Trace Element Determination by Combining Solid-Phase Microextraction Hyphenated to Elemental and Molecular Detection Techniques

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Abstract

The state of the art of analytical procedures based on solid-phase microextraction (SPME) and its applications to tin, mercury, arsenic, antimony, chromium, selenium, and lead determination in abiotic and biotic matrixes are critically reviewed from 1994 to present. First, sample pretreatment prior to SPME is evaluated, including a description of the most usual leaching procedures for sediment, soil, and biological samples. Because most organometallic species lack volatility, a derivatization step is mandatory prior to gas chromatographic (GC) determination, except for the volatile organometallics that can be directly extracted from the sample headspace or liquid phase by SPME. The most common derivatization procedures used in alkylation and hydridization reactions used for mercury, lead, and tin, as well as other procedures for the determination of total chromium and arsenic [i.e., trifluoroacetylacetonates for chromium (III) and thioglycol methylate for organic arsenic species] are reviewed. Critical variables usually evaluated along with the method development to improve the sensitivity of the extraction methods based on SPME, such as sampling size, stirring procedures, sampling temperature and pressure, polymer coating, and thermal desorption are reviewed. In addition, figures of merit of the different detection systems used in SPME combined with GC are evaluated. The validation of the reported analytical procedures with reference materials are also discussed in terms of precision and accuracy. Finally, future developments in the application of SPME to speciation are highlighted. Moreover, the capability of SPME automation for the derivatization–extraction procedures are also presented.

Introduction

Sample handling and, more specifically, analyte extraction are topics of continuous development in trace analysis. Sample size miniaturization, hazardous solvent elimination, and minimization of the number of steps are the most significant trends. In this regard, solid-phase microextraction (SPME), developed by Pawliszyn et al. (1,2), is one of the extraction procedures that meets with the described requirements, and a large number of applications have been developed, including trace element speciation. Additional SPME advantages, such as (*i*) nonexhaustive extraction technique, (*ii*) low cost, (*iii*) solventless, and (*iv*) the full automation of the entire process, cannot be neglected. A large number of applications in many fields (i.e., environmental, foods, pharmaceuticals, flavors, fragrances, and forensics) have been developed using this technique. They were primarily focused on organic trace analysis. Moreover, its application to trace element speciation has been one of the areas of fast development since mid 1990s (3,4). Most of the reported analytical procedures based on SPME in trace element speciation involve a derivatization step to transform the ionic species into neutral compounds that are equilibrated with a fiber by its exposure into the headspace (HS) followed by thermal desorption in the injector port of a gas chromatograph (GC). Therefore, the sensitivity and selectivity are primarily achieved by both the type of polymer used in SPME and the detection system [flame photometric detector (FPD), microwave induced plasma (MIP)-atomic emission spectrometry (AES), inductively coupled plasma (ICP)-mass spectrometry (MS), ICP-AES, sector field (SF)-ICP-MS, cold vapor (CV)-atomic fluorescence spectrometry (AFS), atomic absorption spectroscopy (AAS), glow discharge (GD), ICP-time of flight (TOF)] coupled to GC. Moreover, SPME has also been used for total element determination in combination with a derivatization reaction, followed by thermal desorption in ICP-MS.

In addition to SPME, two ancillary extraction techniques, namely stir bar sorptive extraction (SBSE) (5) and in-tube SPME (6), have been developed, but only applications to speciation have been reported for the latter. Indeed, in-tube SPME is mainly focused on high-performance liquid chromatography (HPLC) coupling, so it will not be covered in the present review.

Indeed, this review will focus on the analytical procedures based on SPME for lead, mercury, arsenic, chromium, antimony species, and organotin compounds published from 1994

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to July 2005, including abiotic and biotic matrices, updating former reviews published in 1999 (7) and 2001 (8). Critical steps and figures of merit of the different analytical procedures will be evaluated and compared with conventional methods. Recent trends involving multielemental speciation and sample size miniaturization will be also presented.

Discussion

Sample pretreatment prior to SPME

Aqueous samples

Sample pretreatment in aqueous matrices is a critical issue in trace element speciation because of adsorption to the sample container and biotic or abiotic processes that can lead to a redistribution between chemical species. Several authors have investigated the aqueous sample storage conditions to minimize the degradation–adsorption processes, which can lead to biased results if not properly evaluated. SPME can be a promising approach for sample storage of trace element species because they can be sorbed onto the SPME fibers, preventing or minimizing the transformation or decay processes as demonstrated for pesticides (9).

Determination of trace elements in aqueous samples comprises several steps. Usually, SPME involves the following: (*i*) surrogate addition, (*ii*) pH adjustment, (*iii*) derivatization-extraction, and (*iv*) determination (Tables I–III). Conversely to other extraction techniques, filtration is not necessary, avoiding analyte adsorption onto the filter (10).

Aqueous-phase derivatization and SPME are simultaneously performed under vigorous stirring to accelerate both the reaction and extraction kinetics (see the Derivatization reactions used in trace element speciation section). Then, the derivatized organometallic species are extracted by the SPME fiber, and the underivatized species remains in solution because they exhibited a much lower distribution coefficient between the fiber and the aqueous phase.

Solid matrices

Sediment and soil. Speciation analysis in solid samples requires a mild digestion or leaching technique to liberate the trace element compounds adsorbed onto the matrix into the liquid phase. Only highly volatile species (i.e. $HgMe_2$, $SnMe_4$, Et_4Pb) can be extracted directly from the HS in equilibrium with the solid sample; otherwise, a leaching step is mandatory prior to the SPME extraction. The leaching procedure depends on the matrix, but it usually involves an acid or basic conditions followed by a pH adjustment to perform the derivatization reaction. When the leaching process is completed, an aliquot of the digested sample (subsample) is transferred to another vessel where the derivatization reaction and SPME are performed. The amount of digested sample used depends on the matrix complexity and the type of coextractants that can inhibit the derivatization reaction. Accordingly, the subsample–reagent amount should be optimized specially in case of samples exhibiting low analyte concentrations or samples very small in size.

For organomercury speciation, MeHg was extracted from marine sediments using microwave-assisted acid extraction or digestion (11). Alternatively, MeHg was extracted from soil with subcritical water extraction (12), immersion in acetic acid–acetate buffer solution (pH = 3, 24 h) with few drops of concentrated nitric acid for sediment (13), and soil (14).

For butyltin extraction from sediment, sonication with HCl in methanol (15,16), glacial acetic acid by mechanical stirring or sonication (17), and microwave-assisted acid digestion (18) have been described.

Biota. For the determination of mercury species in biological matrices, some methods use either HCl leaching from human hair (19), basic digestion under sonication (3), or shaking for 4 h (20). HCl 3M (1 h) was used for fish tissue (21) and methods of immersion in acetic acid–acetate buffer solution (pH = 3, 96 h) with few drops of concentrated nitric for mink hair or skin (13) were described. Alternatively, microwave digestion has also been developed for the determination of MeHg in biological specimens (22).

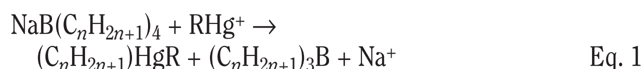
Similarly to sediment extraction, butyltin species from biological samples have been leached by sonication with HCl in methanol (15) and glacial ethanoic acid by mechanical stirring (17).

Derivatization reactions used in trace element speciation

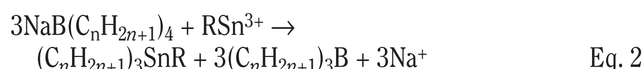
Because most organometallic species lack volatility, a derivatization step is mandatory prior to GC determination. Furthermore, the derivatization reaction allows obtaining lipophilic species, which can be effectively preconcentrated by SPME with non-polar or moderately polar polymers.

Alkylation-phenylation reactions

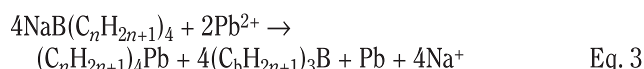
Tables I–III summarize the derivatization procedures used in the SPME–GC methods. Although a variety of alkylation reactions have been used in trace element speciation, the most widely used method for tin, mercury, and lead is by far ethylation and, to lesser extent, propylation by using sodium tetraalkylborates (i.e., $NaBEt_4$ or $NaBPr_4$). The alkylation reactions used in the derivatization of tin, lead, and mercury are:



$$NaB(C_nH_{2n+1})_4 + RHg^+ \rightarrow (C_nH_{2n+1})HgR + (C_nH_{2n+1})_3B + Na^+ \quad \text{Eq. 1}$$



$$3NaB(C_nH_{2n+1})_4 + RSn^{3+} \rightarrow (C_nH_{2n+1})_3SnR + 3(C_nH_{2n+1})_3B + 3Na^+ \quad \text{Eq. 2}$$



$$4NaB(C_nH_{2n+1})_4 + 2Pb^{2+} \rightarrow (C_nH_{2n+1})_4Pb + 4(C_bH_{2n+1})_3B + Pb + 4Na^+ \quad \text{Eq. 3}$$

where n = 2 or 3 for the alkylation reaction. The working pH range for the derivatization reaction is from 4.0 to 5.3, depending on the target trace element. A clear advantage of tetraalkylborates over other derivatization reagents is that derivatization can be performed in the aqueous phase, whereas other alkylating reagents (as Grignard reagents) require strictly anhydrous conditions. Propylation reaction allows the determination of ethyllead, which could not be determined by the most commonly used ethylation reactions. However, one of the

main problems with $NaBEt_4$ is its short lifetime in the presence of oxygen and moisture. Thus, it should be stored in an inert atmosphere, such as argon in a dryer, to avoid its degradation according with the storage time. Moreover, $NaBEt_4$ must be properly disposed of because it is flammable in contact with organic matter such as cellulose. The proposed reactions for the alkylation of mercury, tin, and lead with SPME are indicated in equations 1–3.

