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SPECIAL ISSUE PAPER

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Comparison of sodium tetraethylborate and sodium tetra(n-propyl)borate as derivatization reagent for the speciation of organotin and organolead compounds in water samples

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Abstract The influence of pH on the propylation with sodium tetra(n-propyl)borate of butyl- and phenyltins as well as for trimethyl- and triethyllead was investigated. Ethylation and propylation with tetraalkylborates were compared with regard to derivatization yields and figures of merit for organotin compounds in real water samples. Similar results for limit of detection (3–12 ng/L as tin), derivatization yield (40–100%) and relative standard deviation of the method (3–10%) were achieved for derivatization with the two tetraalkylborates. Propylation is thus the preferred method for the simultaneous determination of environmentally relevant organotin and organolead compounds. The handling of the hygroscopic and air sensitive reagents $NaBEt_4$ and $NaBPr_4$ was simplified by dissolving them in tetrahydrofurane. The reagent solutions in tetrahydrofurane can be stored for at least one month at 4 °C in the dark without observing any decrease in the derivatization efficiency.

Introduction

Over the last years, sodium tetraethylborate ($NaBEt_4$) has gained great popularity as derivatization reagent in the speciation analysis of organometallic compounds for the conversion of ionic polar species into their fully alkylated forms which then can be separated by gas chromatography [1–3]. The derivatization with $NaBEt_4$ is carried out in aqueous solution which is one of the main advantages in comparison to the Grignard reaction where the analytes first need to be extracted into an apolar aprotic solvent and the extract dried before derivatization. Thus, an in-situ derivatization is impossible when using Grignard reagents. Recently, De Smaele et al. [4] have introduced sodium tetra(n-propyl)borate ($NaBPr_4$) as derivatization reagent for this purpose. $NaBPr_4$ combines two major advantages: (1) easy handling and in-situ derivatization and extraction like the ethylation with sodium tetraethylborate ($NaBEt_4$) and (2) the possibility to determine the important ethyl derivatives of lead and mercury without losing the information about the individual species originally present in the sample.

Alkylation of organometallic compounds with tetraalkylborates is known to be strongly pH dependent. Therefore, the pH needs to be optimized for each compound separately. While the derivatization conditions for the ethylation are well established and optimum pH values for the ethylation of some organotin [5–7] and organolead [8–10] compounds are published, the propylation has not yet been investigated in detail. Only De Smaele et al. [4] published results for the propylation of butyltin compounds, some organolead and organomercury compounds.

The objective of this work was to optimize the reaction conditions for the propylation of butyl- and phenyltin compounds, trimethyl- and triethyllead with respect to the pH. Furthermore, the two derivatization methods using $NaBEt_4$ and $NaBPr_4$ were compared in terms of derivatization efficiencies, repeatability and limit of detection.

Since $NaBEt_4$ and $NaBPr_4$ are hygroscopic and air sensitive reagents, they need to be stored under argon to prevent them from rapid degradation. Due to these properties it is necessary to work under protective gas atmosphere, at least when preparing the aqueous solutions, which extremely complicates the handling of those reagents. Therefore, an alternative procedure for storage and handling of these air and moisture sensitive solids is presented here.

Experimental section

Reagents

All solvents and reagents used were of at least analytical reagent grade except of tetrahydrofurane (THF, Aldrich, Steinheim, Germany) which was of HPLC grade without stabilizer. Sodium

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tetraethylborate ($NaBEt_4$) was obtained as solid or as 20% (w/w) solution in tetrahydrofurane from Witco (Bergkamen, Germany) and sodium tetra(n-propyl)borate ($NaBPr_4$, >95%) by GALAB (Geesthacht, Germany). Monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPT), diphenyltin (DPT) and triphenyltin (TPT) were obtained as chlorides with a purity of >98% from the IVM, Free University of Amsterdam (Netherlands), tripropyltin chloride (TPrT, >98%) from Merck (Darmstadt, Germany) and tricyclohexyltin chloride (TCyT, >99%) from Witco. Tetrabutyltin (TeBT, >98%, Fluka, Buchs, Switzerland) and tetraethyllead (TeEL, >99.99% Aldrich, Steinheim, Germany) were used as internal standards. Trimethyllead (TML) and triethyllead (TEL) were obtained as chlorides from Johnson Mathey Alfa (>75%, Karlsruhe, Germany). Since the exact purities of TML and TEL were not known, only relative results can be given and the determination of derivatization yields for the organolead compounds was not possible.

Deionized water was generally used for the preparation of aqueous solutions.

