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Journal of Chromatography A, 938 (2001) 225–236

JOURNAL OF
CHROMATOGRAPHY A

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Derivatization of organometal(loid) species by sodium borohydride Problems and solutions

U.M. Grüter*, M. Hitzke, J. Kresimon, A.V. Hirner

Institute of Environmental Analytical Chemistry, University of Essen, D-45141 Essen, Germany

Abstract

Like other derivatization techniques, hydride generation is a chemical reaction that produces side-reactions leading to analytical problems. Demethylation of dimethylarsinic acid was observed to be dependent upon the pH level of the hydride generation reaction mixture. If the reaction mixture was acidic, then in addition to $(\text{CH}_3)_2\text{AsH}$, the monomethyl arsenic hydride $[(\text{CH}_3)\text{AsH}_2]$ could be detected. Demethylation and also the formation of an unidentified arsenic species were noted when trimethyl arsenic oxide was used as derivatization educt. All of these effects depend on the pH level of the hydride generation mixture. We observed significant levels of organometal(loid) species of elements such as Ge, As, Sn, Sb, Hg and Bi in blank hydride generation mixtures. The organometal(loid) contamination was irreproducible even during 1 day using a single solution of sodium borohydride in deionized water. We concluded that the organometal(loid) contamination arises directly from the derivatization agent, sodium borohydride, itself. Use of helium purging and various adsorptive materials to decontaminate the sodium borohydride solution prior to analysis did not result in a significant decrease in organometal(loid) contamination levels. Use of a palladium-cluster stabilised with 1,10-phenanthroline as alternative hydride generation derivatization agent was not found to be suitable, since reaction yields were poor and transmethylation reactions were noted. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Derivatization, GC; Sodium borohydride; Organometallic compounds; Organoarsenic compounds; Organotin compounds

1. Introduction

Hydride generation by sodium borohydride is a frequently used derivatization technique to volatilise organometal(loid) compounds from liquid or solid environmental samples prior to gas-chromatographic separation followed by element specific detection. Derivatization of organometal(loid) compounds with gaseous products has the significant advantage that interferences caused by matrix compounds are eliminated.

In liquid and solid environmental samples the majority of organometal(loid) species exist in quasi-

ionic polar forms with relatively high boiling points. Hence, prior to gas chromatographic separation, these species require conversion to volatile compounds. A number of derivatization methods exist: (i) volatilisation of inorganic and relatively small organometal(loid)s by hydride generation and ethylation in aqueous media, (ii) larger alkyl metal(loid) cations can be converted with Grignard reagents to saturated non-polar species, and (iii) ionic species can be converted to volatile chelates (e.g. dithiocarbamate, trifluoroacetone) [1]. The choice is dependent upon the concentration of the analyte of interest, the sample matrix and the sample throughput required. Hydride generation active elements are Hg, Ge, Sn, Pb, Se, Te, Sb, As, Bi, Cd. In the case of

*Corresponding author.

arsenic, selenium and antimony the hydride generation efficiency of the inorganic forms is dependent upon their oxidation state. Using sodium borohydride as hydride generation agent it is possible to convert many organometal(loid) compounds into their volatile counterparts: Methyl compounds of germanium, arsenic, tin, antimony, mercury, lead and bismuth, ethyl-, butyl- and phenyltin compounds and phenylarsonic acid [2]. Additionally, the hydrogen, in situ generated during the reaction, seems to submit a very efficient purge effect of peralkylated organometal(loid) species. Sodium borohydride derivatization followed by gas chromatographic separation and multielement detection offers a screening speciation analysis of multiple elements in one measurement: We have previously reported the application of this technique to the detection and identification of 29 organometal(loid) species [3]. To form volatile arsine from waterworks, hydride generation can be performed by a modified Marsh test [4]. Hydride generation using sodium borohydride offers the possibility to perform a selective reduction of different arsenic species by reaction media containing e.g. thioglycolic acid (total arsenic), hydrochloric acid (inorganic As^{III} and As^V), citric acid/sodium hydroxide buffer (inorganic As^{III}) and acetic acid (As^{III} and dimethylarsinic acid) [5]. Gas-chromatographable species can also be formed by derivatization with sodium tetraethylborate. Methyl-, butyl- and phenyltin compounds react with NaB(C₂H₅)₄ to volatile organometal(loid) species. Purging of organometal(loid) species out of the reaction mixture is increasingly difficult with alkyl groups larger than methyl. Alkyllead species do ethylate, however only methylated species can be unambiguously discriminated in contrast to hydride generation because ethyl- and inorganic compounds in the case of ethylation form tetraethyllead, the perethylated species. Selenium(IV), inorganic- and methylmercury can be determined by this method. Derivatization with tetraalkyl(aryl)borates like sodium tetraphenyl borate, tetrapropylborate, tetramethylammonium tetrabutylborate seem to be promising but not readily available [1]. An alternative is the Grignard reaction that requires an aqueous-free medium. Some typical gas-chromatographic methods involve conversion of inorganic and methylated arsenic species into their trimethylsilyl derivatives prior to the separation [6].

