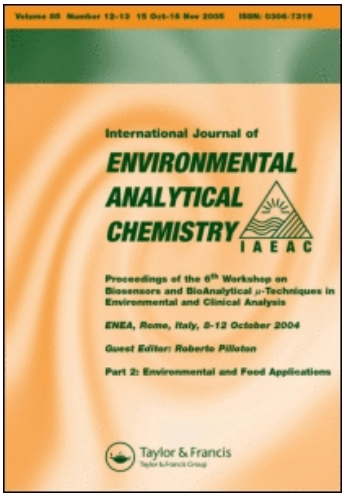

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Developments in the speciation and determination of alkylmetals (Sn, Pb) using volatilization techniques and chromatography-atomic absorption spectroscopy†

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The behavior and fate of heavy metals in the environment is related to the reactivity of their chemical species in the water phase. Further, alkylmetals are more toxic than their free ionic counterparts and usually their toxicity and impact on the biota increase with the size of the alkylgroup. However, their low concentrations in the environment (ng to pg/L) require highly sensitive techniques. We have developed several sensitive methods for the speciation and determination of alkyltins and alkylleads from aqueous samples. All are derived from volatilization of alkylmetals, preconcentration by cryogenic trapping on chromatographic packing material, speciation by mild thermal desorption, detection in a quartz heated furnace aligned in the beam of an atomic absorption spectrometer and electronic integration of the signal. This paper summarizes optimizing and limiting conditions from the different methods developed. Environmental application on these techniques on extractions of methyltin compounds from sediments are presented and discussed.

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INTRODUCTION

Tin is unsurpassed in the multiplicity of its applications in organic chemistry and is used in a wide variety of products such as stabilizers, industrial catalysts, and agricultural biocides.[1] Alkylated forms of metals are usually more toxic than their inorganic counterparts.[1,2] Results in France show that alkyltins inhibit the development of oysters[3] and alkylleads are believed to be responsible for the mortality of sea birds in England.[4] Like their inorganic forms,[5] toxicity and pathways of alkylmetals will be regulated by their partitioning between gaseous/aqueous phases and dissolved/particulate equilibrium in aquatic systems.

In addition to direct anthropogenic inputs, natural alkylation may occur through chemical or enzymatic methylations.[6] Successive environmental methylations of tin by a CH_3^- carbanion could yield all intermediate products leading to air transportable $(CH_3)_4Sn$.[7] Dismutation and disproportionation reactions contribute also to the distribution of tin and lead between soluble $(CH_3)_x \times (Sn, Pb)^{(4-x)+}$ and volatile $(CH_3)_4(Sn, Pb)$ species[6] and therefore control metal fluxes of metals between aqueous and gaseous phases of aquatics systems. The size of the alkylgroup also regulates the dissolved/particulate equilibrium in water. Under simulated estuarine conditions, methylated tin compounds behave differently. Most of $(CH_3)SnCl_3$ is adsorbed to suspended matter and $(CH_3)_2SnCl_2$ partitions between particulate and dissolved phases. The most toxic form, $(CH_3)_3SnCl$ stays mostly in solution and hence presents an immediate threat to the biota.[8]

Recent developments in analytical chemistry shed some light on these pathways. Volatilization of alkylmetals by derivatization, trapping and speciation on chromatographic packing material and detection with an element selective detector allow to address their low concentrations in the environment.[9] Methyltin and methyllead compounds can be derivatized after reaction with a Grignard reagent.[10,11,12] Butyltins are converted to their *n*-pentyl derivatives.[13] These methods require several steps and may lead to errors. Reduction of methyltin compounds with $NaBH_4$ is a simpler procedure.[1] We have initially developed a method for the determination of subnanograms amounts of methyl- and butyltin compounds using hydride generation, trapping in liquid N_2, speciation on chromato-

graphic packing material and detection in a quartz furnace aligned in the beam of an atomic absorption spectrophotometer.[14] A.A.S. was chosen for its ease of operation and high selectivity. This technique has been further improved for enhanced sensitivity with butyltin ions in water.[15] Slight modifications of the apparatus and the use of a new derivatization method allow the detection of picograms of methylated lead ions after a straightforward ethylation reaction.[16] We want to summarize in this paper methods developed on the same apparatus in order to outline critical parameters for the optimization of the signal and discuss limiting conditions. Environmental applications of the technique on preliminary extractions of methyltin compounds from sediments are presented and discussed.

