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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

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Abstract

The versatility of sodium tetra(*n*-propyl)borate, $NaBPr_4$, as aqueous in situ derivatization reagent for organometallic compounds is demonstrated. With this new derivatization reagent it is now possible to derivatize the important ethyl derivatives of lead and mercury which until now had to be derivatized by Grignard alkylation or hydride generation. The synthesis of $NaBPr_4$ is described in detail. Derivatization parameters such as pH, reaction time, amount of reagent and stability of the aqueous $NaBPr_4$ solution were investigated. Different organometallic compounds of tin, mercury and lead were simultaneously determined by an inductively coupled plasma mass spectrometer coupled to the capillary GC system using a laboratory-developed interface. Good linearity was obtained for all components with detection limits in the ng/l range (without preconcentration). The reproducibility of the complete procedure, i.e. derivatization, extraction and injection, is better than 10% R.S.D. The analysis of the PACS-1 Reference Material after derivatization with $NaBPr_4$ showed the accuracy of this method. © 1998 Elsevier Science B.V.

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1. Introduction

Today, the interest in metal speciation is still increasing. Accurate and precise determination of total concentrations of trace and ultratrace amounts of metals in all kinds of samples is no longer sufficient. Chemists want to know the exact concentrations of the different compounds containing the trace element of interest since its toxic behaviour and the impact on the environment is highly dependent on the chemical structure [1]. Metal speciation, however, is impossible without the use of modern high-tech hyphenated techniques, in which highly sensitive and selective elemental detection systems like atomic absorption spectrometry (AAS), inductively coupled plasma and microwave-induced plasma atomic emission spectrometry (ICP-AES, MIP-AES, respectively) and inductively coupled plasma

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mass spectrometry (ICP-MS) are coupled to modern chromatographic separation systems like gas chromatography (GC), high-performance liquid chromatography (HPLC), supercritical fluid chromatography (SFC) and recently capillary zone electrophoresis (CZE) [2–7]. Especially, the advanced hyphenation with ICP-MS is important since the multi-element capabilities and extreme sensitivities of the ICP-MS can be fully exploited, leading to very short analysis times [8–19]. Moreover, with ICP-MS, isotopic information is available whenever necessary, which opens up the possibilities of stable isotope dilutions in metal speciation [20].

The most important and abundant organometallic species in the environment are organomercury, -lead and -tin compounds which are most effectively analysed by capillary GC–MIP-AES and –ICP-MS.

GC, however, requires volatile species, and most of the organomercury, -lead and -tin species occur in ionic form in the environment. Therefore, derivatization into volatile species is necessary. For many years, hydride generation in combination with cryogenic trapping of the volatile species [21–23] has been used. Hydride generation suffers from interferences during the derivatization and the obtained species are often unstable. Another widely used derivatization technique is Grignard reaction [24–26]. In this method, the organometallic species are peralkylated into apolar volatile species. The main advantage is its versatility, because many different alkylations such as ethylation, propylation and pentylation are possible so that nearly all alkyllead, -mercury and -tin species can be derivatized and determined by capillary GC (cGC). The most important drawback of Grignard derivatization is the sensitivity of the reagent towards water. As a consequence, the organometallic species have to be extracted prior to derivatization into an apolar solvent, by use of complexation reagents such as tropolone or sodium diethyldithiocarbamate. This makes the whole sample preparation tedious and time consuming. Another disadvantage is that Grignard reagents are extremely air sensitive and are mostly insufficiently pure for use in ultratrace metal speciation.