The alkylation reaction yield depends on the pH of the medium. Usually the acetic–acetate buffer is used to bring the pH ca. 5. Cai and Bayona (23) have optimized the pH range for the ethylation reaction of organotins. The amount of $NaBEt_4$ is strongly dependent on the matrix because it can react with some of its components. In addition, alkaline ions also might depress the derivatization yield, which can be particularly relevant in the case of speciation studies in seawater. In the case of aqueous matrices, the amount needed is in the range of 0.8–1.0 mL of 1% (w/v) solution for a 150-mL sample. The reaction time is approximately 5 min under mechanical agitation.

Table I. SPME Methods for Mercury Speciation with GC Separation*

Species	Sample type	Derivatization	Fiber, extraction time, extraction mode	Detector	Detection limit (ng/L)	RSD (%)	Reference
DMeHg Hg^{2+}	Gas condensate	DS	100 µm PDMS, 30 s, HS	MIP-AES	240 560	NR	(42)
DMeHg-DEtHg DMeHg-DEtHg	Water	DS HS	100 µm PDMS, 20 min, HS	MIP-AES	30–144 25–123	2.7–4.0 14.8-14.9	(75)
Hg^{2+} MeHg	Seawater	$NaBEt_4$, acetate buffer (pH 5)	100 µm PDMS, 5 min, HS	ICP-MS	1.6 0.11	4.1 4.8	(30)
Hg^{2+} MeHg	Seawater	$NaBPr_4$, acetate (pH 5)	100 µm PDMS, 5 min, HS	ICP-MS	0.35 0.17	2.4 3.6	(30)
Hg^{2+} MeHg, EtHg	Seawater	$NaBPh_4$–acetate (pH = 5)	100 µm PDMS, 5–45 min, HS	MIP-AED	100–300	3-11	(34)
MeHg	Water fish tissue	$NaBEt_4$ –acetate buffer (pH 4.5)	100 µm PDMS, 5 min, HS	AFS	3.0 6.6	9.1	(20)
Hg^{2+} MeHg	Water fish tissue	$NaBEt_4$ –acetate (pH 4.5)	100 µm PDMS, 15 min, HS MeHg and DI	EI-MS	3.5–8.7 7.5–6.7	NR	(3)
MeHg EtHg PhHg	Soil	Hydride generation KBH_4–acetate (pH 3)	Fused silica, 1.5–2 h, HS	AAS	NR	NR	(14)
Hg^{2+} MeHg	Biological	$NaBPh_4$–acetate buffer (pH 5)	100 µm PDMS, 15 min, HS and DI	MIP-AES	860 120	16.3 8.3	(35)
Hg^{2+} MeHg	Fish tissue	$NaBEt_4$ –acetate buffer (pH 5)	100 µm PDMS, 2 min, HS and DI	FAPES	0.7 ng/g 1.5 ng/g	3.8 4.3	(70)
MeHg DEtHg	Fish tissue	DS HS	65 µm PDMS–DVB, 10 min	ICP-MS	160 190	2.7 2.4	(21)
MeHg	Biological samples, sediments	Hydride generation KBH_4–acetate buffer (pH 3)	Fused silica, 1.5–2 h, HS	AAS	NR	NR	(13)
Hg^{2+} MeHg	Urine	$NaBEt_4$ –buffer (pH 4)	100 µm PDMS, 15 min, HS	EI-MS	93 303	NR	(62)
MeHg	Biological samples	$NaBEt_4$ –buffer (pH 4)	100 µm PDMS, 15 min, HS	ICP-MS	4.2 pg/g	2	(22)
Hg^{2+} MeHg	Human hair	$NaBEt_4$ –acetate buffer (pH 4.5)	100 µm PDMS, 10 min, HS	CVAFS	80 ng/g 50 ng/g	15	(19)

* Abbreviations: methylmercury, MeHg; direct immersion, DI; ethylmercury, EtHg; phenyllmercury, PhHg; dimethylmercury, DMeHg; diethylmercury, DEtHg; sodium tetraethylborate, $NaBEt_4$; sodium tetrapropylborate, $NaBPr_4$; sodium tetrahydroborate, $NaBH_4$; headspace, HS; direct sampling, DS; and not reported, NR.

Table II. SPME Methods for Tin Speciation with GC Separation*

Species	Sample type	Derivatization	Fiber, extraction time, extraction mode	Detector	Detection limit (ng/L)	RSD (%)	Reference
TeMT, TMT DMT MMT	Water, seawater	$NaBEt_4$–acetate (pH 4.0)	100 µm PDMS, 20 min, HS	FPD	8.4–41	NR	(4)
MBT DBT TBT	Seawater	$NaBH_4$–HAc and NaAc (pH 3.3)	100 µm PDMS, 20 min, HS	FPD	0.5–19.4	6.8–11.1	(76)
MBT, DBT TBT, MPhT DPhT, TPhT	River water	$NaBEt_4$–ethanoic acid (pH 4.8)	100 µm PDMS, 60 min, DI	FPD	1–4	7–11	(77)
MBT, DBT TBT, MPhT DPhT, TPhT	River water	$NaBEt_4$–acetate (pH 5.3)	100 µm PDMS, 30 min, HS	RTL-GC–MS	0.4–1.1	2.9–6.3	(72)
TeMT, TMT DMT, MMT MBT, DBT TBT, TeBT MPhT, DPhT TPhT, MOcT DOcT, TOcT	Water, fish tissue,	$NaBEt_4$–acetate (pH 4.0)	75 µm carboxen–PDMS, 30 min, HS	PFPD	0.01–56	9–25	(15)
MBT, DBT TBT, MPhT DPhT, TPhT	Spiked water and urban waste water	$NaBEt_4$–ethanoic acid (pH 4.8)	100 µm PDMS, 30-45 min, HS	ICP–AES	2–7	3–18	(78)
MBT, DBT TBT	PACS2	$NaBEt_4$–acetate (pH 4.0)	100 µm PDMS, 60 min, HS	FID	900–1200	8.7–9.6	(16)
MBT, DBT TBT	PACS2	$NaBEt_4$–acetate (pH 4–5)	100 µm PDMS, 60 min, HS	MIP-AES	0.01–0.1	NR	(11)
Sn MBT, DBT TBT	River estuary sediment	$NaBEt_4$–acetate buffer (pH 4.3)	100 µm PDMS, 15 min, HS	FID	NR	NR	(65)
MBT, DBT TBT, MPhT, DPhT, TPhT	PACS2	$NaBEt_4$–ethanoic acid (pH 4.8)	100 µm PDMS, 40 min, HS	FPD	0.006–0.583	3–16	(17,49)
MBT, DBT TBT, MPhT DPhT, TPhT	Harbor sediment	$NaBEt_4$–acetate buffer (pH 5.3)	100 µm PDMS, 30 min, HS	RTL-GC–MS	0.3–1.9	1.73–4.76	(72)
MBT, DBT TBT, MPhT DPhT, TPhT	PACS2	$NaBEt_4$–ethanoic acid (pH 4.8)	100 µm PDMS, 40 min, HS	MIP-AES	0.009–0.415	4–18	(17)
MBT, DBT TBT, MPhT DPhT, TPhT	PACS2	$NaBEt_4$–ethanoic acid (pH 4.8)	100 µm PDMS, 40 min, HS	PFPD	0.001–0.200	4–18	(17)
MBT, DBT TBT. MPhT DPhT, TPhT	PACS2	$NaBEt_4$–ethanoic acid (pH 4.8)	100 µm PDMS, 40 min, HS	ICP-MS	0.0006–0.020	8–25	(17)

* Abbreviations: monobutyltin, MBT; dibutyltin, DBT; tributyltin, TBT; monophenyltin, MPhT; diphenyltin, DPhT; triphenyltin, TPhT; monomethyltin, MMT; dimethyltin, DMT; trimethyltin, TMT; tetramethyltin, TeMT; tetrabutyltin, TeBT; monooctyltin, MOcT; dioctyltin, DOcT; trioctyltin, TOcT; sodium tetraethylborate, $NaBEt_4$; sodium tetrapropylborate, $NaBPr_4$; sodium tetrahydroborate, $NaBH_4$; direct immersion, DI; NR, not reported; and retention time locked, RTL.

Taking into consideration the variability in the derivatization yield, in accordance with the matrix, a structurally related compound or isotopicaly labeled surrogate is strongly recommended to correct concentration by their recovery. Nevertheless, if the surrogate does not possess a similar reactivity, the recovery correction can lead to biased results.

Furthermore, multielement speciation of mercury, lead, and tin has been achieved with $NaBEt_4$ derivatization because these elements are reactive to tetraalkylborates (See Multi-element speciation section). However, one of the main limitations of the ethylation technique is that it cannot be applied to the speciation of ethylated lead species because the triethyllead and inorganic lead react with $NaBEt_4$, both of them leading to the tetraethyllead formation. This limitation could be overcome by utilizing perdeuterated $NaBEt_4$ for the derivatization of organolead species (24) or a propylating agent such as sodium tetrapropylborate ($NaBPr_4$) instead of $NaBEt_4$.