Tetraalkylborates. The solids $NaBEt_4$ and $NaBPr_4$ as they were received were stored at 4 °C in the dark until first usage. After opening the sealed bottle once, the reagent was stored under argon in a desiccator filled with silica gel as drying agent at room temperature. All handling of the solid reagent was carried out under argon. For the investigation of possible effects of the way the reagent is added for derivatization, the 0.5% (w/w) aqueous solution was freshly prepared before use by dissolving the solid in water (reference procedure). As alternative procedure, the 5% and 20% (w/w) tetraalkylborate solutions in THF were prepared once and stored in glass bottles with PTFE-coated septum caps at 4 °C in the dark.

Buffer solutions (0.1 M). For the study of the pH influence on the derivatization yield, solutions with pH values between 1 and 10 were prepared. To obtain pH 1 and 10, diluted solutions of HCl and NaOH were used, respectively. For the other pH values the following buffer systems were used: $H_2PO_4^-/H_3PO_4$ (pH 3), CH_3COO^-/CH_3COOH (pH 4–6), $HPO_4^{2-}/H_2PO_4^-$ (pH 7).

Water samples. Water samples were collected from the Danube channel in Vienna and the March River in Marchegg, Austria. They were acidified to pH 2 with 1 mL concentrated HCl (37%) per liter sample and stored at 4 °C in the dark. Before derivatization 1 g sodium acetate was added to 100 mL acidified water sample and the pH was adjusted to 5 with concentrated acetic acid (100%).

Standard solutions. Stock solutions with concentrations of approximately 1 to 3 g/L as metal and dilutions with concentrations of approximately 10 and 1 mg/L as metal were prepared by weight in methanol and stored at –20 °C in the dark. Stock solutions were prepared monthly and for each substance separately. The first dilution (10 mg/L as metal) was prepared monthly combining the butyl and phenyltin chlorides in one solution. It has to be mentioned that solutions of organolead compounds need to be stored for each compound separately to prevent rearrangement reactions (exchange of alkylchains between organolead compounds), which had been observed in standard mixtures after 2 weeks of storage[1]. Therefore, these compounds were combined only in the final dilution (1 mg/L and 0.1 mg/L as metal, respectively) used as spiking solution. The spiking solution was freshly prepared before use, except for the stability study where the same solution of only organotin chlorides was used throughout the whole period of 4 weeks.

Instrumentation

The GC-AED system (Hewlett Packard, PA, USA) consists of a gas chromatograph (HP 5890 Series II) equipped with a splitless injection port and an autosampler (HP 7673 A) and is coupled to a microwave induced helium plasma atomic emission detector (HP 5921 A). The operating conditions are described in Table 1. In addition to the simultaneous detection of tin and lead, carbon was monitored to obtain extra information on the origin of occasionally occurring interferences on the Pb-trace. Typical chromatograms of buffer solutions spiked with environmentally relevant organotin and organolead compounds and derivatized using $NaBEt_4$ and $NaBPr_4$, respectively, are given in Fig. 1. One has to be aware that derivatization of organotin compounds with alkylation reagents of different chain length may effect the elution order since the retention times basically depend on the number of carbon atoms of the derivative. Some unidentified substances occurred on the tin trace which may origin either from transalkylation reactions between the organometallic compounds present in the spiking solution or from impurities of the derivatization reagent.

Table 1 Instrumental parameters for the GC-AED system

HP 5890 Series II gas chromatograph	
Injection technique	Splitless (purge delay: 1 min)
Injection volume	1 µL for optimization experiments 5 µL for the determination of the analytical figures of merit
Inlet temperature	280 °C
Column	HP 1 (25 m × 0.32 mm × 0.17 µm film thickness)
Carrier gas flow	2.6 mL/min constant flow
Carrier gas	Helium (purity >99.9996%)
Oven program	Initial temp.: 50 °C (ethylation), 65 °C (propylation), initial time: 3 min, rate: 50 °C/min, final temp.: 280 °C, final time: 6 min
HP 5921A atomic emission detector	
Transfer line temperature	280 °C
Wavelength	Sn 270.651 nm, Pb 261.418 nm, C 247.857 nm
Hydrogen pressure	500 kPa
Oxygen pressure	70 kPa
Cavity pressure	10 kPa
Helium total flow	250 mL/min
Spectrometer purge flow rate	0.1 L N_2/min
Cavity temperature	280 °C
Solvent vent off	2.5 min

