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A Novel Technique for Direct Derivatization of Ionic Organotin and Alkyl-lead Compounds in Sediment: Simultaneous Determination of Organotin and Alkyl-lead Compounds in Sediment by Gas Chromatography–Plasma Atomic Emission (GC–AED) Dual-channel Detection

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A direct derivatization carried out on sediment slurries and simultaneous speciation of organotin and alkyl lead in sediments is described. Simultaneous determination was performed using dual-channel operation of the AED detector. Direct contact of phentylmagnesium bromide with the sediment improved drastically the recovery of the monobutyltin (MBT) species. The combined complexation/extraction/derivatization procedure and the dual-channel AED operation reduced the analysis time. Analysis of a Certified Reference sediment, PACS-1, demonstrated the accuracy of the method. The absolute detection limits (3 × noise level) are 0.5 pg and 0.2 pg respectively for tin and lead. The relative detection limits for sediment (1 g sample) are 2.5 ng g^{-1} and 1 ng g^{-1} respectively for organotin and alkyl-lead, expressed as the metal. The results of the analysis of some environmental samples are given. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

The determination of organometallic compounds in environmental materials generally involves extraction of the analytes by a complexing agent followed by derivatization of the compounds for GC separation and final quantification with an element-specific detector. This basic procedure of sample preparation and speciation for organometallic compounds in environmental samples has been used over the last decade for organotin and alkyl-lead compounds. Reviews of the different extraction and derivatization techniques are available.[1, 2]

The extraction of analytes from sediment for speciation analysis has always been a challenging problem for analytical chemists, and organometallic compunds are no exception. For the non-polar, tetra-substituted organometallic compounds, such as R_4Pb, R_4Sn (R = alkyl or aryl groups) etc., extraction with solvent alone can generally isolate them from water, from sediment and even from biological matrices. However, for the ionic organometallic species such as $R_nPb^{(4-n)+}$ and $R_nSn^{(4-n)+}$, a complexing agent is usually required to isolate them from the matrices for further derivatization. Examples are tropolone for organotin compounds, and sodium diethyldithiocarbamate (NaDDC) for organotin and alkyl-lead compounds. All such methods developed over the recent years have followed a similar pattern.

Recently, new techniques such as supercritical fluid extraction (SFE)[3–5] and microwave-assisted extraction[6, 7] have been introduced for the extrac-

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tion of butyltin compounds from sediment. These techniques have reduced the operation time and improved the extraction recovery of some species that are difficult to extract, e.g. monobutyltin.[8]

Numerous developments have also been made in analytical techniques to achieve specificity and sensitivity. In addition to earlier element-specific GC–AAS systems, more sophisticated systems such as GC–ICP, HPLC–ICP–MS etc., have been applied. The recent microwave plasma emission detection system (AED) has lowered the detection limit to the picogram level.

Many analytical methods have been reported for the determination of organotin and alkyl-lead in sediment. However, publications on simultaneous determination of both alkyl-lead and butyltin in sediment are extremely scarce.[9, 10] The two published methods have their disadvantages. The first[9] used micellar electrokinetic capillary chromatography (MECK) to determine two trialkyl-lead and two trialkyltin compounds in solid samples after supercritical and subcritical fluid extraction, but the compounds studied did not include important species such as dibutyltin (DBT), monobutyltin (MBT) and the other dialkyl-lead species which are the corresponding degradation products of the tributyltin and trialkyl-lead species. The second study[10] directly derivatized the organometals (lead, mercury, tin) in an aqueous sediment suspension with sodium tetraethylborate, followed by GC–ICP–MS determination. However, the major drawback was the use of the ethylation-derivatization technique, which is not able to differentiate some environmentally important ethyl-lead species originally present in the sample.

Plasma atomic emission detection has the multi-element feature which can simultaneously and selectively determine several elements by using their discrete channels. If both organolead and organotin can be extracted and derivatized by the same reagents, the extract then can be analysed by simultaneous operation of the lead and tin channels.

The present study reports a novel approach to avoid the extraction and isolation steps for the analytes from sediment, by simultaneously carrying out the complexation/extraction and derivatization of the ionic organotin and alkyl-lead species. The advantages are fewer operations, improved recovery of the mono- and di-butyltin species which were often limited by extraction, and time savings because of the simultaneous two-channel operation. Applications of the techniques to environmental samples are presented.