A further problem is the significant ability of organometal(loid) compounds to undergo transalkylation reactions, which may result in side-reactions. Carbonell-Barrachina et al. [7] noted that arsenic speciation in sludge ecosystems has a complex biogeochemistry. Chemical and microbial processes are highly dependent upon pH–eH conditions. pH conditions have been reported to have an influence on antimony speciation when sodium borohydride is used as derivatization agent [8]. Nevertheless, not only the pH affects arsenic speciation of real samples, other factors such as kinetics and complexation are also involved [9]. In the present study we report the effect of reaction pH upon the sodium borohydride derivatization reaction, with particular regard to establishing organometal(loid) levels in blank samples and transmethylation side-reactions during volatilisation of dimethylarsinic acid (DMAA) and trimethyl arsonic oxide (TMAO).

1.1. Blank samples

The quality of an analytical method is highly dependent upon minimisation of interference arising from the blank samples. If there is background interference, the results of the sample analysis have to be corrected. After determining a blank sample using hydride generation (HG)/LT-GC/inductively coupled plasma (ICP)-MS coupling which has recently been published [2] including hydride generation with sodium borohydride, a usual blank occurs containing various inorganic and organic hydrides of the elements Ge, As, Sn, Sb, Hg, Bi. In particular, the variety and amounts of the different tin species was a problem doing tin speciation in aqueous samples. Following our experience even in the same charge from the same brand differences of the blank sample contamination occur. After many investigations to find the reasons, the blanks could be identified as contamination of the sodium borohydride solution itself. Reports of arsenic and tin contamination of sodium borohydride solutions have also been made [10,11]. In one study in 20 mg NaBH₄ up to 26 ng of total tin was detected suggested to have occurred as a tin transport from the tin containing canister through a closed plastic repository [12]. It is possible however, that the tin contamination of the sodium borohydride arises

during technical synthesis of the reducing agent, for example by tin containing educts. Previous studies have identified the often added sodium hydroxide as an additional blank increasing factor [10].

1.2. Catalytic hydride generation

Catalytic hydride generation with hydrogen at noble metal-catalysts is frequently used to generate hydrides from organic compounds. Hydride generation from alkynes to *cis*-alkenes for example using the Lindlar-catalyst (palladium containing) is possible in the presence of hydrogen. By using a Pt/H₂ system, primary amines are formed from nitro-compounds by reduction. All these processes include the catalytic-induced movement of one hydrogen atom to another atom resulting in the formation of a covalent bond.

There are two common mechanisms describing heterogenic catalytic reactions: (a) following Langmuir-Hinshelwood, both reactants (A+B) adsorb on two neighbouring grid places and react prior to desorption of the formed compound directly after formation of the new bond; (b) in the Eley-Rideal mechanism only reactant A is adsorbed on the surface of the catalyst and reacts with reactant B that is part of the surrounding medium. Which mechanism is relevant in the case of the catalytic hydride generation of organometal(loid) compounds using the presented catalytic system has not been clarified as yet.

The H₂/catalyst system tested in this study contains the catalytic active metal (Pd) as a conglomeration of three or more atoms, each chemically bonded with two or more atoms of the group, a cluster. Of special interest are the so-called “full-shell-clusters” containing a metal-structure with perfect geometry and high stability. This type of catalyst is usually used to perform hydride generation of organic compounds in liquid and solid phase [13]. Pd 7/8 clusters are more active in hydride generation of organic compounds than commercially available Pd catalysts because of their small particles (3.3–3.8 nm).

1.3. Decontamination of sodium borohydride

A number of methods to decontaminate aqueous

sodium borohydride solutions have previously been reported [10]. Some were repeated here for comparison purposes.

1.4. Decontamination by separation of solid and liquid phase

Castillo et al. [12] reported a reduction of the organometal(loid) contamination after sedimentation and filtration of the white residue from the sodium borohydride solution followed by hydride generation atomic absorption spectrometry (HG-AAS) determination. Because of the high solubility of sodium borohydride in water (550 g/l) [14] this residue cannot consist of unsolubilised sodium borohydride.

1.5. Decontamination by purging with a carrier gas

In another study, the decontamination of an aqueous sodium borohydride solution by purging the solution with an inert gas was noted to be effective [10]. The decontamination in this case is however possibly due to hydride generation of the contaminants during the study period at neutral pH level.