Derivatization of spiked buffer solutions

100 mL of the buffer solution was filled into a narrow-necked extraction flask [10] and spiked with 100 µL of the spiking solution (approximately 1 mg/L as metal) containing the analytes of interest, resulting in concentrations of approximately 1 µg/L as metal for each analyte. 100 µL of the internal standard solution (approximately 1 mg/L as metal) was added to correct for volume errors due to vaporization losses and sensitivity variations during detection. TPrT and TCyT were added in order to reveal potential matrix effects on the derivatization efficiency. After addition of 1 mL hexane and (A) 100 µL of 5% (w/w) sodium tetraalkylborate solution in THF or (B) 1 mL of 0.5% (w/w) sodium tetraalkylborate solution in water ($NaBEt_4$ and $NaBPr_4$, respectively) the reaction vessel was closed and shaken vigorously for 5 min. After phase separation the hexane layer was transferred into an autosampler vial and stored at –20 °C in the dark until analysed by GC-AED.

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[1] Mothes S (1998) University of Leipzig, pers. commun.

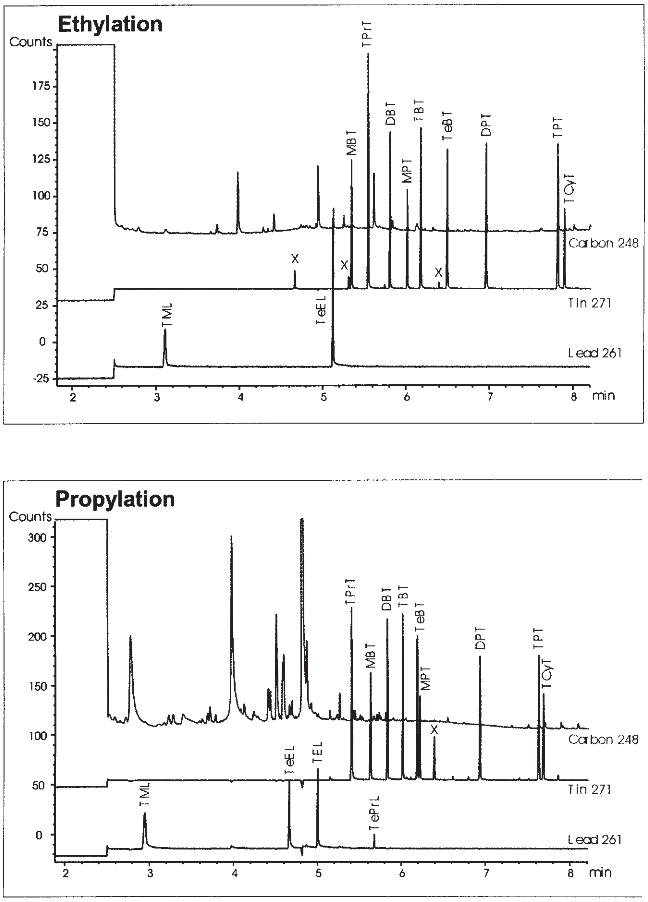

Fig. 1 Element specific GC-AED chromatograms of simultaneously detected ethylated and propylated derivatives of organotin and organolead compounds in a spiked buffer solution (conc. ~1 µg/L as tin or lead) X… unidentified substances

Results and discussion

pH optimization

The alkylation of organometallic compounds with tetraalkylborates is known to be strongly pH dependent and needs to be optimized for each compound separately. Figure 2 shows the influence of the pH value on the relative derivatization efficiency of butyl- and phenyltin compounds as well as for TML and TEL for the propylation.

At pH 1 and 10 highly irreproducible results were obtained and were therefore not further considered. The unsatisfactory repeatability of the derivatization can be explained by fast hydrolysis of the reagent, especially at low pH values [1].

For TML and TEL similar results as in the study of De Smaele et al. [4] were found which showed the highest response at pH 4. For MBT and MPT a very narrow optimum around pH 4–5 and 5, respectively, was observed. The pH value is less critical for the di- and trisubstituted organotin compounds which showed only little variations within a pH range of 4 to 7. These findings indicate a less pronounced dependence of the derivatization efficiency