EXPERIMENTAL

Apparatus

The GC–AED system consists of a gas chromatograph (HP model 5890, Series II, Hewlett–Packard, PA, USA) equipped with a split/splitless injection port, an HP microwave plasma atomic emission detector (model 5921A) and an HP automatic sampler (Model 7673A). A megabore column (DB-17ms), coated with 50% phenyl, 50% methyl-polysiloxane (medium polarity) was supplied by J & W Scientific, Falsom, CA, USA. The system was computer-controlled using the HP3592A ChemStation software. Optimal operation parameters of the GC–AED system for tin and lead are given in Table 1. An ultrasonic processor, Vibra cell model VC 600 (CT, USA) was used for sample sonication.

Reagents

Solvents and common reagents were of analytical grade. Distilled water further purified by a Milli-Q (Millipore, Bedford, MA, USA) system was used throughout. The carrier gas for the GC–AED system was high-purity helium (99.999%). Reagent gases for the AED were oxygen (99.999%) and hydrogen (99.999%), all supplied by Canox Ltd (Mississauga, Canada). Butyltin chlorides (tributyltin (TBT), DBT, MBT), trimethyl-lead chloride, triethyl-lead acetate and tripropyl-lead acetate were obtained from Alfa Chemicals (Ward Hill, MA).

Stock standard solutions of organotin and trialkyl-lead compounds (100 μg/ml^{-1} as the metal) were prepared in toluene or in methanol and diluted for subsequent use. These stock solutions, when stored in amber glass bottles in the refrigerator, are stable for periods of up to several months without noticeable deterioration. The standard trialkyl-lead solutions (100 μg Pb ml^{-1}) for preparing the dialkyl-lead standard solutions were made up in distilled water. The corresponding dialkyl-lead stock solutions (100 μg Pb ml^{-1}) were prepared by adding three drops of iodine monochloride solution (ICl) to 3–4 ml of the above trialkyl-

Table 1. GC–AED operation parameters for lead and tin compounds

GC parameters	
Injection port	Splitless
Injection port temperature	250 °C
Column	DB-17ms, 30 m × 0.25 mm i.d.
Column head pressure	He, 150 kPa (22 psi)
Temperature programme	70 °C (0.5 min)–20 °C min–320 °C (2.5 min)
AED parameters	
Transfer line	DB-17ms
Transfer line temperature	320 °C
Cavity temperature	320 °C
Solvent vent off time	3 min
Spectrometer purge gas	N_2 at 2 l min^{-1}
He make-up gas	250 ml min^{-1}
Pb wavelength	261 nm
Sn wavelength	271 nm
H_2 pressure	482 kPa (70 psi)
O_2 pressure	138 kPa (20 psi)

lead standards. The trialkyl-lead compounds were rapidly converted to the corresponding dialkyl-lead species.[11] The addition of a small amount of ICI did not significantly change the concentration of the trialkyl-lead standards. The standard solutions of dialkyl-lead were prepared by diluting the stock solutions with methanol. The dialkyl-lead solutions so prepared are stable for at least seven days at room temperature. However, dialkyl-lead solutions prepared in this manner should not be mixed with the trialkyl-lead standards in case the residual ICI acts on the trialkyl-lead.

Iodine monochloride was prepared by adding potassium chloride (11 g) to 40 ml of water containing 44.5 ml of concentrated HCl. Potassium iodate (7.5 g) was slowly added with stirring until the iodine so formed gradually redissolved to give a light brown solution. This solution can be kept for months at room temperature in an amber glass bottle.

The Certified Reference sediment PACS-1 was obtained from the National Research Council of Canada, Ottawa (NRCC).