EXPERIMENTAL

Apparatus and methods

The apparatus and methods (Figure 1) have been described previously.[14–16] Briefly, alkyltin hydrides are generated on the system in 100 mL round bottom pyrex flask by injection of $NaBH_4$ through an injection port. Alkylleads are derivatized in separate 120 mL hypovials sealed with crimp-on-Teflon lined septa. These vials are connected to the system by punching 2 needles through the septum

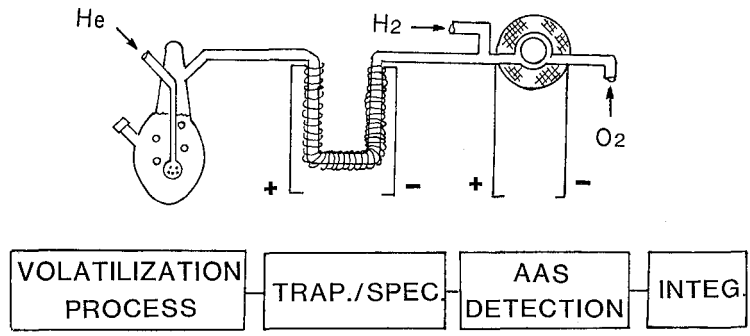

FIGURE 1 Schematic set up for the speciation and determination of organotin or organolead compounds.

allowing for the inlet and outlet of the carrier gas. The reaction flask can be by-passed with a four way valve. Teflon transference lines (2.5 mm id) are heated if necessary, inserted in Tygon or Teflon tubing wrapped with Nichrom wire (28 gauge). An optional water trap is immersed in a dry ice/acetone bath (−78°C). Volatile species are trapped on chromatographic packing material in liquid nitrogen (−196°C). This trap is wrapped with Nichrom wire (26 gauge) and is heated by a Variac after removal from the liquid nitrogen. Alkyl metals elute according to their boiling points and are detected in a quartz furnace aligned in the beam of an A.A.S.

The furnace (11 cm × 1.2 cm) is heated by 26 gauge wire supplied by a Variac and is wrapped by 2 rows of asbestos (0.8 cm). Helium is used as a carrier gas and hydrogen and oxygen are introduced in the furnace to optimize atomization. Alkyltins and alkylleads are determined with a 503 Perkin Elmer A.A.S. The electronic signal is filtered with a low pass filter (1.3 or 13 Hertz) amplified 10 times and integrated with a Hewlett–Packard 3392 A integrator.

Reagents

Deionized distilled water (DDW) was used in all experiments. $NaBH_4$ and $NaBEt_4$, methyl- and butyltins were purchased from Alpha Ventron (Danvers, MA, U.S.A.) and used without further purification. Methylleads were donated by the Ethyl Corporation (Baton Rouge, LA, U.S.A.) and prepurified before use. HCl, HNO_3 and NaOH were Fisher analytical grade. All glassware was soaked for 12 hours in 7% HNO_3 and rinsed before use.

Sediments extractions

Extractions of methylated tin compounds were performed on different types of sediments chosen for their different geochemical matrices. Surface (1–2 cm) sediments were collected with a Schipeck sampler in the Great Bay estuary (NH, U.S.A.) or in the Leman Lake (Switzerland). They were dried at 60°C and ground before storage. Reproducibility on total metal analyses (Cu, Zn) is better than 10% RSD. As little information is available on aqueous extraction procedures used for methyltin ions,[17] we have applied 3 different simple digestion methods. 0.5 g of dried sediments were digested with

either 5 mL of 5 N HNO_3, 5 mL of 5 N HCl or 10 mL of 0.1 N NaOH in 100 mL Pyrex centrifuge tubes. After addition of the leaching reagent, all tubes were sonicated for 1 hour and shaken for 12 hours in the dark at room temperature. Volumes were adjusted for 50 mL with DDW and centrifuged for 10 min. After centrifugation, leachates were collected in 50 mL volumetric flasks and stored at 4°C in the dark. Alkaline digestion leachates were acidified to pH 2 with concentrated HNO_3 prior storage. Alkyltin determinations were made on 20 mL aliquots.