In a validation study of aqueous ethylation with $NaBEt_4$, using isotopically labeled methylmercury where the spiked

Table III. SPME Methods for Lead and Multielement Speciation with GC Separation*

Species	Sample type	Derivatization	Fiber, extraction time, extraction mode	Detector	Detection limit (ng/L)	RSD (%)	Reference
TEL	Gasoline	DS	100 µm PDMS, 10 min, HS	QF-AAS	230	6	(41)
Pb^{2+} TEL	Spiked water	$NaBEt_4$–acetate (pH 4.0)	100 µm PDMS, 15–20 min, HS	EI-MS	200	NR	(40)
Pb^{2+} TML, TEL, TeEL	Water	Deuterated $NaBEt_4$–acetate (pH 4.0)	100 µm PDMS 10 min, HS	EI-MS, FPD	83–130	3.9–6.6	(24)
Pb^{2+}	Blood, urine	$NaBEt_4$–acetate (pH 4.0)	100 µm PDMS, 15 min, HS	EI-MS	2000–3000	NR	(79)
Multielemental							
MeHg TML, DML MBT, DBT,TBT	Water sediment*	$NaBEt_4$–acetate (pH 5.0)	100 µm PDMS, 10 min, HS	ICP-MS	3.70 180 pg/g 0.13-0.15 19–60 pg/g 0.38–1.2 6.5–7.5 pg/g	17 12–25 18–19	(63)
MBT, DBT, TBT TML, TEL	Spiked water	$NaBEt_4$–acetate buffer (pH 4.5)	100 µm PDMS, 5 min, HS	GD-OES	21-75 30–150	6.0-7.8 7.8–8.7	(54)
MeHg, Hg^{2+} TML, TEL MBT, DBT, TBT	River and seawater	$NaBEt_4$–acetate (pH 5.3)	50 or 30 µm DVB–CAR–PDMS, 30 min, HS	MS	3.1-–2.3 0.4–0.2 1.4–16.8	5,–3 3–5 20	(51)
MBT, DBT, TBT MeHg TML	Sediment	$NaBEt_4$–acetate (pH 5.3)	100 µm PDMS, 10 min, HS	ICP-MS	0.34–2.10 4.30 0.19	5.2–14 11 8.2	(47)
MeHg, Hg^{2+} TML, DML, TMT, TMT, DMT, MMT, MBT, DBT, TBT	Sediment	$NaBEt_4$–acetate (pH 5)	75 µm CAR–PDMS, 7 µm PDMS, 30 µm PDMS, 100 µm PDMS, PDMS–DVB, CW–DVB, PA, 30 min, HS	MCGC–ICP-TOF-MS	1.3–2.0 pg/g below pg/g	< 5	(46)
MBT, DBT, TBT MeHg, Hg^{2+} TML	Urine	$NaBEt_4$–acetate (pH 5.3)	100 µm PDMS,10 min, HS	EI-MS–MS	9–13 22,18 7	14.9–6.6 3.8, 15 13.1	(55)

* Abbreviations: TML, trimethyllead; TEL, triethyllead; TeEL, tetraethyllead; $NaBEt_4$, sodium tetraethylborate; $NaBPr_4$, sodium tetrapropylborate; $NaBH_4$, sodium tetrahydroborate; DI, direct immersion; quarz furnace, QF; and not reported, NR.

compound was $Me^{201}Hg^+$ followed by GC–ICP-MS determination, it was found that, in halide-containing solutions, a dealkylation of methylmercury into elemental mercury occurred during ethylation (25). That reaction does not occur with sodium tetrapropylborate ($NaBPr_4$) (26). Moreover, $NaBPr_4$ has already been tested for the determination of tributyltin (TBT) in sediments by SPME using isotope dilution (ID)–GC–MS (27) and for the determination of methylmercury in fish tissues (28,29). Moreover, mercury speciation in seawater at sub-part-per-trillion levels with detection limits down to a few picograms per liter for both mercury and methylmercury have been achieved (30).

Despite the fact that ethylation with $NaBEt_4$ is currently the most widely used derivatization reagent, phenylation with sodium tetraphenylborate ($NaBPh_4$) (31–33) has been evaluated. The advantages of using phenylation with $NaBPh_4$ over ethylation with $NaBEt_4$ are few. The preference of the latter reagent allows MeHg, ethylmercury (EtHg), and inorganic mercury (Hg^{2+}) to be distinguished and concurrently determined. In fact, the phenylic forms of mercury do not occur in nature, and the anthropogenic sources of phenyl mercury derivatives are negligible. In addition, these forms are relatively stable and the reagent has a low cost. Nevertheless, their use for final SPME applications has been tested for inorganic and organomercury compounds in seawater (34) and biological samples (35,36)

Hydridization reaction

Hydridization reaction can also be performed in the aqueous media, which led to the formation of more volatile derivatives than ethylated counterparts. The higher reactivity of metal hydrides in comparison with alkylated species has restricted its applicability to elements that are not able to react with alkylating agents. In this regard, multielement determination of arsenic, selenium, antimony, and tin amenable to hydride generation was achieved by SPME preconcentration with carboxen (CAR)–polydimethylsiloxane (PDMS) followed by thermal desorption and ICP-MS determination (37).

Other derivatization reactions

Several derivatization reactions have been developed for the determination of trace elements such as chromium and arsenic. Unfortunately, most of these derivatization reactions allow only the determination of the total element but an increased sensitivity in complex matrices such as seawater is achieved. Isobaric interferences occurring when direct liquid introduction of trace elements is attempted to be determined by ICP-MS and are minimized when SPME of hydrides is used.

The derivatization reaction used in case of Cr(III) determination consists of the reaction with 1,1,1-trifluoroacetylacetone $(Htfa)_3$ to obtain the volatile trifluoroacetylacetonate (38) (Figure 1). On the other hand, the determination of several methyl arsenic compounds (i.e., dimethylarsinic and monomethylarsonic) has been achieved by derivatization with thioglycol methylate (Figure 2). The method has been successfully applied to human urine samples (39).

Direct determination

Neutral organometallic species that are sufficiently volatile can be sampled by SPME and determined by GC without a derivatization step (8). Direct determination of tetraethyllead in water by HS–SPME was developed by Gorecki and Pawliszyn in 1996 (40). Tetraethyllead was also extracted from gasoline (leaded and unleaded) and water (41). For mercury species, a method for the determination of dimethylmercury in natural gas condensates with very short sampling times (30 s) was developed (42). However, serious problems were reported because of the extremely complex matrix analyzed, including volatile organic material, which is also extracted with the dimethylmercury. Volatile organo-selenium species [dimethylselenide (DMSe), diethylselenide (DEtSe), and dimethyldiselenide (DMDSe)] have also been determined by SPME followed by their direct determination in yeast by using a variety of atomic selective techniques (43).

Speciation of Hg, Pb, and Sn with SPME

Speciation studies for tin, mercury, and lead by SPME have been carried out primarily using PDMS as a preconcentration polymer because trace element species are basically analyzed as

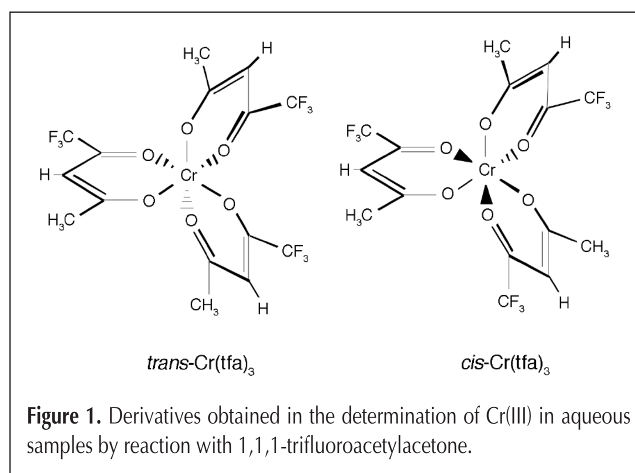


Figure 1. Derivatives obtained in the determination of Cr(III) in aqueous samples by reaction with 1,1,1-trifluoroacetylacetone.

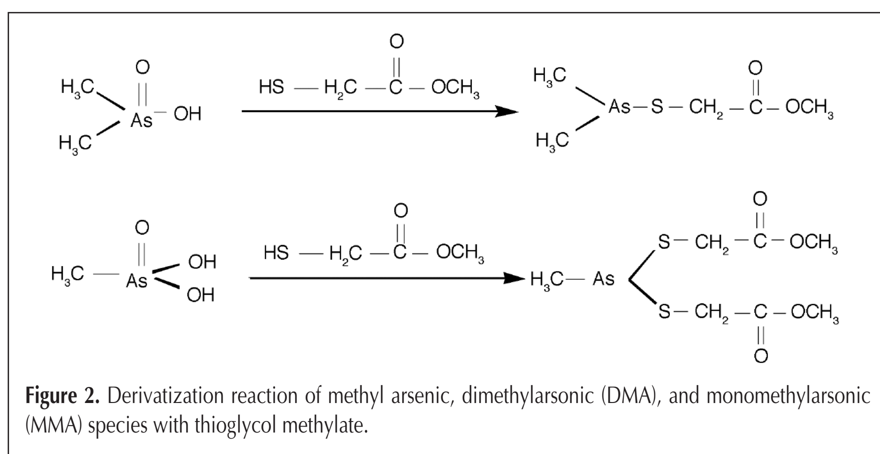


Figure 2. Derivatization reaction of methyl arsenic, dimethylarsonic (DMA), and monomethylarsonic (MMA) species with thioglycol methylate.

methyl or ethyl derivatives. The species determined and the analytical conditions according to the element are reported in Tables I–III.