1.6. Decontamination by contact with an acidic rinsed zeolite

Addition of an acidic zeolite to an aqueous alkaline (pH 14) sodium borohydride solution offers a very effective contact of a small amount of protons to react a proportion of the borohydride with the contaminants and resulting in volatilisation to the gaseous phase.

A zeolite is a crystalline aluminosilicate with a defined framework. Aluminosilicates consist of total networked SiO_{4/2}-tetraeders in which some Si-atoms are replaced by Al. Because of this replacement the network is negatively charged. The charge is compensated by corresponding cations (e.g. alkali ions). Inside a zeolite there are some cavities in the structure suffering an exchange of cations against water molecules. The unsealed structure and capacious zeolite surface allows ease of movement of solution ions. Zeolites can react as acidic catalyst after replacement of for example Na⁺ by protons. The resulting Brønsted acid permits the production

of small acidic spheres in an alkaline sodium borohydride solution. These acidic spheres are short-lived because of the surrounding high OH^- concentration. Contamination can be volatilised by hydride generation. During contact of the zeolite with an alkaline sodium borohydride solution, three different competition reactions can occur:

(1) Neutralisation of protons on the zeolite surface by the surrounding OH^- ions;

(2) Decomposition of some BH_4^- ions at the acidic centres resulting in H_2 formation;

(3) Hydride generation of inorganic and organometal(loid) compounds.

The precise processes during the contact of an aqueous alkaline sodium borohydride solution with an acidic zeolite have not been established, but are likely subject to complicated kinetics.

1.7. Side reactions during hydride generation

Demethylation of methylated antimony compounds in acidic aqueous medium has been reported to occur [8]. Koch et al. [8] detected after hydride generation of a methylated antimony compound $(\text{CH}_3)_3\text{SbCl}_2$, all methylated stibines in addition to the corresponding stibine trimethylantimony $[(\text{CH}_3)_3\text{Sb}]$. After hydride generation of the compound mentioned above using sodium borohydride, four stibines $[\text{SbH}_3, (\text{CH}_3)\text{SbH}_2, (\text{CH}_3)_2\text{SbH}$ and $(\text{CH}_3)_3\text{Sb}]$ were detected. Thorough investigations revealed a pH dependence of the detected molecular transformation processes. The most significant transformation rates were detected at pH 0.83 to pH 1.4 of the hydride generation reaction mixture (transformation of trimethylantimony species up to 25%). At pH 6.1 to pH 6.76, no significant molecular transformation processes were detected (up to 3% using ICP-MS detection). Depending on the chemical similarity of arsenic and antimony, similar transformation processes using hydride generation with sodium borohydride for arsenic species were proposed.

The molecular transformation behaviour of DMAA and TMAO were investigated by variation of the pH conditions during hydride generation using sodium borohydride.

2. Experimental

2.1. Catalytic hydride generation

The catalyst used is a 7/8-shelled Pd cluster saturated with 1,10-phenanthroline for stabilisation and is spread in the amount of 1% on Silikalith as substrate (synthesized by Schmid et al. [13]).

In a special reaction vessel, 200 mg of the catalyst on Silikalith was reacted with an aqueous multi species tin standard solution that contained SnCl_4 (Merck 1 g Sn/l in 5 mol/l HCl), $(\text{CH}_3)_2\text{SnCl}_2$ (Aldrich, 97%), $(\text{CH}_3)_3\text{SnCl}$ (Merck-Schuchard, 98%), $(\text{C}_4\text{H}_9)\text{SnCl}_3$ (Aldrich, 95%) and $(\text{C}_2\text{H}_5)_3\text{SnBr}$ (Alfa) in an amount of 10 ng tin for each species. The reaction vessel was built up in such way that allows purging the reaction slurry consisting of the catalyst powder and the standard solution very effectively through the whole reaction vessel bottom with helium as carrier and purging gas (10 min, 200 ml/min) or with hydrogen as reaction gas (60 min, 380 ml/min). The volatilised organotin compounds were purged out of the reaction vessel by the gas flow and cryofocused in an U-shaped glass tube (length: 22 cm, I.D. 10 mm) that was half-filled with 10% SP-2100 on Supelcoport (80–100 mesh) (Supelco) and wrapped with a resistance heating wire (WSD, resistance alloy following DIN 17471, Monacor). This trap was placed in a Dewar flask filled completely with liquid nitrogen.

The hydride generation experiment was repeated using a commercially available palladium catalyst (Pd on activated carbon, Aldrich, 10%Pd).

2.2. Decontamination of sodium borohydride

Sodium borohydride (Aldrich, 99%) was prepared as a 5% solution in deionised water. All studies were performed on 20-ml aliquots. The sodium borohydride used belongs to one charge of one brand.

A decontamination by separation of solid and liquid phase was tested. After sedimentation overnight, the solution was decanted and filtered (Schleicher+Schuell, roundfilter 597).