EXPERIMENTAL PROCEDURES

Extraction and derivatization of ionic organometallic compounds (tin and lead) in sediment

Sediment samples were freeze-dried and stored in amber glass bottles at 4 °C before analysis. Chelation/extraction/derivatization was carried out on sediment (1 g) suspensions in 10 ml of toluene containing 0.02 g sodium diethyldithiocarbamate (NaDDC) in a 40-ml Teflon tube. After addition of 100 μl of a 10 μg Sn ml^{-1} tripropyltin solution as internal standard, the mixture was placed in a cold-water bath in a 100-ml beaker and sonicated for 5 min at a pulse rate of 60% at power level 7 in the ultrasonic processor. The resulting sediment slurry was placed on a vibrator while 2 ml of 2 M pentylmagnesium bromide was added dropwise to the slurry. The mixture was allowed to stand for 10 min, then 10 ml of 0.5 M H_2SO_4 was added to destroy the excess pentylmagnesium bromide. After centrifugation at 4000 rpm for 3 min, the organic layer was removed quantitatively into a 50-ml glass tube and washed with 10 ml of 1 M NaOH to remove the diethyldithiocarbamic acid and other acidic impurities from the sediment. The organic layer was then transferred to a 50-ml round-bottomed flask and evaporated in a rotary evaporator almost to dryness. Two aliquots of 1 ml hexane were added to dissolve the residues. The dark solution was cleaned up with an alumina column (1 cm Na_2SO_4 was placed on top of 5 cm alumina in a 1.5-cm diameter column) which was eluted with 25 ml of hexane. The eluate was reduced to 1–2 ml under reduced pressure, transferred to a test tube and evaporated to 1 ml with nitrogen; 1 μl was injected into the GC–AED system for analysis.

Reference sediment (PACS-1) was used to evaluate the validity of the procedure for the butyltin species. Because there was no reference sediment for alkyl-lead compounds, spiked sediment samples were used to assess the alkyl-lead recovery.

RESULTS AND DISCUSSION

Optimization of GC–AED operation parameters

For efficient separation of a large number of organotin compounds, a mid-polarity capillary chromatographic column (DB-17ms) was used. It has a higher efficiency in separating the 15 species of pentylated organotin compounds, in particular for the cyclohexyltin and phenyltin, which have the same carbon number and which are not clearly separated on some non-polar columns. DB-17ms also has a higher maximum operating temperature (320/340 °C compared with 280/300 °C with DB-17) which facilitated earlier emergence of the late-component peaks and shortened the analysis time.

The optimal make-up gas flow for both organotin and alkyl-lead components was determined by repeated injections of a mixed standard solution containing three pentylated butyltin (MBT, DBT, TBT) and four alkyl-lead species (Me_3Pb^+, Me_2Pb^{2+}, Et_3Pb^+, Et_2Pb^{2+}) to observe the signal response with changes in make-up gas flow. Similar patterns of response with make-up gas flow rates were observed for the three butyltin and the four alkyl-lead compounds. For simplicity, only the chromatograms of pentylated tributyltin (Bu_3PeSn) and triethyl-lead (Et_3PePb) were selected for presentation (Fig. 1) to show the effects. The optimum flow rate of 250 ml min^{-1} was chosen for simultaneous determination of both elements. The make-up flow rate was measured at the cavity vent outlet, with the reagent gases and spectrophotometer window purge gas turned off.

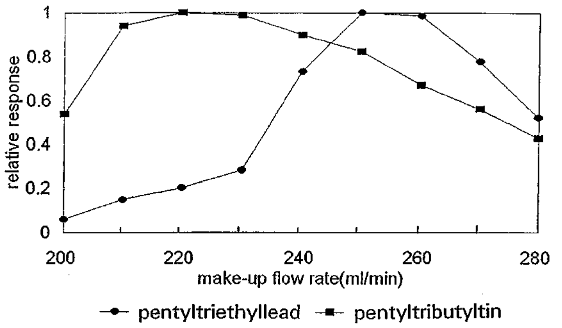

Figure 1 Optimization of make-up gas flow for pentylated tributyltin and pentylated triethyl-lead; 1 μl injection contained 100 pg as the metal.