The following variables have been evaluated to improve the extraction efficiency of the methods based on SPME.

Extraction procedure

Two different sampling procedures are possible for trace element speciation with SPME, HS, or direct sampling from the aqueous sample. Provided that ethylated trace element species have a relatively high volatility, HS sampling is the preferred extraction procedure because the carryover effect is minimized and fiber lifetime is increased. Derivatization reagents are used in the aqueous phase, and they affect the fiber stability when it is exposed to high temperatures in the injector port during the desorption process (3,4,44). The sensitivity in HS analysis depends on their distribution coefficients, the longer the alkyl chain, the higher the sensitivity because they possess a higher distribution coefficient. The highest sensitivity was obtained for the propylated and phenylated derivatives (Tables I–III). The differences in the SPME response among the different organometallics, according to the alkylation degree, are even higher if they are underivatized and are analyzed as chlorides. In this case, the monosubstituted species have a very low response because their lipophilicity is too low to be preconcentrated by nonpolar polysiloxanes (45). The use of adsorption fibers, such CAR–PDMS or PDMS–divinyl benzene (DVB), allows a higher extraction yield in comparison with PDMS for the shorter alkylchain organometallics and hydride derivatives (46).

Extraction time in SPME depends on the sample diffusion and the sampling procedure, either HS or direct sampling by immersion of the SPME fiber in the aqueous sample. In some cases, HS sampling is more time consuming than direct immersion, and equilibrium conditions are not completely reached, but it is preferred in terms of sensitivity and fiber lifetime.

The salting out effect has been evaluated in the case of mercury (3), tin (4), and lead (47), but it did not increase the extraction efficiency of the target analytes.

Stirring procedure

Agitation during the extraction is needed to reduce the boundary layer thickness between the fiber and the solution (48). Although magnetic stirring is usually the most common procedure because of its simplicity, Potin-Gautier et al. have demonstrated that mechanical stirring (i.e., elliptical table) could be more efficient than magnetic stirring in case of organotin speciation (49). Although the exact mechanism is unknown, it could be attributable to the competitive adsorption of derivatized organotin species on the PTFE coated stir bar versus the SPME fiber.

Extraction pressure and temperature

No differences in the extraction yield for methylmercury and methyltins from 25°C and 50°C (3,4) have been found. The equilibrium between the analyte sorbed into the SPME fiber coating and the concentration in the sample solution depends on both the solubility of the analyte in the aqueous phase and its sorption affinity onto the SPME fiber coating. Increasing the temperature will increase the partial vapor pressure of the analytes in the HS, but it will simultaneously decrease the distribution constant on to the fiber HS. However, in the case of less volatile compounds, such as dibutyl- and tributyltin, an increase in the extraction yield was found when the sampling temperature was increased from 20°C to 60°C (47) but decreased at higher temperatures. Mechanical stirring and reduced pressure result in simultaneously higher efficiency (detection limits lowered especially for phenyltins up to an eight-fold reduction) and shorter sampling time (two-fold reduction) (50).

Polymer coating and fiber film thickness

Probably the most important feature determining the analytical performance of SPME is the type and thickness of the coating material. The fiber film thickness plays an important role in the extraction and desorption kinetics. Therefore, thicker coatings result in longer extraction times because diffusion is slow within the polymer extraction phase. Subsequently, when a thicker film is employed, the adsorption process is slower and higher desorption temperatures are needed (45).

To date, several experimental coatings have been prepared and evaluated for a wide range of applications. PDMS is the most widely used coating material because of its high stability. PDMS extracts samples via absorption of analytes, which dissolve and diffuse into the coating material.

In addition to liquid polymeric coatings, other materials have been developed. Then, carbowax–DVB, PDMS–CAR, PDMS–CAR–DVB, and PDMS–DVB are mixed coatings where the extraction occurs via adsorption of analytes. Finally, the PDMS–CAR coating is a special case comprising a mixed carbon-phase containing micro and mesopores and has been particularly effective for the MeHg extraction (46).

In summary, it is important to use the appropriate coating for a given application and any specific compounds. The use of a thicker fiber requires a longer extraction time, but the recoveries are generally higher. Accordingly, when thinner fibers are used (7 µm), the amount of analyte absorbed is lower and, for most of the applications, the 100-µm film thickness is used because trace level determination of trace element species is needed. Maximum operational temperatures depend on the polymer coating.

For organomercury, organotin, and organolead species, PDMS (100 µm) has been successfully employed. Also, PDMS–DVB (65 µm) was used for the determination of methylmercury and diethylmercury in fish tissues (21). Direct immersion or HS sampling achieve similar detection limits and relative standard deviations (RSDs) (%). Potin-Gautier et al. performed a rapid determination of methyl-, butyl-, phenyl-, and octyltin species using PDMS–CAR (75 µm) (15). Finally, DVB–CAR–PDMS was applied for multielement determination [MeHg, Hg^{2+}, trimethyllead (TML), triethyllead (TEL), TERM monobutyltin (MBT), dibutyltin (DBT), and tributyltin (TBT)] (51).

Jiang and He (13,14) developed a new pretreatment of the

silica fiber as an alternative to commercial polymer-coated fibers by immersing the bottom 5 cm of a fused-silica fiber in concentrated hydrofluoric acid. The adsorption efficiency increased initially with the pretreatment time, reaching a maximum between 3 and 4.5 h, but if the pretreatment process was longer than 4.5 h, the extraction efficiency dropped quickly because the fiber surface can be destroyed by concentrated hydrofluoric acid. In this case, extraction, which is based on surface interactions between the organomercury hydrides and the treated glass fiber, was reported to be too long (2 h) and predominantly is an adsorption phenomenon. Later on, Mester et al. (37) studied two different fibers for sampling volatile metal and metalloid hydrides (As, Se, Sn, and Sb) coupled with ICP-MS detection. PDMS–CAR fiber (adsorption-based extraction) provided better sensitivity than PDMS fiber (absorption-based extraction). Moreover, the desorption process from the PDMS coating was significantly slower than from the CAR coating.

Thermal desorption

The injector temperature is a key parameter because thermal stability is rather limited. However, in order to minimize the carryover effect, it is necessary to increase the injector temperature. Butyltins and tetraethyllead are rather stable at 250°C, and it is reported that they can be completely desorbed following 1 min of desorption time in the GC injector port at that temperature. It offers a good compromise between complete desorption and carryover effects. At lower temperatures, carryover effects were detected for the less volatile compounds such as butyl- and phenyltins (52). In the case of methylmercury, lower injector port temperatures (i.e., 170°C for PDMS) are strongly recommended in order to minimize thermal degradation (68).

Multielement speciation

Applications of SPME to target individual trace elements have been fully described in Tables I–III; however, few papers dealing with its application to multielement speciation studies have been reported (Table III). Development of a multielement speciation method with the ultimate aim of simultaneously determining various organometallic compounds of mercury, lead, and tin is covered to a lesser degree in the literature. Because of the different characteristics of the several species involved in the multielement speciation, it required a compromise during the optimization conditions for the method. Thus, extraction mode selection (direct or HS), fiber coating selection, and extraction conditions (time and temperature) are critical parameters. Another important aspect is the chromatographic resolution between the derivatized species. Although standard capillary GC columns allow a sufficient resolution between species, multicapillary GC has been introduced to reduce the analysis time to less than 1 min (46).

Selection of the fiber coating is also critical. For example, in Table I, it should be observed that the limit of detection (LOD) for organomercury compounds is at least a factor of 10 higher than those of organotin and lead. This is because of the less efficient absorption of the more volatile organomercury species onto the fiber in comparison with the others. Furthermore, the lower ionization efficiency for Hg in the plasma will contribute to this higher value.

It is known that PDMS (100 µm) is the most useful liquid-type coating, but Sanz-Medel et al. (51) evaluated a dual fiber containing the DVB–CAR–PDMS (50/30 µm) coating for the simultaneous determination of various organometallic compounds of mercury, lead, and tin. As expected, a temperature increase in the extraction medium of the target species (MeHg, Hg^{2+}, TML, TEL, and butyltins) lead to a decrease of the amount extracted by the fiber, except for the butyltins, which increase because of their higher boiling points (47,51)

Extraction time optimization is another critical variable because for different species, the equilibrium is reached at different times. For example, for the more volatile compounds, MeHg, Hg^{2+}, and TML, equilibrium is reached after 30 min (longer than those reported previously) (47,53–55), but for TEL, DBT, and TBT, more than 60 min is needed (51).

Results

Linearity range, detection systems, selectivity, and sensitivity

Linearity range in the trace element speciation has been evaluated in several analytical techniques such as GC–FPD in the tin selective mode, GC–MS in the SIM mode for mercury (i.e., quadrupolar analyzer), and GC–flame ionization detection (FID) for tetraethyllead. It also depends on the SPME coating used for the preconcentration. Adsorption coatings usually possess less sample capacity and suffer from competitive adsorption, leading to displacement of the lesser affinity analytes by the higher affinity ones. That behavior has been evidenced in the organotin extraction according with time (49). Hereafter, a description and evaluation of the analytical techniques will follow.