The sample preparation for organometal speciation has drastically been simplified by the introduction of the aqueous in situ derivatization by Ashby et al. [27–29]. Ethylation takes place in the aqueous phase by addition of sodium tetraethylborate ($NaBEt_4$). In this way, derivatization into apolar volatile species and extraction into the organic solvent can take place simultaneously within one handling step. The derivatization reaction can be described as:

$$R_nM^{(4-n)+} + (4-n)NaBEt_4 \rightarrow R_nEt_{4-n}M + (4-n)BEt_3 + (4-n)Na^+ \quad (1)$$

with R = methyl (Me), butyl (Bu); M = Sn, Pb; $n = 1, 2, 3$

$$MeHg^+ + NaBEt_4 \rightarrow MeEtHg + BEt_3 + Na^+ \quad (2)$$

Inorganic Sn, Hg and Pb also react with $NaBEt_4$. These reactions are given in detail by Rapsomanikis and co-workers [30–33]. Other metals that react with $NaBEt_4$ are cadmium [34] and selenium [35]. The main disadvantage of sodium tetraethylborate is that the important ethyllead and -mercury species cannot be distinguished from inorganic Pb and Hg after ethylation. Alternative aqueous in situ methods are butylation, using the commercially available sodium tetrabutylammonium tetrabutylborate ($NaBu_4NBBu_4$) as reported by Bergmann and Neidhart [36], and phenylation with sodium tetraphenylborate [37]. The latter reagent, however, only reacts with inorganic mercury and alkylmercury species, while the former cannot be used for the analysis of butyltin compounds.

To the best of our knowledge, no procedures have been reported that allow similtaneous derivatization of all organotin, -mercury and -lead compounds, including the ethyl derivatives. Sodium tetra(*n*-propyl)borate has been synthesized in our laboratory for the simultaneous aqueous in situ derivatization of methyl and ethyl derivatives of lead and mercury, and for derivatization of the butyl derivatives of tin. Using this novel reagent, the multi-element features of the cGC–ICP-MS hyphenated technique can be fully exploited.

2. Experimental

2.1. Reagents

Monobutyltin trichloride ($MBTCl_3$, 97% purity), dibutyltin dichloride ($DBTCl_2$, 97% purity), tributyltin chloride (TBTCl, 96% purity) and triethyltin bromide (TETBr, 97% purity) were purchased from

Aldrich (Sigma-Aldrich Belgium, Bornem, Belgium). Methylmercury chloride (MMCl, 98% purity) and ethylmercury chloride (EMCl, analytical-reagent grade) were from Merck (Darmstadt, Germany). Trimethyllead chloride (TMLCl, analytical-reagent grade) was obtained from ABCR (Karlsruhe, Germany) and triethyllead chloride (TEL, analytical-reagent grade) from Alfa (Johnson Matthey Germany, Karlsruhe, Germany). Dimethyllead dichloride ($DMLCl_2$) and diethyllead dichloride ($DELCl_2$) were prepared by the reaction of iodine monochloride (ICl) on TMLCl and TELCl, respectively [38]. Stock solutions of 1 g/l (as metal) were separately prepared in ethanol (EtOH, analytical-reagent grade, Merck). Mixed organomercury, -tin and -lead standard solutions were prepared in and further diluted with EtOH to concentrations varying between 1 and 100 μg/l as metal and stored in the dark at 4°C. Sodium tetraethylborate ($NaBEt_4$) was purchased from Strem Chemicals (Bischheim, France). Milli-Q water (Millipore, Bedford, MA) was used to prepare all aqueous solutions.

Buffer solutions with pH values between 2 and 8 were prepared by mixing appropriate amounts of 0.2 mol/l acetic acid (HOAc, analytical-reagent grade, Merck) and sodium acetate (NaOAc, analytical-reagent grade, UCB, Leuven, Belgium) solutions. HCl (analytical-reagent grade, 12 *M*) was purchased from UCB, and further purified by subboiling distillation, and NH_4OH (analytical-reagent grade, 25%) was from Merck.

For the synthesis of the sodium tetra(*n*-propyl)borate ($NaBPr_4$), 1-bromopropane (PrBr, 99%), 1-chloropropane (PrCl, 99%), boron trifluoride diethyl etherate ($BF_3.OEt_2$) were purchased from Aldrich and freshly distilled before use. Magnesium turnings were from UCB, sodium (lump, analytical-reagent grade in light petroleum) and diethyl ether (Et_2O, analytical-reagent grade) from Merck.