Decontamination by purging with a carrier gas was performed by flushing the sodium borohydride solution with helium (200 ml/min) for 30 min.

Different adsorption examinations performed are summarised in Table 1.

2.3. Decontamination by contact with an acidic rinsed zeolite

Zeolite (Fluka, molecular sieve UOP type 13X) was acidified in 1 M HCl (Merck, 30%, Suprapur) overnight. This was followed by rinsing with deionised water until neutral pH was achieved and drying

(38°C) overnight. Different quantities of the zeolite (3, 4, 4.5, 9 g) were added to 20-ml aliquots of an alkaline (1% NaOH, Roth, 99%) NaBH₄ solution (Aldrich, 99%). The acidic zeolite was added to the sodium borohydride solution under vigorous stirring and continuously purging with helium (600 ml/min, 120 min). After centrifugation of the mixture (800 rpm, 30 min, 10°C), the sodium borohydride solution was decanted and adjusted to pH 14 by adding NaOH.

All blank sample measurements were performed

Table 1
Decontamination of an aqueous sodium borohydride solution by adsorption

Adsorption material	Contact	Preparation	Result
10% SP-2100 (separation column filling material)	3 days stirring of ca. 3 g NaBH ₄ powder in an aqueous solution of 20 ml	Membrane filtration	No decontamination effect
Active coal	3 days stirring of ca. 3 g NaBH ₄ powder in an aqueous solution of 20 ml	(1) centrifugation, (2) filtration	No decontamination effect
Active coal particle (coated with wax)	3 days stirring of ca. 3 g NaBH ₄ powder in an aqueous solution of 20 ml	(1) centrifugation, (2) filtration	No decontamination effect
Barium sulfate	Precipitate of 5 × 125 mg BaSO ₄ in an aqueous solution of 20 ml (pH 14)	Filtration [glass filter (D4)]	No decontamination effect
Glass surface of the stocking flask	Sedimentation for 4 weeks (following Dedina and Tsalev [10], 1 day is enough)	Not required	No decontamination effect
Florisil (cation-exchange material, commercially available)	Chromatographic: 5 ml aqueous solution in 15 s through 1 g of Florisil (pH 14)	Not required	No decontamination effect
Florisil (cation-exchange material, commercially available)	Chromatographic: 5 ml aqueous solution in 60 s through 4 g of Florisil (pH 14)	Not required	No decontamination effect
Florisil (cation-exchange material, commercially available)	Chromatographic: 5 ml aqueous solution in 5 min through 1 g of Florisil (pH 5)	Not required	No decontamination effect
Sodium zeolite (type 13X, Na ₈₆ [(AlO ₂) ₈₆ (SiO ₂) ₁₀₆] · xH ₂ O)	7 days stirring of ca. 3 g NaBH ₄ powder in an aqueous solution of 20 ml (pH 14)	Centrifugation	No decontamination effect

using 1 ml of a 5% sodium borohydride solution (deionised water).

2.4. Side reactions during hydride generation

Each reaction was performed using standard solutions (10 ng As/species, 1 ml 5% aqueous NaBH_4 solution). Hydrochloric acid (pH 1) and different buffers [(pH 2, 3, citrate–HCl, Merck), (pH 4, sodium citrate–HCl, Kraft), (pH 5, 6, citrate–NaOH, Merck), (pH 7, phosphate buffer, Kraft)] were used to adjust the different pH levels (pH 1, 2, 3, 4, 5, 6, 7). Each analysis was performed five times. Dimethylarsinic acid was from Strem Chemicals (98%) and trimethylarsenic oxide was from Tri Chemical Laboratory (100%).

After cryofocusing of the volatile compounds, an identification and quantification via an LT-GC/ICP-MS multi-element speciation technique was performed as described previously [2].

3. Results and discussion

3.1. Blank samples

No decrease in the organometal(loid) contents was noted when NaOH (stabilising agent) was absent

from the sodium borohydride solution. To underline the supposition that sodium borohydride itself is the source of the organometal(loid) contamination, the increase in the blank tin species contents using 3, 8, 10 and 20 mg NaBH_4 in aqueous solution to create the blank was tested. The total element contamination found in the blanks could be correlated with the levels in a certificated charge of sodium borohydride (Fig. 1).

Analysis of a blank by LT-GC/ICP-MS technique revealed a number of different organometal(loid) species of various elements (Fig. 2).

Table 2 shows the average level of the species usually found in a blank. It should be noted that the variation between repeat analyses was significant.

To reduce the organometal(loid) contamination of the blank, we used two strategies: an alternative hydride generation technique was developed, and additionally, different cleaning procedures of an aqueous sodium borohydride solution were tested to reduce the levels of different organometal(loid)s in the blank samples.