Organomercury compounds

Speciation of organomercury compounds is most commonly performed by GC coupled to MS, AAS, AFS, CV-AFS, ICP-MS, MIP-AES, or furnace atomization plasma emission spectrometry (FAPES) with excellent sensitivity and selectivity.

GC coupled with MIP-AES detection is a highly sensitive technique for the determination of dimethylmercury and diethylmercury with a working range in the µg/L and ng/g levels. For mercury and methylmercury quantitation in seawater samples, the lowest detection limits were obtained using ICP-MS. Ethylated and propylated mercury species analysis were tested to achieve detection limits (30) down to 2 ng/L for both, and the precision was always better than 5% at a level of 100 ng/L of both species (Table I). The lowest detection limits were achieved by ICP-MS-TOF (46).

Organotin compounds

The SPME procedure followed by GC with specific detection has been developed in most studies for the speciation of butyl-

and phenyltins in environmental samples (Table II). Most of the developed analytical procedures are based on GC separation coupled to element-specific detection systems, such as MIP-AES, FPD, or a specific MS detector such as ICP-MS. Pulsed-flame photometric detection (PFPD) has been widely used because of its higher sensitivity than single or dual FPD.

The performances of these four specific detectors used for the speciation of organotin compounds after SPME and GC separation were evaluated by Potin-Gautier et al. (17). In general, with these detectors, very low detection limits (less than 500 pg/L for all the compounds) can be reached.

ICP-MS is the most sensitive detector (LOD ranging from 0.6 to 20 pg/L); however, the rather selective and sensitive PFPD appears to be a good alternative, with LOD only approximately 2–10 times higher than for ICP-MS. PFPD could be especially adequate for butyltins (LOD ranged from 1 to 4 pg/L), considering its low cost and the reduced operational expenses. Although GC–FPD and GC–MIP-AES are the most common detectors used for organotin determination, their LODs are very low (less than 200 pg/L except for TPhT). The linearity range for all detectors is from the LOD to 400 ng/L, corresponding to the highest concentration typically found in environmental samples.

Organolead compounds

There is a broad selection of methods applied to the speciation of organolead species. GC with MS detection is a generally well-accepted approach to speciation analysis of organolead compounds. Other systems include GC coupled to element specific detection systems, such as AAS, FPD, or electron impact ionization (EI)-MS. The lowest LOD has been attained using ion trap (IT)-MS in the EI mode. On the other hand, as shown in Table III, this is the most useful method for organolead speciation. Górecki and Pawliszyn (40) reported detection limits for TEL of 100 ppt when using FID and 5 ppt when using IT-MS. The detection limit for Pb^{2+} was 200 ppt. IT-MS offered excellent sensitivity and selectivity, but the calibration curves were nonlinear when the m/z = 295 ion was used for quantitation. Later, full speciation and determination of alkyllead and inorganic lead in water was accomplished by in situ derivatization with deuterium-labeled sodium tetraethylborate (24). The extracted analytes were determined by GC–MS or GC–FID. RSD values were less than 7%, which is acceptable considering the complexity of the speciation. Duplicate five-point calibration curves for every one of the species were obtained from 0.1 to 100 parts per billion (ppb) using GC–MS.

Direct determination of tetraethyllead in gasoline and water with detection by quartz furnace AAS after thermal desorption from the SPME fiber was also proposed (41). In this case, detection limits are in the sub-ppb range (0.23 ng/mL), with a good reproducibility (RSD = 6%; n = 5) and linear range (0–100 ng/mL).

Organoarsenical, chromium, antimony, and selenium compounds

There are only a few methodologies applied for the speciation of those compounds (Table IV). The use of SPME with GC coupled to microwave-induced plasma (MIP)-AED is described for selenite [Se(IV)] speciation. Aqueous standards were derivatized with sodium tetraethyl- or tetrapropylborate and extracted by SPME. Under optimized conditions, both derivatization methods gave comparable detection limits (3000 ng/L Se for ethylation and 2000 ng/L Se for propylation) and RSD (7% and 4%, respectively). The method is linear up to a concentration of at least 200,000 ng/L Se (56). Nevertheless, with the coupling of SPME–GC–MIP-AES, a simple and economic method for organo-selenium speciation was presented. Detection limits obtained were 570, 470, and 190 ng/L for DMSe, DEtSe, and DMDSe, respectively (57).

The determination of trace Cr(III) in aqueous solution by SPME coupled with GC–FPD was achieved with the limit of detection for Cr(III) of 2000 ng/L. This value is about 10 times lower than that of the SPME–HPLC–UV method (58) but about two orders of magnitude higher than that of the SPME–GC–SF-ICP-MS method (59) or the SPME–GC–ECD method (60).

For organoarsenic compounds, a method for roxarsone based on SPME–GC–MS-PFPD provided a linear calibration over an environmentally relevant range (0.0–100,000 ng/L) (61). Detection limits obtained by PFPD were 600 and 220 ng/L for monomethylarsonic (MMA) dimethylarsonic (DMA) , respectively. In contrast, detection limits for MMA and DMA using the SPME–GC–MS method (39) were 290 and 120 ng/L, respectively. The method is linear in the 1 to 200,000 ng/L range.

Direct coupling of SPME with ICP-MS was used for the non-selective determination of arsenic, selenium, antimony, and tin species amenable to hydride generation. PDMS–CAR showed better extraction capacity and enhanced selectivity for tin hydrides. SPME provided good sensitivity and an approximately 3.5-decade linear response range. Detection limits for As, Se, Sn, and Sb using a PDMS–CAR were 70, 5300, 8, and 310 ng/L, respectively. The method was validated for total arsenic using SLRS-4 (Riverine water) and CASS-4 (Nearshore seawater) reference materials.

Multielement detection

To perform simultaneous speciation and determination of the target trace element, the most common approach for this purpose is GC coupled with ICP-MS, MIP-AES, or MS. (3,24,55,62)

In terms of detection limits and precision (Table III), the HS–SPME–GC–MS method presents good analytical performance characteristics (51). Detection limits obtained are around one order of magnitude higher (except for MeHg) than those reported using HS–SPME–GC–ICP-MS (63). However, GC–MS permits the identification and verification of molecular species, which is not possible using element-specific detection by ICP-MS. The observed RSDs ranged between 3% and 5% for Hg and Pb compounds and increased (up to 20%) for organotin derivatives. The linear range was found to be from 50 ng/L to 250 µg/L.

Validation

A point of primary importance before the application of the

developed analytical procedures is their validation. Reference materials (RMs) are available for butyltins in sediment and mussel tissue, methylmercury in fish, and trimethyllead in urban dust (64). Until now, developed speciation studies using SPME have been validated in the case of butyltin in marine sediment by PACS-1 (marine sediment) (11,47) and PACS-2 (marine sediment) (11,17,27,65), butyltin in fish by NIES 11 (17), methylmercury in biological samples by DORM-2 (Dogfish muscle), DOLT-2 (Dogfish liver), TORT-1 or TORT-2 (Lobster hepatopancreas) (11,20,66), standard reference material (SRM) 1566b (methylmercury in oyster tissue) (11, 22) and SRM 1946 Lake Superior Fish Tissue (22) and sediments SRM 1646a (11) or methylmercury in human hair by NIES 13 (19,67).

Two sediments (SRM PACS-1 and PACS-2) with certified values for butyltin compounds are currently used. Because several authors reported problems with the indicated (not certified) concentration of monobutyltin in PACS-1, even with other techniques, it was replaced in 1997 by PACS-2. Afterwards, marine sediment PACS-2 was used to validate several SPME methods (Table V). The microwave-assisted extraction SPME–GC–MIP-AES (11,17) is possibly the

Table IV. SPME Methods for Antimony, Arsenic, Chromium, and Selenium in Environmental Matrices*

Species	Sample type	Derivatization	Fiber, extraction time, extraction mode	Detector	Detection limit (ng/L)	RSD (%)	Reference
As Se Sn Sb	Seawater	$NaBH_4$	100 µm PDMS, 30 min	TD-ICP-MS	320 12000 3200 1800	NR	(37)
As Se Sn Sb	Seawater	$NaBH_4$	75 µm CAR–PDMS, 30 min	GC–MS	60 5300 8 310	NR	(37)
SbH_3 Me_2Sb Me_3Sb	Cryptococcus humicolus	$NaBH_4$	100 µm PDMS, 10 min, HS	GC–MS	50–3490	6.8	(80)
MMA DMA 3-NHPAA	Fortified environmental surface water samples	PDT	65 µm PDMS–DVB, 15 min	GC–MS-PFPD	220–2690	1.70–10.9	(61)
MMA, DMA	Aqueous samples	TGM	100 µm PDMS, 40 min	GC–MS	120–290	7.2–9.2	(39)
Cr(III)	Aqueous solution	acetate buffer (pH 6.0) sodium–sulfite reducing agent–$(Htfa)_3$	polyimide-coated silica fiber	GC–FPD	2000	7	(38)
Cr(III)	Aqueous solution	25% TFA in MeOH–NH_4Ac (pH 5.2)	100 µm PDMS	ID GC–SF-ICP-MS	20	7	(60)
Se(IV)	Aqueous solution	NH_4Ac–HAc and buffer; $NaBEt_4$ $NaBPr_4$	100 µm PDMS 70 µm CAR–PDMS 65 µm CW–DVB 85 µm PA	GC–AED	2–3	4–7	(56)
DMSe, DEtSe, DMDSe	Biological matter, such as lupine, yeast, Indian mustard and garlic	DS	75 µm CAR–PDMS 35 min	MC–MIP-AES	190–570	7	(43) (57)

* Abbreviations: monomethylarsonic acid, MMA; dimethylarsinic acid, DMA; roxarsone (3-nitro-4-hydroxyphenylarsonic acid, 3-NHPAA; 1,1,1-trifluoroacetylacetone, $(Htfa)_3$; dimethylselenide, DMSe; diethylselenide, DEtSe; dimethyldiselenide, DMDSe; stibine, SbH_3; monomethylantimony dimethylantimony, Me_2Sb; trimethylantimony, Me_3Sb; 1,3-propanedithiol, PDT; and thioglycol methylate, TGM.

method that gives the most accurate results for all three butyltins.