For the liquid–liquid extraction isooctane (analytical-reagent grade, UCB) was used. Tributylpentyltin was obtained by Grignard pentylation (pentylmagnesium bromide, 2 *M* in diethy lether, Aldrich) of TBTCl.

2.2. Synthesis of sodium tetra(n-propyl)borate

Sodium tetra(*n*-propyl)borate was synthesized according to the method described by Honeycut and Riddle [39] for the synthesis of sodium tetraethylborate. The synthesis consists of the following steps:

$$3PrBr + 3Mg + BF_3.OEt_2 \xrightarrow[Et_2O]{} Pr_3B + 3MgBrF \quad (3)$$

$$Pr_3B + 2Na + PrCl \xrightarrow[Et_2O]{} NaBPr_4 + NaCl \quad (4)$$

In the first step, tri(*n*-propyl)borane, BPr_3 is prepared [39–41]. In the second step BPr_3 is converted into sodium tetra(*n*-propyl)borate, $NaBPr_4$. The first step is necessary since tri(*n*-propyl)borane is not commercially available.

2.2.1. Synthesis of tri(n-propyl)borane

In a 1-l three-necked flask fitted with a reflux condenser and placed onto a magnetic stirrer, Mg turnings (9.73 g, 400 mmol) and a teflon stirring bar were added. The Mg was activated by heating the turnings under a nitrogen atmosphere. Subsequently, $BF_3.OEt_2$ (14.2 g, 100 mmol) freshly distilled over CaH_2, a crystal of I_2 and 100 ml of anhydrous diethyl ether were added to the Mg turnings, maintaining the N_2 atmosphere. The reaction was initiated by dropwise addition of 4.7 ml of 1-bromopropane while stirring the reaction mixture. The remainder of 1-bromopropane (36.9 g, 300 mmol added in total), taken into 55 ml of anhydrous diethyl ether, was added slowly over a period of 30–45 min, such that the ether refluxed gently. The mixture was subsequently stirred for another 1.5–2 h. After allowing the reaction mixture to settle for phase separation, the clear supernatant ether layer was separated into a distillation flask. The insoluble Mg salts were washed with 200 ml of anhydrous ether and the ether portion added to the distillation flask. The ether was distilled off at atmospheric pressure, and the residual tri(*n*-propyl)borane was distilled under reduced pressure (b.p. 54–56°C/12 mmHg; 1 mmHg = 133.322 Pa) and stored under nitrogen until further use.

2.2.2. Synthesis of sodium tetra(n-propyl)borate

Into a 500-ml round-bottomed flask, the tri(*n*-propyl)borane, obtained in step one, was transferred together with approximately 300–400 ml of anhydrous diethyl ether at 4°C, and an equimolar amount of PrCl was added. Na sand was freshly prepared by grinding the lump in refluxing toluene. While stirring, a double molar amount of Na sand was added in small portions over approximately 2 h. The

temperature was maintained at 4–10°C during the addition. Subsequently, the mixture was allowed to warm up to room temperature (≈25°C) and was filtered to remove NaCl. The ether was removed under reduced pressure and the remaining sodium tetra(*n*-propyl)borate etherate was heated to 110°C at 1 mmHg to yield sodium tetra(*n*-propyl)borate. The $NaBPr_4$ was stored under nitrogen at 4°C.

2.3. Optimization of the aqueous derivatization conditions

Ten ml of buffer solution were pipetted into 15-ml glass test tubes. Two hundred and fifty μl of a 100-μg/l solution of alkyltin (MBT, DBT, TBT), alkylmercury (MM, EM) and alkyllead (TML, TEL) and (DEL, DML) standard were added together with 100 μl of a 500 μg/l of triethyltinchloride (TET) as internal standard, and 500 μl of isooctane, containing 100 μg/l Bu_3PeSn. Bu_3PeSn was used to correct for injection volume errors (manual injection). Next, 500 μl of an aqueous 1% (m/v) $NaBPr_4$ solution were added. The test tubes were closed and shaken vigorously. After spontaneous phase separation (10 min) the isooctane layer was pipetted into GC glass vials and stored at 4°C until GC–ICP-MS analysis.