3.2. Catalytic hydride generation

It has been shown that the Pd cluster catalyst is more active in hydride generation than a commercially available Pd catalyst. The commercially avail-

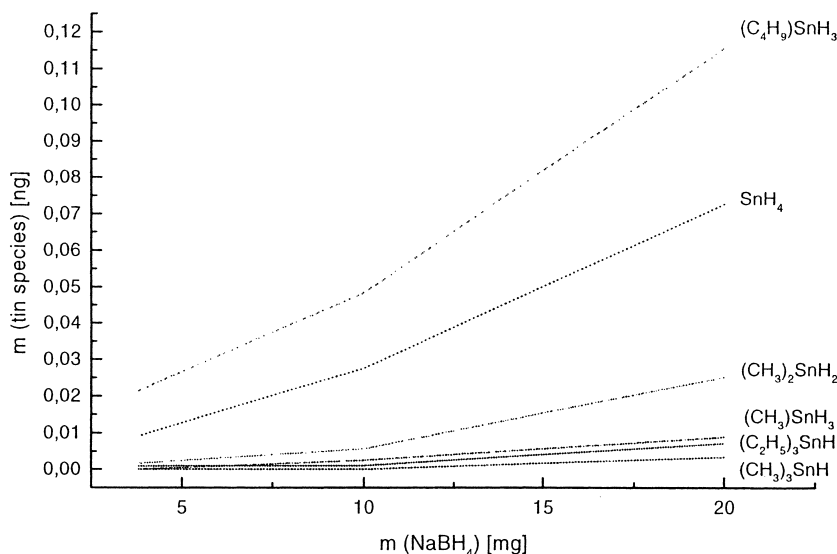


Fig. 1. Tin species in blank samples with various amounts of NaBH_4 .

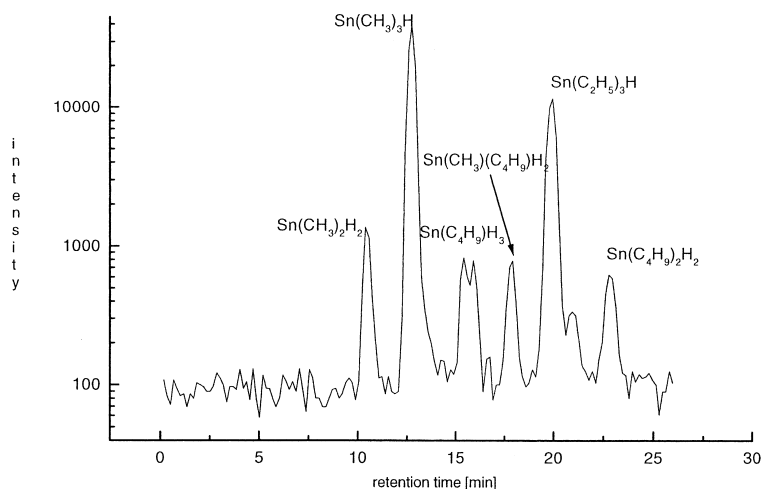


Fig. 3. Tin species determined after catalytic hydride generation using a Pd/H₂ catalyst.

tion reactions. Hence in conclusion, hydride generation using this Pd-catalyst system is possible but of no practical relevance because of transmethylation reactions and poor reaction yields (Fig. 3).

3.3. Decontamination of sodium borohydride

None of the decontamination investigations using separation of solid and liquid phase, purging with helium and adsorption with different materials resulted in a reduction of the organometal(loid) contamination.

The reason for the inefficient purging effect using helium may be the poor hydride generation efficiency as a result of the rather slow decomposition of sodium borohydride in aqueous solution at neutral pH. In the present study, a more acidic pH level to increase the decomposition rate is not reasonable because the hydride generation solution would lose its reduction reactivity.

3.4. Decontamination of sodium borohydride by contact with an acidic rinsed zeolite

Investigations by adding protons by dropping a defined amount of hydrochloric acid into the alkaline sodium borohydride solution showed that efficient contact of the acid and reaction mixture could not be reached by stirring of the solution only, since the

contact surface of the hydrochloric acid drops is too small. The contact surface can be significantly increased by adding the acid as an acidic zeolite. Cationic compounds additionally can be adsorbed at the anionic centres of the zeolite. These effects can simultaneously contribute to an elimination of metal(loid) inorganic and organic contaminants from an aqueous sodium borohydride solution.

Addition of different quantities of acidic zeolite (3, 4, 4.5 g) resulted in significant contamination reduction. Use of 9 g acidic zeolite unfortunately resulted in total inactivation of the NaBH₄ solution (Table 3).