Calibration

The concentration of organotin compounds could be calculated either from internal standard tripropyltin (Pr_3Sn^+), or by using an external standard. The concentration of alkyl-lead compounds was calculated by using an external standard (Et_3Pb^+) directly derivatized with pentylmagnesium bromide. All the organotin compounds have a linear range of 2.5–1000 ng ml^{-1} with correlation coefficents ranging from 0.999 to 1.000; correlation coefficients range from 0.998 to 1.000 for the four ionic alkyl-lead compounds in the concentration range 1–100 ng ml^{-1}. The absolute detection limits (measured at 3×noise level) were 0.5 pg and 0.2 pg, respectively, for tin and lead. The relative detection limits for sediment (1 g) were 2.5 ng g^{-1} for tin and 1 ng g^{-1} for lead.

Extraction of ionic butyltin and alkyl-lead compounds from sediment

The extraction of ionic alkyl-lead species from water and sediment using NaDDC as complexing agent has been known for some time.[12–14] Its application to the extraction of butyltin compounds in water has also been successful, but its application to sediment has not been fully investigated.[15]

Experiments were carried out to evaluate the complexation efficiency of several complexing agents for butyltin compounds from the reference sediment PACS-1. Since the recovery of the TBT and DBT species was always satisfactory, the investigation was focused on the recovery of the MBT species. Other dithiocarbamate complexing agents, including DDDC (diethylammoniumdiethyldithiocarbamate) and APDC (ammonium pyrrolidine dithiocarbamate), were compared for their efficiency in complexing butyltins from sediment because of their higher solubility in toluene than NaDDC (0.095 g/100 ml toluene, 20 °C).[16]

Table 2 shows that neither DDDC nor APDC recovered any MBT from PACS-1. Therefore NaDDC was chosen for further investigation. In studying the efficiency of derivatization with pentylmagnesium bromide (PeMgBr) addition to

Table 2. Determination of MBT (μg Sn g^{-1}) in PACS-1 by different complexing agents[a]

Complexing agent	Method 1[b]	Method 2[c]
DDDC	0	0.343
APDC	0	0.503
NADDC	0.402	0.751

[a] PACS-1, 1 g; DDDC, APDC, NaDDC, 0.02 g in 10 ml toluene.

[b] Method 1: after sonification, the toluene was separated from sediment before pentylation.

[c] Method 2: after sonification, PeMgBr was added directly to the complexing agent/toluene/sediment mixture.

Table 3. Determination of butyltin compounds (μg Sn g^{-1}) in PACS-1 by the present method[a]

	TBT	DBT	MBT
Certified value	1.27 ± 0.22	1.16 ± 0.18	0.28 ± 0.17
This method	1.12 ± 0.03	0.98 ± 0.06	0.76 ± 0.10

[a] $n = 4$; ± standard deviation.

the separated toluene extract (Method 1) versus direct addition of PeMgBr to the complexing agent/toluene/sediment slurry without phase separation (Method 2), it was observed that pentylation of the butyltin species in the presence of sediment distinctly enhanced the recovery of MBT from PACS-1. From the data summarized in Table 2, pentylation carried out on the NaDDC/toluene extract (Method 1) only recovered about half of the MBT species in the sediment, whereas pentylation on the NaDDC/ toluene including the sediment slurry almost doubled the recovery of MBT. Such observations substantiate the fact that MBT has a strong adsorption affinity to the sediment, and that direct contact of PeMgBr with the sediment (Method 2) could facilitate the derivatization of the organometallic species adsorbed or bound to the sediment.

The complexation/extraction of organometallic compounds from sediment involves transportation of compounds from solid to liquid phases, which is a matter of equilibrium thermodynamics. Pentylation derivatization of ionic organometallic compounds is a peralkylation reaction whereby the ionic organometal species $R_nM^{(4-n)+}$ (M = Sn, Pb) are pentylated to the nonpolar, low-boiling, tetra-substituted forms, $R_nPe_{(4-n)}M$, amenable for GC separation. The combined, simultaneous processes of complexation/extraction/derivatization all favour the removal of organometallic compounds from the sediment. To our knowledge, the direct addition of Grignard reagent (alkylmagnesium bromide) to sediment slurries is a novel approach which has not been attempted, although direct *in-situ* derivatization of butyltin species in sediment leachate with sodium tetraethylborate ($NaEt_4B$) has been adopted.[7,10,17,18]