For the study on the influence of the pH on the derivatization buffer, solutions with pH values ranging between 2 and 8 were prepared. To obtain pH 2 and 8, diluted solutions of HCl and NH_3 were used, respectively. Ten ml of each solution was used and treated as described above.

The effect of the amount of $NaBPr_4$ was examined by adding different amounts (250–1000 μl) of a 1% (m/v) solution of $NaBPr_4$ to a spiked buffer solution (pH 4). The mixture was allowed to react for 10 min.

The influence of the reaction time was investigated as follows. To a spiked buffer solution, 500 μl of a 1% (m/v) solution of $NaBPr_4$ was added. The mixture was shaken and the organic phase was pipetted after different reaction times (1–10 min).

The stability of the aqueous $NaBPr_4$ was studied by adding a freshly prepared 1% m/v $NaBPr_4$ solution to the spiked buffer solutions after different times (immediately–5 h delay).

2.4. Analysis of the standard reference material

In order to evaluate the reliability of the new derivatization procedure and of the cGC–ICP-MS analysis, the PACS-1 marine sediment reference material from the National Research Council Canada (NRC) was analysed for organotin compounds. Approximately 0.2 g of sediment was weighed in a 50-ml glass vial, and 5 ml of Milli-Q water were added to moisten the sediment. Subsequently, 1 ml of HOAc and 5 ml of methanol were added. Finally, 100 μl of 500 μg/l TET, used as internal standard, were added. The samples were well shaken and ultrasonically treated for 30 min. After the leaching procedure, 25 ml of HOAc–NaOAc buffer were added to adjust the pH to 4 and 1 ml isooctane was added. Then, 500 μl 1% $NaBPr_4$ were added. The vials were shaken vigorously and, after a reaction time of 10 min, the vials were centrifuged at 4000 rpm for 3 min to facilitate phase separation. Finally, the isooctane layer was pipetted into GC sample vials and stored at 4°C until further analysis.

2.5. Instrumentation

A Perkin-Elmer Autosystem gas chromatograph was coupled to a Perkin-Elmer Sciex Elan 5000 ICP mass spectrometer by means of a laboratory-made transfer line. The transfer line has been described in detail elsewhere [16,17]. The operating conditions are described in Table 1. The isotopes ^{120}Sn, ^{202}Hg and ^{208}Pb were selected for simultaneous detection of Sn, Hg and Pb. To correct for signal drift and instrument instabilities, ^{126}Xe was measured as an internal standard. Xe was present in the H_2 carrier gas of the GC at a concentration of 1% (Air Liquide Belgium, Liège, Belgium). The raw data were further processed with the Chromafile MS software (Perkin-Elmer, LabControl, Köln, Germany).

3. Results and discussion

3.1. Synthesis of sodium tetra(n-propyl)borate

The yield of the synthesis of BPr_3 starting from $BF_3.OEt_2$, Mg and PrBr was 91%. In the second step, the proper $NaBPr_4$ was synthesized [39,42]. The obtained product was a hygroscopic, white to very pale yellow powder and was immediately stored at 4°C under nitrogen. The reaction yield of the second synthesis step was approximately 30%. The

Table 1
Instrumental parameters for cGC–ICP-MS

Gas chromatograph	Perkin-Elmer Autosystem
Column	Fused-silica open tubular, polydimethylsiloxane; 30 m, 0.25 mm I.D., $d_f = 0.50$ μm
Injection technique	Splitless
Injection temperature	250°C
Temperature programme	60°C (1 min)—30°C/min—120°C (0.5 min)—30°C/min—230°C (0.7 min)
Carrier gas; inlet pressure	Xe–H_2 (1:99); 435.1 bar
Transfer line	Laboratory-made; heated stainless steel tube
Transfer line temperature	250°C
ICP-MS	Perkin-Elmer Sciex Elan 5000
RF power	1250 W
Sampling depth	10 mm
Carrier gas flow-rate	1.10–1.25 l/min
Auxiliary gas flow-rate	1.20 l/min
Plasma gas flow-rate	15 l/min
Sampling cone/aperture diameter	Ni/1.125 mm
Skimmer cone/aperture diameter	Ni/0.875 mm
Dwell time	30–50 ms (depending on number of nuclides to be measured) 10 ms (^{126}Xe)