Increasing amounts of the zeolite used to decontaminate the sodium borohydride solution resulted in an increasing decontamination effect. Total decontamination appears unlikely since increasing the amount of the zeolite used results in inactivation of the sodium borohydride solution. To extract all of the tin species out of the solution, hydride generation had to be performed at an acidic pH level, however such reaction conditions would surely result in inactivation of the sodium borohydride solution. The decontamination effect performed using 4.5 g of the zeolite to decontaminate 20 ml of a 5% sodium borohydride solution is significant. The organic tin blank level could be reduced to 3% compared to the usual amounts detected in a blank analysis.

Fig. 4 shows the effect of increasing the amount of

Table 3
Reduction of the amount of tin species found in the blank samples

Species	Content in 1 ml NaBH ₄ solution, average blank (ng)	Percentage part in 1 ml NaBH ₄ solution referring to the average blank; decontaminated with:		
		3 g acidic zeolite	4 g acidic zeolite	4.5 g acidic zeolite
SnH ₄	1.8994	91	1	5
Sn(CH ₃)H ₃	0.0308	–	2	–
Sn(CH ₃) ₂ H ₂	0.2522	80	1	–
Sn(CH ₃) ₃ H	0.0275	4	3	–
Sn(C ₄ H ₉)H ₃	0.3187	74	16	6
Sn(C ₂ H ₅) ₃ H	0.0546	–	11	–
Inorganic tin species	1.8994	91	1	5
Organic tin species	0.6838	70	11	3

the zeolite to the organic tin species usually found in a blank determination. This decontamination effect was also noted for species of other elements usually found in the blank determinations (Table 4).

3.5. Side reactions during hydride generation

After hydride generation of dimethylarsinic acid, in addition to the expected signal for (CH₃)₂AsH, the (CH₃)AsH₂ peak could be detected over the pH range 1–4. The total transmethylation rate was only significant at pH 1 (Fig. 5).

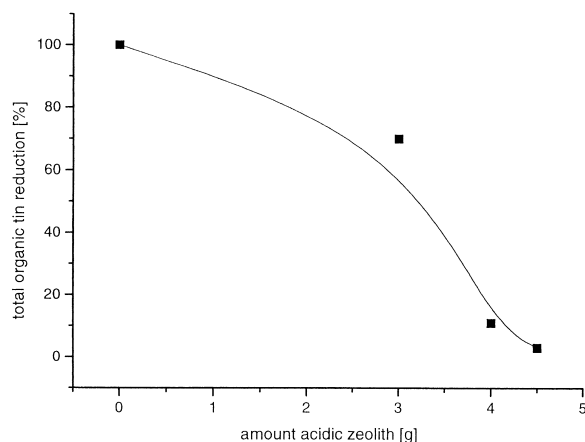


Fig. 4. Reduction of organic tin species in a blank after decontamination procedure using acidic zeolite as decontamination agent.

The total amount of volatilised arsenic detected was dependent upon the adjusted pH level. The acidity of the reaction mixture has a significant effect on the hydride generation efficiency of inorganic and methylated arsenic species. The influence of the pH reaction conditions on the hydride generation efficiency of inorganic As(III) is not significant. The hydride generation efficiency is nearly quantitative at pH 0 to pH 6.7. An effective hydride formation of inorganic As(V) requires strongly acidic reaction conditions (pH ca. 0.5). Hydride formation of monomethylarsonic acid (MMAA) and DMAA requires pH conditions at pH 0–1.5. A decreased hydride formation efficiency was observed, when MMAA and DMAA were hydride generated at pH levels above pH 2 [15]. The efficiency of the hydride formation of DMAA has been previously reported to be relatively constant up to neutral pH levels [10]. In the present study, the hydride forming efficiency decreases after hydride generation of DMAA if the pH level rises (Fig. 6).

The hydride forming efficiency during conversion of TMAO at different pH levels shows a completely different dependency on the pH level of the hydride generation mixture in comparison to the hydride forming efficiency of DMAA. The efficiency increases with increasing pH level (Fig. 7).

The total transmethylation rates of TMAO during hydride generation decrease at increasing pH level, similar to DMAA (Fig. 8).

An unknown arsenic species of a molecular mass

Table 4

Reduction of arsenic, antimony, germanium, bismuth and mercury species in the procedural blanks after decontamination using an acidic zeolite