For methylmercury determination in biological matrices by SPME, DORM-2 has been widely used for validation. The SPME–GC–MIP-AES method also provides a significant improvement compared with previous methods used for the certification of methylmercury in muscle tissues SRMs (68,69). Nevertheless, the GC–FAPES method (70) seems to be the most accurate, offering an improvement over SPME–GC–AFS (20), GC–MIP-AES (11), GC–ICP-MS (21), or isotope dilution (ID) technique, ID–SPME–GC–MS (28), as is shown in Table V. It should be emphasized that the use of ID–GC–ICP-MS (29) provides similar results, but generally is an expensive technique, and isotopic enriched standards are not widely available. In addition, when the ID-SPME–GC–MS is applied with an isotopic element enriched spike, the mass balance equations should take into account the contributions of proton losses from the alkyl substituents, which add complexity into the calculations (51,71). Alternatively, synthesized deuterated organotin analogues were used as internal standards to circumvent the former problem (72).

For the determination of total Cr in seawater by isotope dilution (ID–SF–ICP-MS), a coastal seawater CRM CASS-4 was used as a test sample for method development (59,60). A concentration of 154 ± 13 ng/L (1 SD, n = 4) was obtained for Cr in NRCC seawater CRM CASS-4 using a 1-µL hexane extract, in agreement with the certified value of 144 ± 29 ng/L (95% confidence interval).

Method validation for total arsenic using NRCC SLRS-4 (Riverine Water) and CASS-4 (Nearshore Seawater) reference materials showed good agreement between certified (630 and 990 ng/L) and measured values (680 and 1110 ng/L) (37). Finally, a lack of pure standards and reference materials for organo-selenium species prevents their positive identification and improved method validation.

Conclusion

Future developments in the application of SPME in speciation

The most obvious trend in speciation studies using SPME is the simultaneous determination of organic and inorganic species. In fact, most of the developed procedures are successful for the determination of trace element compounds because the procedures are based on aqueous-phase derivatization, which offer poor yields for the inorganic species. Nevertheless, optimization of the fiber coating (PDMS–DVB) and a high sensitivity detection technique (ICP-TOF) allowed the simultaneous determination of up 10 organometallic compounds of tin, lead, and mercury, including elemental mercury (46). LODs below the pg/g were achieved for most of the species.

Therefore, new derivatization reactions, such as ion-pair or chelate extraction, followed by SPME are needed to extend the speciation to the simultaneous organometallic and elemental determination. The procedure could expand the speciation to other elements of interest in environmental and food safety. In this regard, a methodology to determine total chromium in seawater was developed (59). First, chromium was reduced to Cr-III by addition of SO_2-saturated water and derivatized with trifluoroacetylacetonate (TFA) to form volatile $Cr(TFA)_3$. The derivatized analyte was either extracted into hexane or directly sampled by SPME using a PDMS fiber for GC–ICP-MS or GC–FPD determination.

Until now, the polymers used in trace element speciation studies are similar to those used in the determination of organic compounds. Therefore, both organic and derivatized organometallics are simultaneously extracted during the SPME with conventional polymers, limiting the multielement speciation studies to a few elemental detector systems. A possibility to circumvent the lack of extraction selectivity is the application of an electro-synthesized overoxidized sulfonated polypyrrole film. The polymer film is used for the selective extraction of trace levels of nickel and cadmium ions by an electrochemically driven SPME. The cation uptake and release properties of the overoxidized sulfonated polypyrrole film electrode are controlled by the positive or negative potentials applied to the electrode. The method allowed an increased extraction efficiency and selectivity toward cations (i.e., Cd and Ni) in high saline content waters (73).

Finally, the method automation is another important aspect to increase the sample throughput and reliability of results. Current developments in SPME automation allow the possibility to perform derivatization and extraction sequentially by using two robotic systems (74). Nevertheless, the high cost of this instrumentation prevents its widespread use.

Table V. Validation of the Organotin and Organomercury Content in Sediments and Biological Certified Reference Materials (CRM) by Different SPME Methods

CRM	MBT	DBT	TBT	Reference
PACS-2 (ng/g as Sn)	**450 ± 50**	**1090 ± 150**	**980 ± 130**	**(81)**
GC–MIP-AES (n = 4)	470 ± 60	1070 ± 130	1040 ± 110	(11)
GC–FID (n = 3)	800 ± 130	990 ± 50	890 ± 100	(16)
GC–MIP-AES (n = 6)	566 ± 36	1013 ± 89	964 ± 64	(17)
GC–ICP-MS (n = 6)	1301 ± 27	981 ± 73	931 ± 153	(17)
GC–PFPD (n = 6)	2000 ± 480	1158 ± 148	892 ± 214	(17)
ID–GC–MS			895 ± 15	(27)
	MeHg			
DORM-2 (ng/g as Hg)	**4470 ± 320**			**(82)**
GC–AFS (n = 3)	4060 ± 140			(20)
GC–MIP-AES (n = 2)	4710			(11)
GC–FAPES (n = 3)	4460 ± 20			(71)
GC–ICP-MS (n = 5)	4720 ± 160			(21)
ID–GC–MS (n = 4)	4336 ± 91			(28)
ID–GC–ICP-MS (n = 4)	4484 ± 29			(29)