identity and purity was checked by derivatizing an organometal standard with both $NaBPr_4$ and PrMgBr. The chromatograms obtained with both methods were identical confirmed the identity of the tetra(*n*-propyl)borate. Fig. 1 shows a chromatogram of an organometal mixture derivatized with $NaBPr_4$. The undefined tin peaks probably originate from the internal standard Et_3SnBr, since they do not appear in blank solutions without internal standard. Unidentified organolead peaks, however, are impurities in the tetra(*n*-propyl)borate itself. The signal intensities for the organomercury species is at least a factor of 10 lower than those for the organotin and -lead compounds. This is due to the high first ionization potential of Hg (10.44 eV) in comparison with Sn (7.34 eV) and Pb (7.42 eV) resulting in a less efficient formation of mercury ions in the ICP. A similar trend was observed for ethylation with $NaBEt_4$ so that a possible difference in derivatization yields cannot be the main reason for these systematically lower Hg intensities.

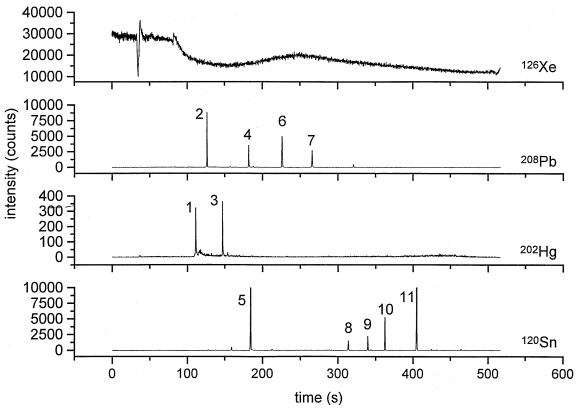

Fig. 1. Chromatogram of an organometal standard after propylation with $NaBPr_4$: (1) MM; (2) TML; (3) EM; (4) DML; (5) TET; (6) TEL; (7) DEL; (8) MBT; (9) DBT; (10) TBT; (11) TBPeT. Measured isotopes: ^{120}Sn, ^{202}Hg, ^{208}Pb, ^{126}Xe.

3.2. Optimization of the extraction parameters

One of the most important parameters in the derivatization reaction is the pH. In Fig. 2, the influence of the pH on the derivatization is shown.

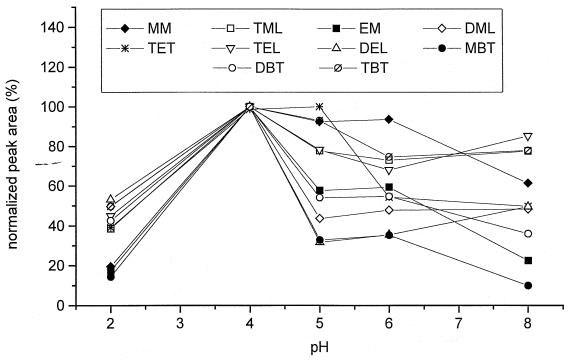

Fig. 2. Influence of pH on the derivatization. Optimum expressed as 100%.

The normalized peak areas of the organometals (normalized to Bu_3PeSn and Xe, to correct for volume errors and instrumental instabilities, respectively) were plotted versus the pH (varying between 2 and 8). The highest derivatization yield for all organometal species was obtained at pH 4, corresponding with absolute derivatization yields ranging between 92 and 100%. At low pH values ($\leq$2), the $NaBPr_4$ is rapidly decomposed to BPr_3 and propane. The optimum pH range for $NaBPr_4$ is thus somewhat lower than that for $NaBEt_4$ (pH 5) [26,28,29,43].