Species	Average content in 1 ml NaBH ₄ solution (ng)	Content in 1 ml decontaminated NaBH ₄ solution (4.5 g zeolite) (ng)	Percentage part in 1 ml decontaminated NaBH ₄ solution (4.5 g zeolite) (%)
AsH ₃	0.1079	0.0282	26
As(CH ₃)H ₂	0.0400	<0.0001	–
As(CH ₃) ₂ H	0.0308	<0.0001	–
As(CH ₃) ₃	0.0245	<0.0001	–
SbH ₃	0.1076	0.1055	98
Sb(CH ₃)H ₂	0.0071	<0.0001	–
Sb(CH ₃) ₂ H	0.0600	<0.0001	–
Sb(CH ₃) ₃	0.0022	<0.0001	–
Hg ⁰	0.1010	0.0371	37
Hg ?	0.0410	<0.0001	–
BiH ₃	0.0185	0.0080	43
GeH ₄	0.0400	<0.0001	–
Ge(CH ₃)H ₃	0.0121	<0.0001	–
Ge(CH ₃) ₂ H ₂	0.1157	<0.0001	–

possibly higher than (CH₃)₃As was detected during hydride generation of TMAO. The quantity of the unknown arsenic species was strongly correlated with the total transmethylation rate of TMAO. The gradient of the formation of the unknown species correlating with the gradient of the total transmethylation of TMAO strongly suggests that this unknown arsenic species is formed from the TMAO itself during the hydride generation process (Fig. 9).

Hydride generation of TMAO at different pH levels revealed that the formation of up to four

arsenic species was dependent upon the pH level of the hydride generation reaction mixture (Fig. 10).

4. Conclusions

To deal with the organometal(loid) contamination in the blank samples, different investigations were performed. A palladium catalyst in the presence of hydrogen was tested to derivatise five inorganic and organic tin compounds. Analysis of the resultant

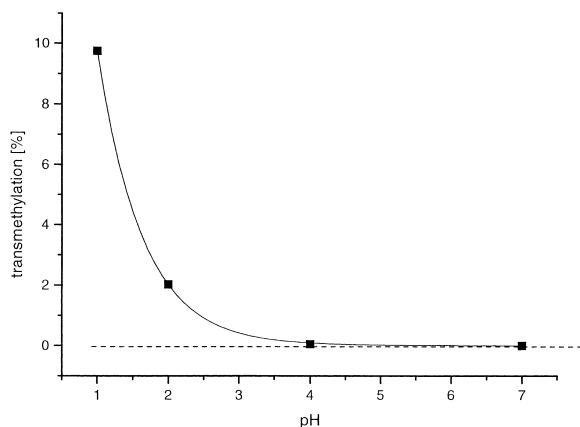


Fig. 5. Total transmethylation of DMAA during hydride generation.

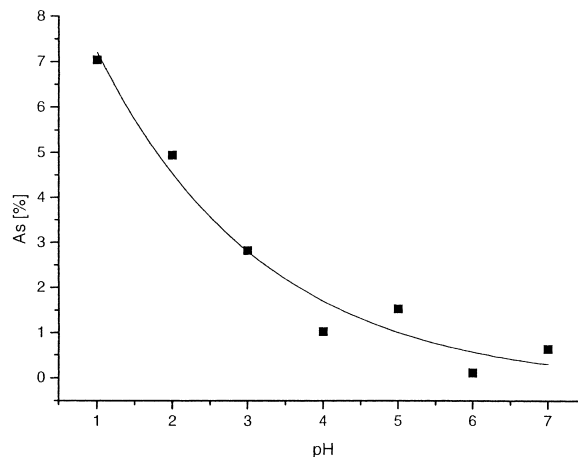


Fig. 6. Hydride forming efficiency during conversion of DMAA.

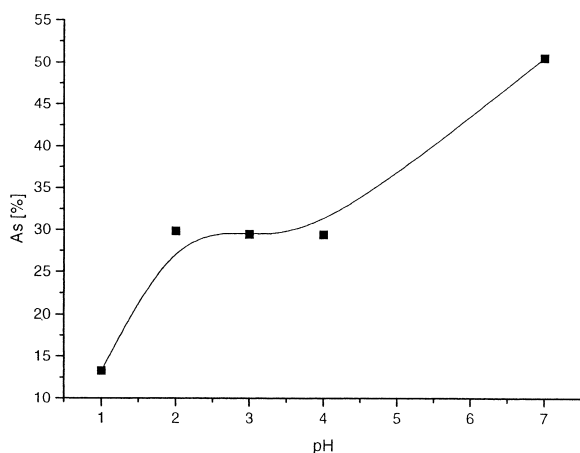


Fig. 7. Hydride forming efficiency during conversion of TMAO.

species showed all corresponding hydrides and additionally two organic tin compounds probably being $(\text{CH}_3)(\text{C}_4\text{H}_9)\text{SnH}_2$ and $(\text{C}_4\text{H}_9)_2\text{SnH}_2$. The formation efficiency of the five hydrides formed from the tin standards was very low, about 5% for the two trimethylated species and 0.2% for the others. The catalyst used seems to have a better hydride generation efficiency for higher alkylated tin compounds, however the hydride forming efficiency is generally too low to analyse samples containing organometal(loid) compounds in the ultra-trace range.