References

1. C.L. Arthur and J. Pawliszyn. Solid-phase microextraction with thermal-desorption using fused-silica optical fibers. *Anal. Chem.* **62:** 2145–48 (1990).
2. R.G. Belardi and J. Pawliszyn. The application of chemically modified fused silica fibers in extraction of organics from water matrix samples, and their rapid transfer to capillary column. *Water Pollut. Res. J. Can* **24:** 179–91 (1989).
3. Y. Cai and J.M. Bayona. Determination of methylmercury in fish and river water samples using in situ sodium tetraethylborate derivatization followed by solid-phase microextraction and gas chromatography–mass spectrometry. *J. Chromatogr. A* **696:** 113–22 (1995).
4. Y. Morcillo, Y. Cai, and J.M. Bayona. Rapid determination of methyltin compounds in aqueous samples using solid phase microextraction and capillary gas chromatography following in-situ derivatization with sodium tetraethylborate. *J. High Resolut. Chromatograpy* **18:** 767–70 (1995).
5. E. Baltussen, P. Sandra, F. David, and C. Cramers. Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. *J. Microcol. Sep.* **11:** 737–47 (1999).
6. J.C. Wu, Z. Mester, and J. Pawliszyn. Determination of tributyltin by automated in-tube solid-phase microextraction coupled with HPLC-ES-MS. *J. Anal. At. Spectrom.* **16:** 159–65 (2001).
7. J.M. Bayona. "Organometallic speciation by combining aqueous phase derivatization with SPME-GC-FPD-MS", in *Applications of Solid-Phase Microextraction*, J. Pawliszyn, Ed. Royal Society of Cambridge, Cambridge, UK, 1999, pp. 284–95.
8. Z. Mester, R. Sturgeon, and J. Pawliszyn. Solid phase microextraction as a tool for trace element speciation. *Spectrochim. Acta Part B* **56B:** 233–60 (2001).
9. Application note 143. "Field sampling for pesticides, using solid-phase microextraction/capillary GC". Supelco, Bellefonte, PA, 2005.
10. S. Zorita and L. Mathiasson. Determination of dissolved and particle-bound PCB congeners at ultra-trace concentrations in water. *Int. J. Environ. Anal. Chem.* **85:** 531–42 (2005).
11. S. Tutschku, M.M. Schantz and S.A. Wise. Determination of methylmercury and butyltin compounds in marine biota and sediments using microwave-assisted acid extraction, solid-phase microextraction and gas chromatography with microwave-induced plasma atomic emission spectrometric detection. *Anal. Chem.* **74:** 4694–4701 (2002).
12. A. Beichert, S. Padberg, and B.W. Wenclawiak. Selective determination of alkylmercury compounds in solid matrices after subcritical water extraction, followed by solid-phase microextraction and GC–MS. *Appl. Organom. Chem.* **14:** 493–98 (2000).
13. B. He, G.B. Jiang, and Z.M. Ni. Determination of methylmercury in biological samples and sediments by capillary gas chromatography coupled with atomic absorption spectrometry after hydride derivatization and solid phase microextraction. *J. Anal. At. Spectrom.* **13:** 1141–44 (1998).
14. B. He and G.B. Jiang. Analysis of organomercuric species in soils from orchards and wheat fields by capillary gas chromatography on-line coupled with atomic absorption spectrometry after in situ hydride generation. *Fresenius' J. Anal. Chem.* **365:** 615–18 (1999).
15. M. Le Gac, G. Lespes, and M. Potin-Gautier. Rapid determination of organotin compounds by headspace solid-phase microextraction. *J. Chromatogr. A* **999:** 123–34 (2003).
16. E. Millan and J. Pawliszyn. Determination of butyltin species in water and sediment by solid-phase microextraction-gas chromatography-flame ionization detection. *J. Chromatogr. A* **873:** 63–71 (2000).
17. S. Aguerre, G. Lespes, V. Desauziers, and M. Potin-Gautier. Speciation of organotins in environmental samples by SPME-GC: comparison of four specific detectors: FPD, PFPD, MIP-AES and ICP-MS. *J. Anal. At. Spectrom.* **16:** 263–69 (2001).
18. S. Aguerre, C. Pecheyran, G. Lespes, E. Krupp, O.F.X. Donard, and M. Potin-Gautier. Optimisation of the hyphenation between solid-phase microextraction, capillary gas chromatography and inductively coupled plasma atomic emission spectrometry for the routine speciation of organotin compounds in the environment. *J. Anal. At. Spectrom.* **16:** 1429–33 (2001).
19. S. Diez and J.M. Bayona. Determination of methylmercury in human hair by ethylation followed by headspace solid-phase microextraction-gas chromatography-cold-vapor atomic fluorescence spectrometry. *J. Chromatogr. A* **963:** 345–51 (2002).
20. Y. Cai, S. Monsalud, K.G. Furton, R. Jaffe, and R.D. Jones. Determination of methylmercury in fish and aqueous samples using solid-phase microextraction followed by gas chromatography-atomic fluorescence spectrometry. *Appl. Organom. Chem.* **12:** 565–69 (1998).
21. Z. Mester, J. Lam, R. Sturgeon, and J. Pawliszyn. Determination of methylmercury by solid-phase microextraction inductively coupled plasma mass spectrometry: a new sample introduction method for volatile metal species. *J. Anal. At. Spectrom.* **15:** 837–42 (2000).
22. W. Davis, S. Vander Pol, M. Schantz, S. Long, R. Day, and S. Christopher. An accurate and sensitive method for the determination of methylmercury in biological specimens using GC-ICP-MS with solid phase microextraction. *J. Anal. At. Spectrom.* **19:** 1546–51 (2004).
23. Y. Cai and J.M. Bayona. Simultaneous speciation of butyltin, phenyltin and cyclohexyltin compounds in aqueous matrices using ethylation followed by solid-phase trace enrichment, SFE and CC determination. *J. Chromatogr. Sci.* **33:** 89–97 (1995).
24. X. Yu and J. Pawliszyn. Speciation of alkyllead and inorganic lead by derivatization with deuterium-labeled sodium tetraethylborate and SPME-GC/MS. *Anal. Chem.* **72:** 1788–92 (2000).
25. N. Demuth and K.G. Heumann. Validation of methylmercury determinations in aquatic systems by alkyl derivatization methods for GC analysis using ICP-IDMS. *Anal. Chem.* **73:** 4020–27 (2001).
26. T. De Smaele, L. Moens, R. Dams, P. Sandra, J. Van der Eycken, and J. Vandyck. Sodium tetra(n-propyl)borate: a novel aqueous in situ derivatization reagent for the simultaneous determination of organomercury, -lead and -tin compounds with capillary gas chromatography-inductively coupled plasma mass spectrometry. *J. Chromatogr. A* **793:** 99–106 (1998).
27. C. Bancon-Montigny, P. Maxwell, L. Yang, Z. Mester, and R.E. Sturgeon. Improvement of measurement precision of SPME-GC/MS determination of tributyltin using isotope dilution calibration. *Anal. Chem.* **74:** 5606–13 (2002).
28. L. Yang, V. Colombini, P. Maxwell, Z. Mester, and R.E. Sturgeon. Application of isotope dilution to the determination of methylmercury in fish tissue by solid-phase microextraction gas chromatography–mass spectrometry. *J. Chromatogr. A* **1011:** 135–42 (2003).
29. L. Yang, Z. Mester, and R.E. Sturgeon. Determination of methylmercury in fish tissues by isotope dilution SPME-GC-ICP-MS. *J. Anal. At. Spectrom.* **18:** 431–36 (2003).
30. L.R. Bravo-Sanchez, J. Ruiz Encinar, J.I. Fidalgo Martinez, and A. Sanz-Medel. Mercury speciation analysis in sea water by solid phase microextraction-gas chromatography-inductively coupled plasma mass spectrometry using ethyl and propyl derivatization. Matrix effects evaluation. *Spectrochim. Acta Part B* **59B:** 59–66 (2004).
31. Y. Cai, S. Monsalud, R. Jaffé, and R.D. Jones. Gas chromatographic determination of organomercury following aqueous derivatization with sodium tetraethylborate and sodium tetraphenylborate–comparative study of gas chromatography coupled with atomic fluorescence spectrometry, atomic emission spectrometry and mass spectrometry. *J. Chromatogr. A* **876:** 147–55 (2000).
32. V. Minganti, R. Capelli, and R. De Pellegrini. Evaluation of dif-