The amount of $NaBPr_4$ is far less critical. As with $NaBEt_4$, an excess of derivatizing reagent is used in real life samples such as waters and sediments since matrix components also react with the alkylborates. One ml of a 1% (m/v) aqueous solution is a sufficient excess to derivatize approximately 50 ng (as metal) of alkyltin, -mercury and -lead.

For routine analyses, it is important that the total analysis time, including the sample preparation, is as short as possible. The reaction time was therefore investigated. In Fig. 3, the derivatization yields of the organometal species are plotted versus the reaction time. As can be seen, complete derivatization is achieved after only 5 min for most of the organometallic species. For TEL, however, the propylation obviously proceeds much slower. Therefore, a reaction time of 10 min was chosen as a compromise.

The stability of the aqueous $NaBPr_4$ solution was checked by using freshly prepared solutions as well as solutions that were allowed to stand for 1–5 h. As can be deduced from Fig. 4, there is no overall

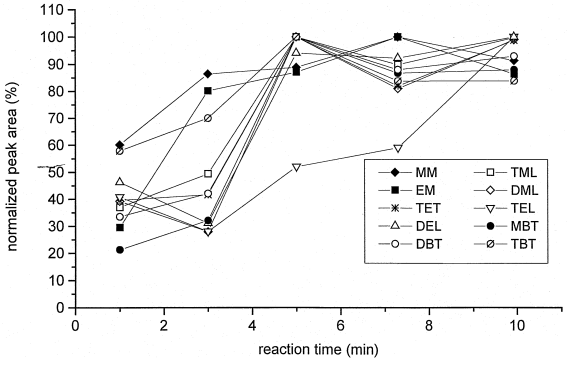

Fig. 3. Influence of the reaction time on the derivatization. Optimum expressed as 100%.

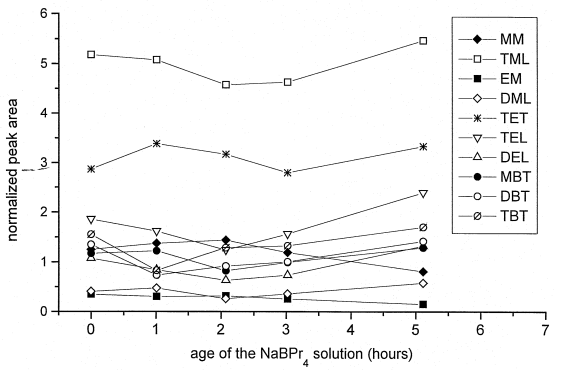

Fig. 4. Stability of the aqueous $NaBPr_4$ solution: influence on derivatization as a function of the solution age.

decrease of the reaction yield with increasing age of the $NaBPr_4$ solution. This is in agreement with the statements reported by Damico [42], who concluded that lithium tetraalkylborate compounds are fairly stable in water and are decomposed for only 0.5–13% at 35°C after 16 h. Decomposition due to hydrolysis only occurs in a strong acidic medium:

$$NaBR_4 + H^+ \rightarrow Na^+ + BR_3 + RH \quad (5)$$

3.3. Linearity

Calibration graphs for the different organometallic species were obtained by derivatizing/extracting buffer solutions, spiked with 250 μl mixed standard solutions, with concentrations between 0.1 and 100 μg/l (0.1, 0.5, 10, 50, 100 μg/l as metal) after propylation with $NaBPr_3$. Linear calibration curves were obtained with regression coefficients ranging between 0.990 and 0.998.

3.4. Reproducibility and limits of detection

The reproducibility of the aqueous in situ propylation was investigated by 10 subsequent derivatizations of 10-ml buffer solutions spiked with 250 μl of a 100 μg/l (as metal) mixed standard solution. The results are summarized in Table 2 and vary between 4 and 10%.