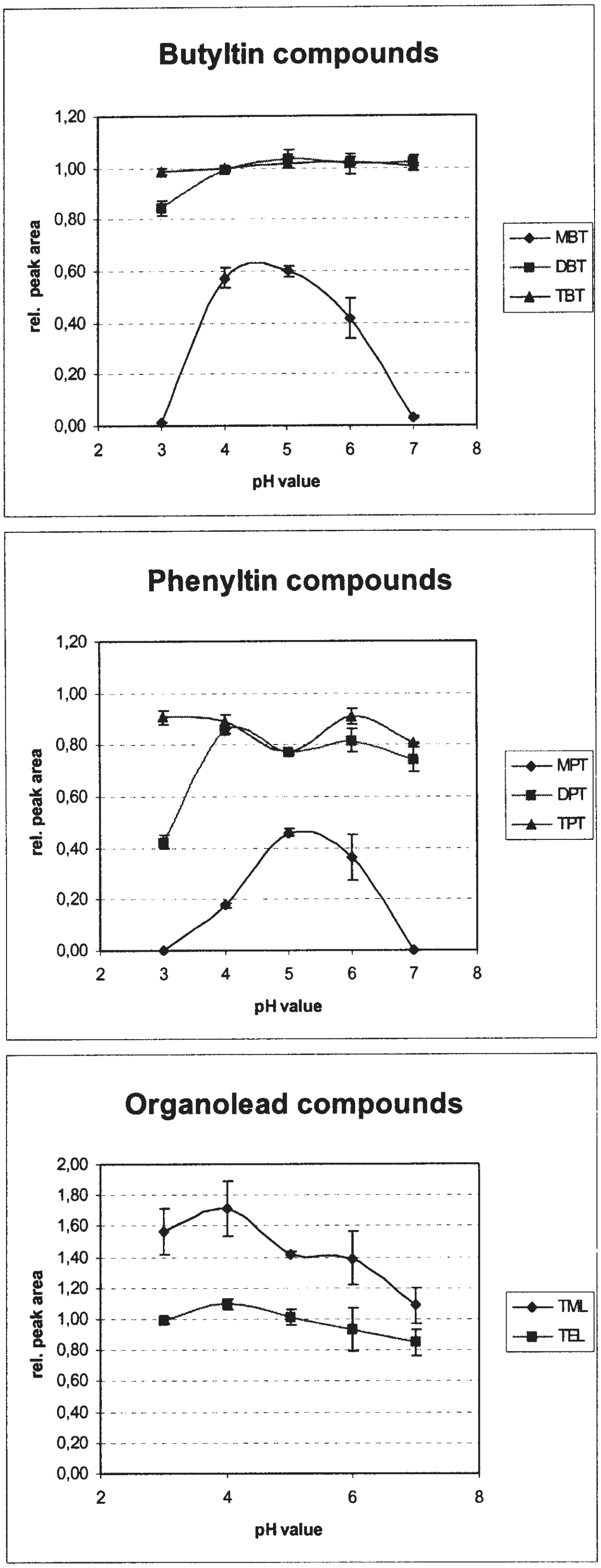

Fig. 2 Influence of pH on the propylation of organotin and organolead compounds with $NaBPr_4$. Relative peak areas are related to the internal standards TeBT and TeEL, respectively

for the di- and trisubstituted compounds than was reported by De Smaele et al. [4], who found an optimum pH of 4 for all investigated compounds.

According to the presented pH optimization study a pH value of 5 allows simultaneous derivatization of all investigated organotin and organolead compounds with satisfactory derivatization yields.

The comparison of the optimum pH values for the derivatization with $NaBEt_4$ [5,7–9] and $NaBPr_4$ (this work and [4]) does not reveal significant differences. For this reason, derivatization was carried out with both reagents under identical conditions.

Handling of the reagent

$NaBEt_4$ and $NaBPr_4$ are hygroscopic white powders which easily decompose and therefore need to be handled only under protective gas. The mechanism of the hydrolysis and oxidation of tetraalkylborates was summarized by Rapsomanikis [1] who reviewed the ethylation with $NaBEt_4$ for the speciation of organometallic compounds. In most cases the derivatization reagent is applied as a 0.3 to 1% solution in water but the aqueous solutions are unstable and need to be prepared freshly before use.

To simplify the handling of the reagent, the tetraalkylborates were dissolved in THF and directly applied to the derivatization as a 5% solution. The tetraalkylborate solution was stored in a glass vial with a septum cap, which allows an easy transfer via a syringe without handling under inert gas. The two ways of storage and addition of the reagent were compared during a period of 2 weeks. No differences were found between derivatization by the reference procedure (adding 1 mL of a 0.5% aqueous solution) and by the easier way of adding 100 µL of a 5% solution in THF (see Fig. 3).