ferent derivatization methods for the multielement detection of Hg, Pb and Sn compounds by gas-chromatography microwave-induced plasma-atomic emission-spectrometry in environmental-samples. *Fresenius' J. Anal. Chem.* **351:** 471–77 (1995).
33. H.E.L. Palmieri and L.V. Leonel. Determination of methylmercury in fish tissue by gas chromatography with microwave-induced plasma atomic emission spectrometry after derivatization with sodium tetraphenylborate. *Fresenius' J. Anal. Chem.* **366:** 466–69 (2000).
34. A.M. Carro, I. Neira, R. Rodil, and R.A. Lorenzo. Speciation of mercury compounds by gas chromatography with atomic emission detection. Simultaneous optimization of a headspace solid-phase microextraction and derivatization procedure by use of chemometric techniques. *Chromatographia* **56:** 733–38 (2002).
35. R. Rodil, A.M. Carro, R.A. Lorenzo, M. Abuin, and R. Cela. Methylmercury determination in biological samples by derivatization, solid-phase microextraction and gas chromatography with microwave-induced plasma atomic emission spectrometry. *J. Chromatogr. A* **963:** 313–23 (2002).
36. Z. Jokai, L. Abranko, and P. Fodor. SPME-GC-pyrolysis-AFS determination of methylmercury in marine fish products by alkaline sample preparation and aqueous phase phenylation derivatization. *J. Agric. Food Chem.* **53:** 5499–5505 (2005).
37. Z. Mester, R.E. Sturgeon, and J.W. Lam. Sampling and determination of metal hydrides by solid phase microextraction thermal desorption inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.* **15:** 1461–65 (2000).
38. T. Ding, H. Lin, and C. Whang. Determination of chromium(III) in water by solid-phase microextraction with a polyimide-coated fiber and gas chromatography-flame photometric detection. *J. Chromatogr. A* **1062:** 49–55 (2005).
39. Z. Mester and J. Pawliszyn. Speciation of dimethylarsinic acid and monomethylarsonic acid by solid-phase microextraction-gas chromatography-ion trap mass spectrometry. *J. Chromatogr. A* **873:** 129–35 (2000).
40. T. Gorecki and J. Pawliszyn. Determination of tetraethyllead and inorganic lead in water by solid-phase microextraction gas chromatography. *Anal. Chem.* **68:** 3008–14 (1996).
41. S.M. Fragueiro, F. Alava-Moreno, I. Lavilla, and C. Bendicho. Determination of tetraethyllead by solid phase microextraction-thermal desorption-quartz furnace atomic absorption spectrometry. *J. Anal. At. Spectrom.* **15:** 705–709 (2000).
42. J.P. Snell, W. Frech, and Y. Thomassen. Performance improvements in the determination of mercury species in natural gas condensate using an on-line amalgamation trap or solid-phase micro-extraction with capillary gas chromatography-microwave-induced plasma atomic emission spectrometry. *Analyst* **121:** 1055–60 (1996).
43. C. Dietz, J. Landaluze, P. Ximenez-Embun, Y. Madrid-Albarran, and C. Camara. SPME-multicapillary GC coupled to different detection systems and applied to volatile organo-selenium speciation in yeast. *J. Anal. At. Spectrom.* **19:** 260–66 (2004).
44. C.M. Barshick, S.-A. Barshick, M.L. Mohill, P.F. Britt, and D.H. Smith. Elemental and organometallic analyses of soil using glow discharge mass spectrometry and gas chromatography/mass spectrometry. *Rapid Commun. Mass Spectrom.* **10:** 341–46 (1996).
45. S. Tutschku, S. Mothes, and R. Wennrich. Preconcentration and determination of Sn- and Pb-organic species in environmental samples by SPME and GC-AED. *Fresenius' J. Anal. Chem.* **354:** 587–91 (1996).
46. P. Jitaru, H. Infante, and F. Adams. Simultaneous multi-elemental speciation analysis of organometallic compounds by solid-phase microextraction and multicapillary gas chromatography hyphenated to inductively coupled plasma-time-of-flight-mass spectrometry. *J. Anal. At. Spectrom.* **19:** 867–75 (2004).
47. L. Moens, T. De Smaele, R. Dams, P. Van Den Broeck, and P. Sandra. Sensitive, simultaneous determination of organomercury, -lead and -tin compounds with headspace solid phase microextraction capillary gas chromatography combined with inductively coupled plasma mass spectrometry. *Anal. Chem.* **69:** 1604–11 (1997).
48. J. Pawliszyn. *Solid Phase Microextraction: Theory and Practice*. Wiley-VCH, New York, NY, 1997, p. 247.
49. S. Aguerre, C. Bancon-Montigny, G. Lespes, and M. Potin-Gautier. Solid phase microextraction (SPME): a new procedure for the control of butyl- and phenyltin pollution in the environment by GC-FPD. *Analyst* **125:** 263–68 (2000).
50. J. Darrouzes, M. Bueno, C. Pecheyran, M. Holeman, and M. Potin-Gautier. New approach of solid-phase microextraction improving the extraction yield of butyl and phenyltin compounds by combining the effects of pressure and type of agitation. *J. Chromatogr. A* **1072:** 19–27 (2005).
51. G. Centineo, E. Blanco Gonzalez, and A. Sanz-Medel. Multielemental speciation analysis of organometallic compounds of mercury, lead and tin in natural water samples by headspace-solid phase microextraction followed by gas chromatography-mass spectrometry. *J. Chromatogr. A* **1034:** 191–97 (2004).
52. Y. Morcillo, Y. Cai, C. Porte, and J.M. Bayona, *16th International Symposium on Capillary Chromatography*. Hüthig, Heidelberg, Germany, 1994, pp. 864.
53. T. De Smaele, L. Moens, R. Dams, and P. Sandra. Metal speciation by SPME-CGC-ICPMS. *Applications of Solid Phase Microextraction.* Royal Society of Cambridge, Cambridge, UK, 1999, pp. 296–310.
54. N.G. Orellana-Velado, R. Pereiro, and A. Sanz-Medel. Solid phase microextraction gas chromatography-glow discharge-optical emission detection for tin and lead speciation. *J. Anal. At. Spectrom.* **16:** 376–81 (2001).
55. L. Dunemann, H. Hajimiragha, and J. Begerow. Simultaneous determination of Hg(II) and alkylated Hg, Pb and Sn species in human body fluids using SPME-GC/MS-MS. *Fresenius' J. Anal. Chem.* **363:** 466–68 (1999).
56. E. Dimitrakakis, C. Christina Haberhauer-Troyer, Y. Abe, M. Ochsenkuhn-Petropoulou, and E. Rosenberg. Solid-phase microextraction-capillary gas chromatography combined with microwave-induced plasma atomic-emission spectrometry for selenite determination. *Anal. Bioanal. Chem.* **379:** 842–48 (2004).
57. J. Sanz Landaluze, C. Dietz, Y. Madrid, and C. Camara. Volatile organoselenium monitoring in production and gastric digestion processes of selenized yeast by solid-phase microextraction-multicapillary gas chromatography coupled microwave-induced plasma atomic emission spectrometry. *Appl. Organom. Chem.* **18:** 606–13 (2004).
58. A.A. Boyd-Boland. "SPME-HPLC of Environmental Pollutants". In *Applications of Solid Phase Microextraction,* J. Pawliszyn, Ed. Royal Society of Chemistry, Cambridge, U.K., 1999, pp. 327.
59. L. Yang, Z. Mester, L. Abranko, and R. Sturgeon. Determination of total chromium in seawater by isotope dilution sector field ICPMS using GC sample introduction. *Anal. Chem.* **76:** 3510–16 (2004).
60. L. Abranko, L. Yang, R. Sturgeon, P. Fodor, and Z. Mester. Solid-phase microextraction for the determination of chromium in seawater. *J. Anal. At. Spectrom.* **19:** 1098–1103 (2004).
61. A.R. Roerdink and J.H. Aldstadt, III. Sensitive method for the determination of roxarsone using solid-phase microextraction with multi-detector gas chromatography. *J. Chromatogr. A* **1057:** 177–83 (2004).
62. M. Guidotti and M. Vitali. Determination of urinary mercury and methylmercury by solid phase microextraction and GC/MS. *J. High Resolut. Chromatogr.* **21:** 665–66 (1998).
63. T. De Smaele, L. Moens, P. Sandra, and R. Dams. Determination of organometallic compounds in surface water and sediment samples with SPME-CGC-ICPMS. *Mikrochim. Acta* **130:** 241–51 (1999).
64. http://www.irmm.jrc.be/rm/cert-reports/BCR-605_cert.pdf.
65. I. Arambarri, R. Garcia, and E. Millan. Assessment of tin and butyltin species in estuarine superficial sediments from Gipuzkoa, Spain. *Chemosphere* **51:** 643–49 (2003).
66. P. Grinberg, R.C. Campos, Z. Mester, and R.E. Sturgeon. A com-

parison of alkyl derivatization methods for speciation of mercury based on solid phase microextraction gas chromatography with furnace atomization plasma emission spectrometry detection. *J. Anal. At. Spectrom.* **18:** 902–909 (2003).
67. P. Montuori, E. Jover, R. Alzaga, S. Diez, and J.M. Bayona. Improvements in the methylmercury extraction from human hair by headspace solid-phase microextraction followed by gas-chromatography cold-vapour atomic fluorescence spectrometry. *J. Chromatogr. A* **1025:** 71–75 (2004).
68. H. Emteborg, E. Bjorklund, F. Odman, L. Karlsson, L. Mathiasson, W. Frech, and D.C. Baxter. Determination of methylmercury in sediments using supercritical fluid extraction and gas chromatography coupled with microwave-induced plasma atomic emission spectrometry. *Analyst* **121:** 19–29 (1996).
69. M.K. Donais, R. Saraswati, E. Mackey, R. Demiralp, B. Porter, M. Vangel, M. Levenson, V. Mandic, S. Azemard, M. Horvat, K. May, H. Emons, and S. Wise. Certification of three mussel tissue standard reference materials (SRM) for methylmercury and total mercury content. *Fresenius' J. Anal. Chem.* **358:** 424–30 (1997).
70. P. Grinberg, R.C. Campos, Z. Mester, and R.E. Sturgeon. Solid phase microextraction capillary gas chromatography combined with furnace atomization plasma emission spectrometry for speciation of mercury in fish tissues. *Spectrochim. Acta Part B* **58B:** 427–41 (2003).
71. L.R. Bravo-Sanchez, J.R. Encinar, J.I.F. Martinez, and A. Sanz-Medel. Mercury speciation analysis in sea water by solid phase microextraction-gas chromatography-inductively coupled plasma mass spectrometry using ethyl and propyl derivatization. Matrix effects evaluation. *Spectrochim. Acta Part B At. Spectroscopy* **59:** 59–66 (2004).
72. C. Devos, M. Vliegen, B. Willaert, F. David, L. Moens, and P. Sandra. Automated headspace-solid-phase micro extraction—retention time locked-isotope dilution gas chromatography—mass spectrometry for the analysis of organotin compounds in water and sediment samples. *J. Chromatogr. A* **1079:** 408–14 (2005).
73. U. Tamer, N. Ertas, Y. Udum, Y. Sahin, K. Pekmez, and A. Yildiz. Electrochemically controlled solid-phase microextraction (EC-SPME) based on overoxidized sulfonated polypyrrole. *Talanta* **67:** 245–51 (2005).
74. D.R. Parkinson, I. Bruheim, I. Christ, and J. Pawliszyn. Full automation of derivatization-solid-phase microextraction-gas chromatography-mass spectrometry with a dual-arm system for the determination of organometallic compounds in aqueous samples. *J. Chromatogr. A* **1025:** 77–84 (2004).
75. S. Mothes and R. Wennrich. Solid phase microextraction and GC-MIP-AED for the speciation analysis of organomercury compounds. *J. High Resolut. Chromatogr.* **22:** 181–82 (1999).
76. G.B. Jiang, J.Y. Liu, and K.W. Yang. Speciation analysis of butyltin compounds in Chinese seawater by capillary gas chromatography with flame photometric detection using in-situ hydride derivatization followed by headspace solid-phase microextraction. *Anal. Chim. Acta* **421:** 67–74 (2000).
77. G. Lespes, V. Desauziers, C. Montigny, and M. Potin-Gautier. Optimization of solid-phase microextraction for the speciation of butyl- and phenyltins using experimental designs. *J. Chromatogr. A* **826:** 67–76 (1998).
78. S. Aguerre, C. Pecheyran, and G. Lespes. Validation, using a chemometric approach, of gas chromatography-inductively coupled plasma-atomic emission spectrometry (GC-ICP-AES) for organotin determination. *Anal. Bioanal. Chem.* **376:** 226–35 (2003).
79. X. Yu, H. Yuan, T. Gorecki, and J. Pawliszyn. Determination of lead in blood and urine by SPME–GC. *Anal. Chem.* **71:** 2998–3002 (1999).
80. L.M. Smith, W.A. Maher, P.J. Craig, and R.O. Jenkins. Speciation of volatile antimony compounds in culture headspace gases of Cryptococcus humicolus using solid-phase microextraction and gas chromatography-mass spectrometry. *Appl. Organom. Chem.* **16:** 287–93 (2002).
81. Certified Reference Material PACS-2, Marine Sediment; National Research Council Canada: Otawa, Canada; 1997 (http://inms-ienm.nrc-cnrc.gc.ca/calserv/chemical_metrology_e.html#Certified).
82. Certified Reference Material DORM-2, Dogfish Muscle; National Research Council Canada: Otawa, Canada; 1999 (http://inms-ienm.nrc-cnrc.gc.ca/calserv/chemical_metrology_e.html#Certified).

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