Anal. Atom. Spectrom. 9 (1994) 291.
[136] M. Gómez, C. Cámara, M.A. Palacios, A. Lopez-Gonzálvez, Fresenius J. Anal. Chem. 357 (1997) 844.
[137] S. Yalcin, C. Le, Talanta 47 (1998) 787.
[138] J.L. Gómez-Ariza, J.A. Pozas, I. Giraldez, E. Morales, Analyst 124 (1999) 75.
[139] M.L. Mena, C.W. McLeod, P. Jones, A. Withers, V. Minganti, R. Capelli, Ph. Quevauviller, Fresenius J. Anal. Chem. 351 (1995) 456.
[140] Y. Yamini, N. Alizadeh, M. Shamsipur, Anal. Chim. Acta 355 (1997) 69.
[141] D.M. Sánchez, R. Martín, R. Morante, J. Marín, M.L. Munuera, Talanta 52 (2000) 671.
[142] M. Fernández, R. Pereiro, N. Bordel, A. Sanz-Medel, Talanta 41 (1994) 1833.
[143] B. Aizpun, M.L. Fernández, E. Blanco, A. Sanz-Medel, J. Anal. Atom. Spectrom. 9 (1994) 1279.
[144] O.X.F. Donard, B. Lalère, F. Martin, R. Lobinski, Anal. Chem. 67 (1995) 4250.
[145] I.R. Pereiro, V. Schmitt, J. Szpunar, O. Dinard, R. Lobinski, Anal. Chem. 68 (1996) 4135.
[146] C.M. Tseng, A. de Diego, F.M. Martin, O.X.F. Donard, J. Anal. Atom. Spectrom. 12 (1997) 629.
[147] C. Gebersmann, M. Heisterkamp, F.C. Adams, J.A.C. Broekaert, Anal. Chim. Acta 350 (1997) 273.
[148] T. Dagnac, A. Padro, R. Rubio, G. Rauret, Talanta 48 (1999) 763.
[149] I. Rodriguez, M. Santamaria, M.H. Bollain, M.C. Mejuto, R. Cela, J. Chromatogr. A 774 (1997) 379.
[150] I. Rodriguez, M. Santamaria, M.H. Bollain, M.C. Mejuto, R. Cela, Spectroscopy 13 (1997) 51.
[151] C.M. Tseng, A. De Diego, F.M. Martin, D. Amouroux, O.F.X. Donard, J. Anal. Atom. Spectrom. 12 (1997) 743.
[152] I.R. Pereiro, A. Wasik, R. Lobinski, Anal. Chem. 70 (1998) 4063.
[153] V.O. Schmith, A. De Diego, A. Cosnier, C.M. Tseng, J. Moreau, O.F.X. Donard, Spectroscopy 13 (1997) 99.
[154] V.O. Schmitt, J. Szpunar, O.F.X. Donard, R. Lobinski, Can. J. Anal. Sci. Spectrosc. 42 (1997) 41.
[155] I.R. Pereiro, A. Wasik, R. Lobinski, Fresenius J. Anal. Chem. 363 (1999) 460.
[156] W.S. Chao, S.J. Jiang, J. Anal. Atom. Spectrom. 13 (1998) 1337.
[157] Y. Morcillo, Y. Cai, J.M. Bayona, J. High Resolut. Chromatogr. 18 (1995) 767.
[158] Y. Cai, J.M. Bayona, J. Chromatogr. A 696 (1995) 113.
[159] S. Tutschku, S. Mothes, R. Wennerich, Fresenius J. Anal. Chem. 354 (1996) 587.
[160] J. Poerschmann, F.D. Kopinke, J. Pawliszyn, Environ. Sci. Technol. 31 (1997) 3629.
[161] M. Guidotti, M. Vitali, Ann. Chim. 87 (1997) 497.
[162] G. Lespes, V. Desauziers, C. Montigny, M. Potin-Gautier, J. Chromatogr. A 826 (1998) 67.
[163] L. Moens, T. De Smaele, R. Dams, P. Van Den Broeck, P. Sandra, Anal. Chem. 69 (1997) 1604.
[164] M. Guidotti, M. Vitali, J. High Resolut. Chromatogr. 21 (1998) 665.
[165] L. Dunemann, H. Hajimiragha, J. Begerow, Fresenius J. Anal. Chem. 363 (1999) 466.
[166] C.M. Barshick, S.A. Barashick, Ph.-F. Britt, A.D. Lake, Int. J. Mass. Spectrom. 178 (1998) 31.
[167] B. Szostek, J.H. Aldstadt, J. Chromatogr. A 807 (1998) 253.

[168] S. Mothes, R. Wennrich, Am. Environ. Lab. 9 (1997) 5.
[169] Z. Mester, J. Pawliszyn, J. Chromatogr. A 873 (2000) 129.
[170] A. de Diego, C.M. Tseng, T. Stoichev, D. Amouroux, O.F.X. Donard, J. Anal. Atom. Spectrom. 13 (1998) 623.
[171] O.F.X. Donard, B. Lalere, F. Martin, R. Lobisnki, Anal. Chem. 76 (1995) 4250.
[172] M.J. Vázquez, A.M. Carro, R.A. Lorenzo, R. Cela, Anal. Chem. 69 (1997) 221.
[173] J. Szpunar, V.O. Schmitt, R. Lobinski, J. Anal. Atom. Spectrom. 11 (1996) 193.
[174] M. Abuín, A.M. Carro, R.A. Lorenzo, J. Chromatogr. A 889 (2000) 185.
[175] J.L. Gómez-Ariza, D. Sánchez-Rodas, I. Giráldez, E. Morales, Analyst 125 (2000) 401.