The procedure was validated by the analysis of a reference sediment PACS-1 (Table 3). While the recovery of TBT and DBT were satisfactory, the recovery for MBT was higher than the certified value. The high value, however, was in agreement with several other determinations reported in the literature.[7,19,20] All these methods that produced high MBT recoveries employed acidic digestion of the sediment and polar solvents for the extraction. The reason for the low recoveries is probably that MBT is not completely recovered from the sediment by most of the previous procedures. The discrepancy has also been discussed in a recent study.[7]

GC–AED chromatograms in Fig. 2 show the simultaneous determination of a standard solution containing pentylated alkyl-lead and Pb^{2+} together with organotin and Sn^{2+} compounds by the present procedure by two-channel operation of the AED. There are no cross-interferences of signals for the two elements in the chromatograms.

Interference of inorganic lead

In view of the findings of an early study on the interference by inorganic Pb^{2+} in the determination of ionic alkyl-lead compounds by NaDDC extraction followed by GC–AAS determination,[14] experiments were carried out to investigate the effects of Pb^{2+} (100 μg Pbg^{-1}) on the recovery of ionic alkyl-lead (50 ng Pb g^{-1}) and organotin compounds (500 and 50 ng Sn g^{-1}) in sediment.

The standard solutions of orgnotin compounds (1000 ng Sn ml^{-1}) were spiked to 1 g of sediment and allowed to dry in air before analysis. The standard solutions (1000 ng Pb ml^{-1}) of trialkyl-lead compounds (Et_3Pb^+; Me_3Pb^+ in methanol) and the corresponding standard solutions of dialkyl-lead (Et_2Pb^{2+}; Me_2Pb^{2+} in methanol) were spiked to 1 g of sediment and allowed to dry in air at room temperature before the compelxation/derivatization reactions. The recoveries were evaluated against respective