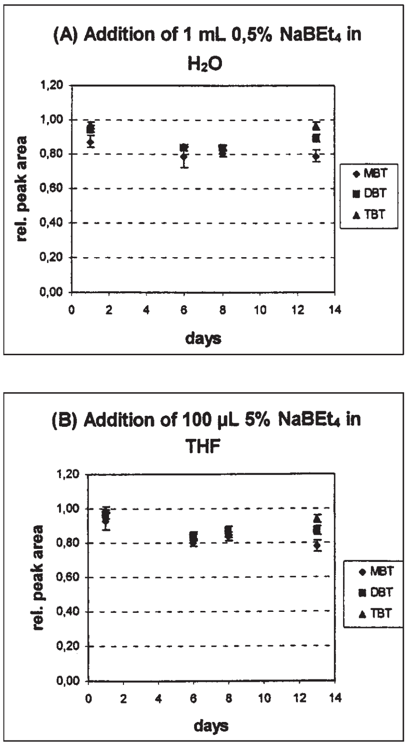

Fig. 3 Comparison of the derivatization yields relative to the internal standard TeBT for the reagent addition (A) as aqueous solution and (B) as solution in THF, monitored over a period of 14 days

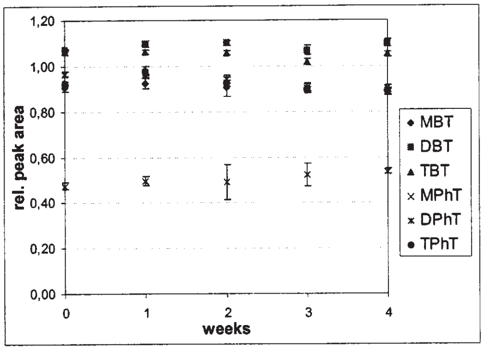

Fig. 4 Stability study of a 20% (w/w) $NaBPr_4$ solution in THF over 4 weeks, used for the derivatization of butyl- and phenyltin compounds

Table 2 Analytical figures of merit of the ethylation and propylation of spiked water samples collected in the Danube channel in Vienna/Austria and in the March river in Marchegg/Austria (analyte concentration: 20–420 ng/L as tin, internal standard: 100 ng/L as tin)

Ethylation	MBT	DBT	TBT	MPT	DPT	TPT
A	4.07	7.78	7.79	6.18	5.60	7.58
B	0.07	0.13	0.01	0.11	0.09	0.15
R^2	0.996	0.997	0.996	0.996	0.998	0.998
RSD	5	4	5	4	4	3
LOD	6	3	3	5	6	6
Yield	60–90	80–100	80–100	40–60	80–100	80–100
Propylation	**MBT**	**DBT**	**TBT**	**MPT**	**DPT**	**TPT**
A	4.30	7.45	7.04	7.28	6.08	8.22
B	0.05	0.28	0.17	0.11	0.12	0.24
R^2	0.998	0.984	0.990	0.981	0.996	0.991
RSD	3	8	8	10	4	7
LOD	10	12	7	8	10	7
Yield	60–90	80–100	80–100	40–60	80–100	80–100

A: slope [rel. peak area/(µg/L as tin)]
B: intercept [rel. peak area]
R^2: correlation coefficient
RSD: relative standard deviation of the method [%]
LOD: limit of detection [ng/L as tin] according to [11]
Yield: derivatization yield [%] calculated respective to the internal standard

A stability study for 20% solutions in THF of both reagents was carried out during a period of 4 weeks. Shortly before use the 20% tetraalkylborate solutions were diluted with THF by a factor of four (v/v). As Fig. 4 shows, the 20% $NaBPr_4$ solution can be stored at 4 °C in the dark for at least 4 weeks without any observable decrease in the derivatization efficiency. Similar results were obtained for $NaBEt_4$.

Analytical figures of merit

The analytical figures of merit for ethylation and propylation of spiked real water samples were determined from calibration data with 5 equidistant concentration levels between 20 and 420 ng/L as tin and two replicates each. A sample volume of 5 μL was injected to achieve lower limits of detection. The LODs were determined by preparing a separated calibration graph with lower concentrations near the detection limit (10–50 ng/L as tin, internal standards at 100 ng/L as tin), using the "calibration method" as suggested in [11]. The internal standards were added always at the same concentration level of 100 ng/L as tin. Calculation of the derivatization yield was based on the sensitivity of the internal standard TeBT and the assumption of substance independent response of the AED.

As can be seen in Table 2 the characteristics of both derivatization methods are comparable in terms of standard deviation and limit of detection. The estimation of the LODs by the "calibration method" is considered more appropriate than by the signal-to-noise ratio, particularly when the matrix can be expected to exhibit a pronounced effect on the derivatization procedure.

Conclusion

The parameters for the aqueous *in-situ* derivatization with $NaBPr_4$ are comparable to those found for the ethylation. Since similar derivatization efficiencies and limit of detection for both methods were observed the propylation is preferred to ethylation due to its wider applicability enabling also the simultaneous speciation of ethyl and butyl derivatives of organometallic compounds. Handling of the hygroscopic and air sensitive reagents is extremely simplified by dissolving and storing in THF.

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