RESULTS AND DISCUSSION

Techniques summarized here (Table I) involved 4 steps (Figure 1). Each of these steps includes several parameters critical for the speciation and sensitivity. Rapid optimization of these steps was made using a Simplex algorithm. Boundary values must be first determined in order to avoid shrinkage of the Simplex. This multivariate approach optimizes the response using a minimum number of experiments.

Volatilization

Major advantages of these techniques rely on the quantitative derivatization of soluble alkylmetals to their volatile species. Concentration by cryogenic trapping contributes to enhance the sensitivity. Hydride generation with a 4% solution of $NaBH_4$ allows the stripping of volatile methyl- and *n*-butyltin hydrides from sample solutions. In either case a buffer was avoided to insure low tin blanks and to allow successive reactions of $NaBH_4$ for butyltin compounds. In the later case, reaction of $NaBH_4$ under very acidic conditions yields a strong production of H_2 and increases the scrubbing efficiency for lower boiling point compounds. The use of He as scrubbing and carrier gas requires high flow rates but increases atomization processes.[18] Continuous agitation with a magnetic stirrer and direct injections of $NaBH_4$ in the sample through the septum port gives good reproducibility and high scrubbing efficiency. Derivatization with $NaBEt_4$ has to be made separately for methyllead ions in sealed hypo-vials. The ethylation

TABLE I

Critical parameters for the speciation and determination of organometallic compounds

		$Me_{(x)}Sn^{(4-x)+}$	$n\text{-}Bu_{(x)}Sn^{(4-x)+}$	$Me_{(x)}Pb^{(4-x)+}$
Volatilization	Flask	100 mL	100 mL	50 mL
	Stripping time	5–10 min	8 min	8.7 min
	pH	2 to 8	1.6–2.2	4.1
	Reactant conc.	1 ml 4% Na BH_4	2×2.5 ml 6% Na BH_4	3 ml 0.43% Na BEt_4
Trapping/speciation	Water trap	45×0.6 (id) cm	none	45×0.5 (id) cm
	Speciation trap	45×0.6 (id) cm Pyrex	35×0.4 (id) cm in *Teflon*	45×0.5 (id) cm Pyrex
	Packing support	2.5 g Chromosorb GAW DMCS 40/60	2.5 g Chromosorb GAW DMCS 40/60	5.2 g Chromosorb WAW DMCS 80/100
	Coating phase	SP 2100 3–10%	SP 2100 3%	SP 2100 10%
	Carrier gas He	400 mL/min	400 mL/min	102 mL/min
	Warming rate	48°C/min	48°C/min (2 min) then 145°C/min	50°C/min
	Temp. Transference lines	25°C	150°C	95°C
Atomization	Temp. Atomization	850°C	750°C	950°C
	Atomization gas: H_2	1200 mL/min	833 mL/min	18 mL/min
	O_2	100 mL/min	21 mL/min	none
	Source lamp	Sn EDL	Sn EDL	Pb Hollow Cathode
	Wavelength	224.6 nm	224.6 nm	217 nm

reaction kinetics are slower than hydride generation but are completed with 10 min of shaking. Hypo-vials can be connected to the system and then follow similar operating conditions described for alkyltins. Preliminary results have also been obtained with methyl mercury after derivatization with $NaBEt_4$.[16] This derivatization method could possibly also be extended to methyltin ions. The scrubbing time, however, is a limiting factor. Long scrubbing times achieve higher recoveries of volatile species from complex sample solutions but bring water to the system. A water trap (−78°C) is used for methyltins and methylleads but irreversibly stops butyltins compounds. For these compounds, the water trap is removed and a compromise has to be found between stripping time and the flow rate of the carrier gas. Deterioration of the packing material occurs rapidly and the speciation trap has to be replaced every 15 runs. The water trap may be used with methyltins and methylleads and 60 runs can be made before replacement of the packing phase.

Trapping and speciation

The high vapor pressure of derivatized compounds allows their concentration by trapping on chromatographic packing material in liquid N_2. This step is critical for both sensitivity and speciation. Separation occurs as a combination of processes and is not a true chromatographic process. Compounds first elute according to their boiling points during initial warming of the trap after its removal from the liquid N_2. Changing the loading on the support does not modify significantly retention time during this period. The flow rate is important in order to allow complete trapping. A high He flow rate will prevent the complete trapping of compounds in the cryogenic trap. Chromatographic separation only occurs after reaching room temperature. Light loading of the SP 2100 non polar stationary phase gives well defined peaks. A 10% coating provides best separation of methyltin compounds but 3% are adequate for most alkylmetal species (Figure 2). Quality of the stationary phase does not only provide separation but also prevents catalytic decomposition of compounds on the solid support. The He flow rate and the mesh of the solid support are also important in achieving good separations. For compounds such as butyltins, the speciation trap undergoes a 500°C temperature change within 4 min., leading to a