As another way to deal with the organometal(loid) contamination in the blank samples, 12 different

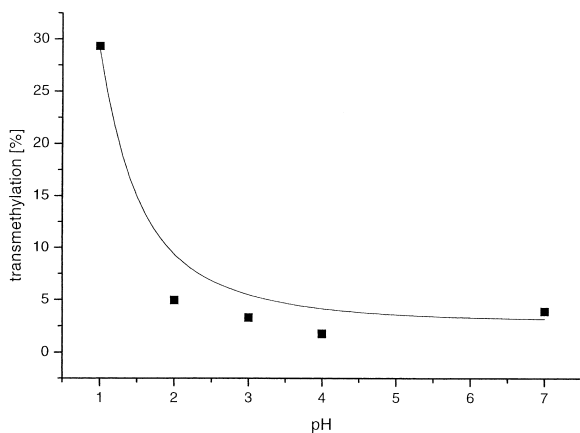


Fig. 8. Total transmethylation of TMAO during hydride generation.

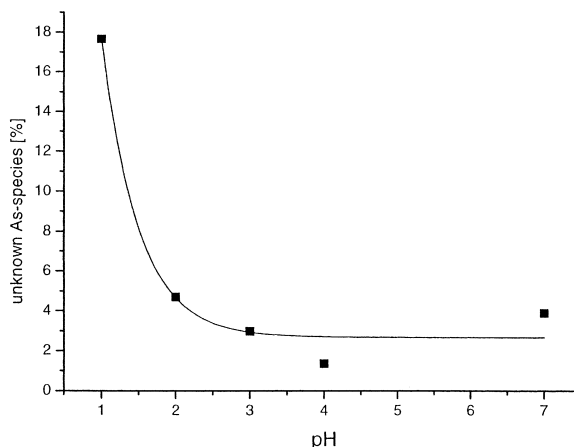


Fig. 9. Formation of an unknown As species during hydride generation of TMAO.

decontamination tests were performed to remove interfering compounds from an aqueous sodium borohydride solution. Only one of these was successful. Use of an acidic zeolite revealed that the organotin contamination of the blank could be reduced to 3% of the usual blank level. The decontamination procedure takes several days and the decontaminated sodium borohydride solution is not as active as before, hence it must be used on the same day as the last step of the decontamination procedure. If it is assumed that all sodium ions are transposed by protons on the zeolite and that there

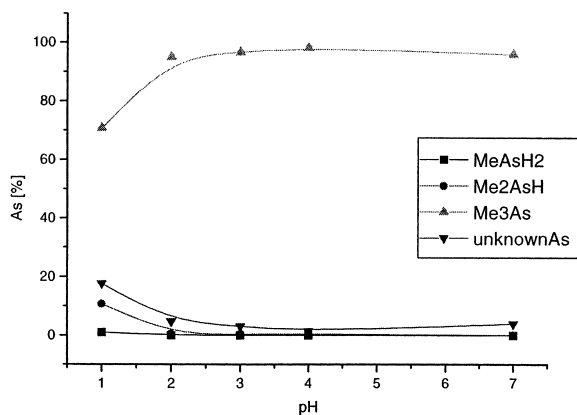


Fig. 10. Distribution of arsenic species detected during hydride generation at different pH levels (reduction of TMAO).

was full contact of all active centres with the sodium borohydride solution then approximately the calculated remaining activity of the sodium borohydride solution is 28, 2 and 0% using 3, 4, and 4.5 g of the acidic zeolite, respectively. It can be recommended first to look at difference of amounts of the organometal(loid) contamination in the blank samples and the sample content of the compounds of interest. If the difference is significant it is sufficient to subtract the blank, if not, it is necessary to use a decontaminated sodium borohydride solution.

Hydride generation of DMAA and TMAO over the pH range of pH 1–7 revealed some differences in the chemical behaviour of these two arsenic species. The hydride forming efficiency of DMAA decreases with increasing pH whilst the efficiency of TMAO increases with increasing pH levels. Both organic arsenic compounds show transmethylation reactions decreasing at increasing pH levels. Transmethylation reactions of DMAA only include demethylation reactions by forming the monomethylated compound. After hydride generation of TMAO, up to four species could be detected including the minor methylated corresponding As species and an unknown possibly organic arsenic species supposed to have a higher molecular mass (late retention time). Derivatization reactions using sodium borohydride are often performed at pH 1. Because of the high degree of observed transformation reaction we recommend derivatization of DMAA and TMAO at a pH level of 2. The adjustment of higher pH levels would once result in a decreasing hydride forming efficiency of dimethylated arsenic compounds that are frequently found in environmental samples. Twice performing hydride generation at pH levels of 3 or more would lead to a higher hydride forming efficiency of TMAO, but again this effect is only

significant at pH 7 whereas this pH level shows a very low hydride formation efficiency for DMAA.

Acknowledgements

The authors are grateful to L. Smith for comments improving the text.

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