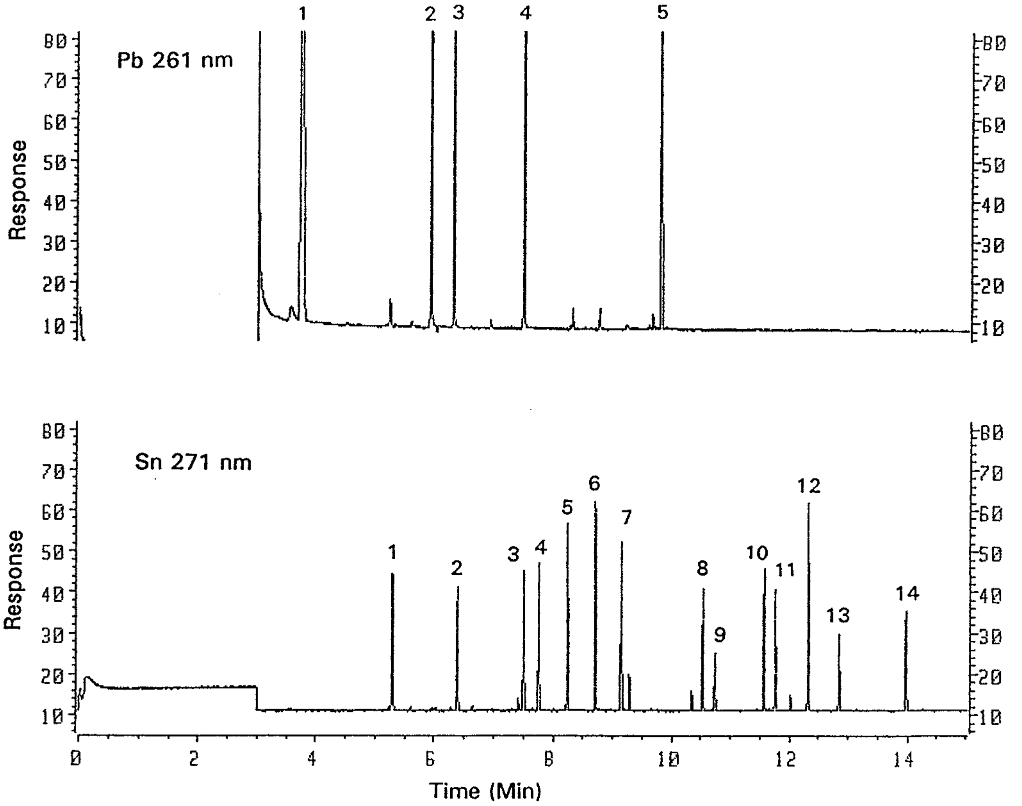

Figure 2 The chromatograms of alkyl-lead and organotin compounds. Alkyl-lead compounds: 1, Me_3PePb; 2, Et_3PePb; 3, Me_2Pe_2Pb; 4, Et_2Pe_2Pb; 5, Pe_4Pb. Organotin compounds: 1, Me_2Pe_2Sn; 2, Pr_3PeSn; 3, $MePe_3Sn$; 4, Bu_3PeSn; 5, Bu_2Pe_2Sn; 6, $BuPe_3Sn$; 7, Pe_4Sn; 8, $OctPe_3Sn$; 9, $PhPe_3Sn$; 10, c-Hex_2Pe_2Sn; 11, Oct_2Pe_2Sn; 12, Ph_2Pe_2Sn; 13, c-Hex_3PeSn; 14, Ph_3PeSn. Each peak represents 100 pg of Pb or Sn.

mixtures of standard solutions as external standards.

Results summarized in Table 4 did not indicate any significant interferences in the determination of organotin by the present procedure due to the presence of high levels of Pb^{2+}. The overall recoveries of 14 species of organotin spiked at two concentration levels were satisfactory.

Similarly, Table 4 also indicates no apparent interferences with the recovery of alkyl-lead compounds from sediment caused by the presence of inorganic Pb^{2+}. The interference with recovery of ionic alkyl-lead species observed in an earlier study[14] was possibly due to the consumption of the complexing agent NaDDC by the large quantity of inorganic Pb^{2+} compounds present in the sediment, resulting in incomplete extraction of the ionic alkyl-lead species for derivatization. The advantage of the present method is to allow a large amount (2 ml) of pentyl Grignard reagent to come into direct contact with the sediment dispersed in an organic matrix containing the complexing agent. Thus the complexation/extraction and derivatization occurred simultaneously. Such a combination of reactions enhanced recovery of strongly adsorbed organometallic species. This may explain why intereference was not observed in the present procedure in the presence of large quantities (100 μg Pb g^{-1}) of Pb^{2+}.

In the course of the investigation of the recovery of spiked alkyl-lead compounds in sediment, it was observed that, in some sediments, the spiked trialkyl-lead compounds (Et_3Pb^+, Pr_3Pb^+) were converted to the corresponding dialkyl species (Et_2Pb^{2+}, Pr_2Pb^{2+}) (Table 5). Parallel experiments run without the sediment did not show such conversions. It is possible that certain metal ions in some types of sediment could cause transalkylation reactions whereby the trialkylmetal transferred part of its alkyl groups to other metal ions. Such reactions

Table 4. Recoveries of organotin and alkyl-lead compounds from spiked sediment[a] (containing 100 μg Pb^{2+}/g sediment)

	Recovery[c] (%)	
Organotin compound[b]	Spike at 50 ng Sn g^{-1}	Spike at 500 ng Sn g^{-1}
DMT	94 ± 13.9	100.0 ± 0.4
TPrT	82.3 ± 11.2	98.2 ± 8.6
MMT	90.0 ± 11.9	94.1 ± 3.1
TBT	87.9 ± 7.1	101.0 ± 1.7
DBT	87.2 ± 9.4	92.4 ± 11.2
MBT	99.4 ± 17.0	93.4 ± 2.6
TPeT	90.1 ± 7.9	100.7 ± 2.7
MOT	94.5 ± 13.4	84.4 ± 0.8
MPhT	102.3 ± 18.8	62.1 ± 2.6
D-c-HT	102.5 ± 8.9	94.9 ± 0.9
DOT	90.0 ± 8.6	91.7 ± 0.7
DPhT	90.6 ± 7.7	94.3 ± 0.3
T-c-HT	91.4 ± 10.6	90.7 ± 0.5
TPhT	92.2 ± 8.1	90.6 ± 1.6
Alkyl-lead compound	Spike at 50 ng Pb g^{-1}	
Me_3Pb^+	87.4 ± 13.6	
Et_3Pb^+	86.7 ± 17.7	
Me_2Pb^{2+}	77.6 ± 11.5	
Et_2Pb^{2+}	97.6 ± 11.6	

[a] Organotin spiked levels: 500 ng Sn/g and 50 ng/Sn/g sediment; alkyl-lead spikes, 50 ng Pb/g sediment; Pb^{2+} added in form of $Pb(NO_3)_2$.