The limits of detection, LODs, were determined as 3 times the standard deviation of the background measured after injection of a blank solution obtained by derivatization of a non-spiked buffer solution

Table 2
Reproducibility of the extraction/derivatization, linearity and limit of detection (LOD) for propylated alkyltin, -mercury and -lead with $NaBPr_4$

Compound	R.S.D.% ($n=10$)	Regression coefficient	LOD (ng/l or fg absolute)
Alkyltin MBT, DBT, TBT	8.1–9.0	0.990–0.998	52–170
Alkylmercury MM, EM	7.1–10	0.992–0.995	210
Alkyllead TML, DML, TEL, DEL	4.4–8.0	0.990–0.993	36–85

(experiment in 10-fold). Table 2 shows that LODs are of the same order of magnitude as those reported by other author using different derivatization agents and different GC-injection methods [15,17,18]. The detection limits reported in this work refer to a sample volume of 10 ml of buffer only, whereas in real life samples at least 250 ml of water sample is taken when applying conventional injection techniques such as split/splitless.

3.5. Accuracy

The reliability of the $NaBPr_4$ as an aqueous in situ derivatization reagent was investigated by the analysis of the PACS-1 reference material (Marine Sediment) from the National Research Council Canada (NRCC) for MBT, DBT and TBT. A chromatogram of the derivatized organotin species is shown in Fig. 5. In Table 3, the results are summarized. The results obtained for DBT and TBT are in good agreement with the certified values. The value for MBT, however, exceeds the certified value by a factor of 2.3. In the past this PACS-1 sediment has been analysed either via classical liquid–liquid extraction and headspace solid-phase microextraction both in combination with aqueous in situ ethylation, and values of 390±110 and 428±76 ng/g were found [15,43,44]. It is well known that the certified value for MBT is far too low. Szpunar et al. found a concentration of 760±50 ng/g after microwave-assisted leaching and aqueous in situ ethylation [45]. The leaching procedure for MBT, rather than the derivatization, is still the main source of error during the analysis of the sediment.

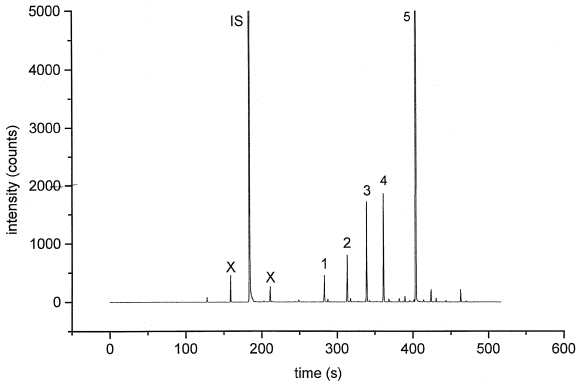

Fig. 5. Chromatogram of PACS-1 Marine Sediment Reference Material for alkyltin (m/z 120). IS, internal standard (TET); (1) inorganic Sn (Pr_4Sn); (2) MBT; (3) DBT; (4) TBT; (5) TBPeT (IS); X, unknown compounds.

4. Conclusions

The proposed aqueous in situ derivatization opens new possibilities for organometallic speciation by gas chromatography. The most important and toxic organometallic derivatives – methyl-, ethyl- and butyl- species of organotin, -mercury and -lead – can be derivatized and analysed with cGC–ICP-MS in only one sample preparation step. With sodium tetra(*n*-propyl)borate it is now possible to derivatize the different ethylleads, originating from anti-knocking additives in fuels, and ethylmercury species in situ without losing information of their chemical identity (which occurs with $NaBEt_4$) and without additional sample handling steps. The chemical behaviour of $NaBPr_4$ and the optimized extraction/

Table 3
Determination of MBT, DBT, and TBT in PACS-1 Reference Material after propylation with $NaBPr_4$

Component	This work	Certified values (ng/g)
MBT	750±210[a]	280±170
DBT	1060±150	1160±180
TBT	1220±190	1270±220

[a]Limit of 95% confidence ($n=3$).

derivatization parameters are comparable to those of $NaBEt_4$. The sample preparation can be reduced to a strict minimum in comparison with Grignard derivatization, and the aqueous in situ derivatization could possibly be combined with advanced extraction techniques such as solid-phase microextraction (SPME) [43].

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