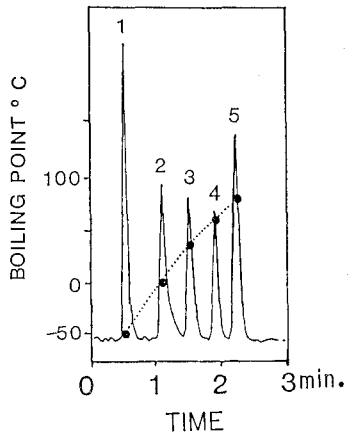

FIGURE 2 Chromatogram of methyltins compounds (as Sn) in waters: 1, SnH_4 (8 ng), 2, $MeSnH_3$(5 ng), 3, Me_2SnH_2(5 ng), 4, Me_3SnH (5 ng), 5, Me_4Sn(7 ng). Packing material: 2.5 g of SP 2100 3% on Chromosorb 40/60 GAW DMCS. He flow rate is 400 mL/min.

rapid expansion of the packing phase and a decrease of the flow rate. These drawbacks may be overcome. Important flow rates of the carrier gas, high pressure in the system and lower mesh size contribute to the good separation of butyltins compounds. A low He flow rate is required for the separation of alkylleads owing to the length of the trap and the size of the packing support used.

Atomization

The use of an A.A.S. as a detector combines high specificity and high sensitivity. Increased sensitivity was achieved by a careful design of the atomization cell[14,19] and by the addition of O_2 and H_2 to the quartz furnace.[14] Table I indicates that flow rates are very different according to elements determined. Methyl- and *n*-butyltin compounds require a high H_2 flow but little amount of O_2 flow. The presence of O_2 is however critical in regulating the sensitivity of the setup. Ratio of atomization gas are not absolute for their need to be slightly readjusted with each furnace replacement. The position of the mixing zone of O_2 and H_2 in the furnace may also affect the overall sensitivity by a factor of 1.5–2. This fact suggests that

atomization processes may occur by collision with free radicals H· as previously described for arsine or selenium.[20,21] Oxygen is not required for the atomization of alkylleads. They may need less energy to be disocciated in the quartz furnace since the Pb—C is much weaker than the Sn—C bond.[22] Further incomplete atomization is very likely for all three methods showing a decrease in sensitivity with increased size of alkylgroups atomized.[14–16] The temperature of the furnace does not have a significant effect on atomization but rather conditions its life time.

Signal processing

Other improvements for gain in sensitivity were achieved with careful processing of the A.A.S. signal. The electronic noise of the apparatus was recorded and a low pass filter (1.3–13 Hz) was designed accordingly to improve the signal to noise ratio. Amplification ($\times 10$) and integration with an H.P. integrator allow the detection of sub-nanograms amounts of Sn or Pb. Surface area mode always gave better results for reproducibility than peak height even with gradual deterioration of the packing phase. The use of an EDL lamp for Sn instead of a hollow cathode contributes to increase the signal to noise ratio, allowing lower detection limits.

Operating conditions

Results of calibration curves, reproducibility and detection limits obtained with DDW are summarized in Table II and are among the

TABLE II

Limits of linearity, reproducibility, and detection limits

Compounds	Limit of linearity-ng	% RSD	Detection limits†. pg.	Reference
$Me_{(x)}S_n^{(4-x)+}$	30	3–8[a]	30	14
$n\text{-}Bu_{(x)}Sn^{(4-x)+}$	8–13	5–18[b]	11–45	15
$Me_{(x)}Pb^{(4-x)+}$	1	9[c]	9	16

†Based on 3σ of blank noise.
[a]For 15 ng as Sn.
[b]For 2 ng as Sn.
[c]For 0.2 ng as Pb.

lowest reported in the literature. Under these conditions no redistribution using mixed standards were observed with all three methods used. Reducing the size of the setup and of the dead volume may account for the improvement achieved with butyltin over methyltins. Highest sensitivity is obtained with methyllead ions in comparison to alkyltin compounds. This difference of sensitivity observed on the same apparatus may occur through higher dissociation of alkyllead in the furnace owing to the weaker Pb—C bond and to the general higher sensitivity of Pb over Sn as observed with graphite furnace atomization.[23]