[b] Abbreviations: DMT, dimethyltin; TPrT, tripropyltin; MMT, monomethyltin; TBT, tributyltin; DBT, dibutyltin; MBT, monobutyltin; TPeT, tripentyltin; MOT, monooctyltin; MPhT, monophenyltin; D-c-HT, dicyclohexyltin; DOT, dioctyltin; DPhT, diphenyltin; T-c-HT, tricyclohexyltin; TPhT, triphenyltin.

[c] $n=3$; ± standard deviation.

Table 5. Recovery (%) of spiked trialkyl-lead compounds from different sediments[a]

Sediment	Me_3Pb^+	Et_3Pb^+	Pr_3Pb^+
Charlottetown Harbour	88.0	86.7	102.0
Thunder Bay	101.0	41.1	47.1
Lake Erie (Long Point)	94.4	49.0	64.4

[a] Sediment samples were free of alkyl-lead; trialkyl-lead spikes, 50 ng Pb/g sediment (50 ppb); $n=2$; values are averages of duplicate determinations.

have been reported in the literature.[21, 22] It is for this reason that tripropyl-lead (Pr_3Pb^+), once considered for use as an internal standard for alkyl-lead, is not deemed suitable for this purpose by this procedure. External standards were used for calibration of the alkyl-lead peaks instead.

Analysis of environmental samples

Sediment samples were collected for analysis by the present method at locations previously found contaminated with alkyl-lead[23, 24] and with butyltin compounds.[25] Alky-lead compounds were rarely observed in the once-polluted areas except in Toronto and Montreal Harbours, and in Blue Church Bay, St Lawrence River, where low concentrations of alkyl-lead still persisted in the sediment. Harbour sediments were found to contain various species of butyltin, and residues of alkyl-lead were detected in these samples (Table 6). It is apparent that the alkyl-lead compounds have gradually degraded to inorganic lead since the regulations on leaded gasoline were introduced in Canada in 1987.

CONCLUSION

The direct derivatization of ionic butyltin and alkyl-lead compounds in sediment followed by dual-channel operation of the GC–AED technique provides an efficient and simple technique

Table 6. Determination of butyltin and alkyl-lead compounds in sediment[a]

Location	Bu_3Sn	Bu_2Sn	BuSn	Mep_3Pb	Me_2Pb	Et_3Pb	Et_2Pb
Toronto Harbour	307.2 ± 32.3	183.5 ± 17.2	35.1 ± 7.2	—	—	—	6.4 ± 0.4
Montreal Harbour	184.8 ± 1.1	100.8 ± 1.9	40.3 ± 1.9	d	9.3 ± 0.1	—	6.6 ± 0.3
Halifax Harbour	1652 ± 7.6	733.2 ± 19.2	200.5 ± 5.6	—	—	—	—
Kingston Harbour	742.0 ± 79.8	498.5 ± 49.7	148.9 ± 22.3	—	—	—	—
Blue Church, St Lawrence River	—	—	—	8.7 ± 0.2	—	4.3 ± 0.9	2.1 ± 0.5

[a] Sediment freeze-dried; averaged concentration in ng (metal)/g dry weight basis; $n=2$ (± deviation); d, detected, not quantified; —, undetectable.

to analyze both butyltin and alkyl-lead simultaneously in one sample preparation. The technique eliminates many conventional extraction and separation steps, with the major advantage of time saving. The present method will find use in areas where leaded gasoline is still in use and in Europe where occurrence of alkyl-lead compounds is still being investigated.[26, 27] The occurrence of tributyltin and its degradation products in harbours, rivers and lakes has been widely studied all over the world because of its use as an antifouling agent in paint formulation.[25, 28–30] In spite of TBT-usage regulations in many countries, butyltin compounds are still found in sediments.

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