Limiting environmental conditions

The determination of methyl- and *n*-butyltin compounds from environmental water samples is now well established.[1,24] In comparison little information is available on methylated tin concentrations in sediments. This compartment of aquatic ecosystem is, however, very important since metal pollutions are often assessed from sediment analyses.[25] The straightforward ethylation technique is inappropriate for the determination of environmental mixed methylated lead species due to direct anthropogenic inputs of some of these compounds but has been applied with success to model environmental conditions.[26] Brinckman *et al.*[27] have detected alkyltin hydrides in waters of the Chesapeake Bay but no results have been reported for sediments. Organotin compounds will require different extraction procedures than used for total metal determination. It is essential to avoid breaking the Sn—C bond in order to assess the real distribution of methyltins in sediments. Table III presents results obtained for 3 different extraction procedures performed on three different sediments. Inorganic tin will be considered as Total Recoverable Inorganic Tin (TRISn) since results indicate very different recovery rates. The total tin concentration is the sum of TRISn and methylated tin species. Extractions with an alkaline digestion procedure achieves highest recovery for total Sn in general. Within different organotin species, TRISn and trimethyltin compounds yield highest leaching rates with the NaOH digestion. This procedure favors the release of organic compounds (notably humic substances) from the sediments[28] and suggest possible preferential affinities of inorganic tin and trimethyltin with the humic fraction of the

TABLE III

Extractions of TRISn and methyltins compounds from sediments (3 replicates) μg/g dry weight

Extractant		Great Bay (est. U.S.A.)		Plaine Centrale (lake Switz.)		Vidy (lake Switz.)	
		$\bar{X}$	% RSD	$\bar{X}$	% RSD	$\bar{X}$	% RSD
HCl	TRISn	0.007	n.s.	0.015	n.s.	0.013	45
	$MeSn^{3+}$	0.083	85	0.354	79	0.023	90
	Me_2Sn^{2+}	0.037	19	0.027	80	0.023	38
	Me_3Sn^{+}	0.395	11	0.445	33	0.328	51
	Total Sn	0.522	—	1.091	—	0.387	—
HNO_3	TRISn	0[a]	n.s.	0	n.s.	0.031	80
	$MeSn^{3+}$	0.215[a]	92	0.017	55	0.028	36
	Me_2Sn^{2+}	0.044[a]	n.s.	0.028	82	0.028	35
	Me_3Sn^{+}	0.548[a]	28	0.422	44	0.403	27
	Total Sn	0.807[a]	—	0.467	—	0.490	—
NaOH	TRISn	0.406	40	0.280	56	0.200	17
	$MeSn^{3+}$	0.042	52	0.056	40	0.042	29
	Me_2Sn^{2+}	0.048	57	0.033	21	0.039	49
	Me_3Sn^{+}	0.741	46	0.543	15	0.552	31
	Total Sn	1.236	—	0.906	—	0.833	—

[a]2 replicates.
n.s.: not significant.

sediment. Trimethyltin is the dominant species and its occurrence is not dependent of the method used. Presence of trimethyltin as predominant organotin species in unpolluted sediments has also been mentioned by Tugrul *et al.*[17] Alkaline leachate also gives more reproducible results but are still generally poor.

These results raised several important questions. First, are these extraction procedures strong enough to quantitatively extract all methylated tin species from the sediment? Results obtained reflect their adsorption capacities.[8] Second, what is the stability of alkylmetals in the digestion leachate? Partially methylated tin species may react with natural S^{2-} ligands to yield volatile $(CH_3)_4Sn$.[29] Dismutation and disproportionation reactions[6] may also artificially modify the initial speciation of tin from the sediment. Further, if interferences from dissolved trace metal are unlikely due to their low concentrations when analyzing water samples with hydride generation, they however, may significantly inhibit the $NaBH_4$ reduction process with sediment leachates enriched in metal.[30] Finally, organotin sulfides react consistently and non-quantitatively with $NaBH_4$ and may account for the poor reproducibility observed.[31] If these methods are suitable for the determination of alkyltins in waters, there is still an urgent need for the determination of alkyltins in solid matrices in order to assess their pathways and speciation within sediments.

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