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Organoarsenic compounds in water samples – the problem of hydride generation atomic absorption spectroscopic method

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ABSTRACT

The limitation of using a standardized method for the determination of total arsenic in water samples containing various organoarsenic compounds by the hydride generation technique in combination with atomic absorption spectrometry is presented in the publication. The study was carried for aqueous solutions of the organoarsenic compounds with significantly different molecular structures such as: dimethylarsinic acid, phenylarsonic acid and *p*-arsanilic acid and mixtures thereof. It was found that, the percentage arsenic concentration determination by hydride generation atomic absorption spectrometry in relation to the total content of the element in the samples depends on the structure of organoarsenic compound. The determination of As by hydride generation in water samples solutions containing various inorganic and organic forms of arsenic species is challenging.

Keywords: Hydride generation atomic absorption spectrometry; Total arsenic; Organoarsenic compounds; Determination

1. Introduction

Arsenic naturally occurs in the environment in various chemical forms and oxidation states. Twenty-five different arsenic compounds have been identified in the aquatic environment. Inorganic arsenic in natural waters can occur in several forms mainly as trivalent arsenite (As(III)) or pentavalent arsenate (As(V)). Organic forms of arsenic are abundant in seafood and include forms such as monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA) and arsenosugars. Organoarsenic compounds in both trivalent and pentavalent forms are used in industry and agriculture [1–4]. Pentavalent arsenate is a form of As with many commercial applications such as agricultural pesticides, glass manufacturing, Cu refining, veterinary drugs and is present in soil under oxidizing conditions [5,6]. As(III) is expected to be the primary form of As found in waste environments and in water-saturated soils or soils containing significant amounts of organic matter. Several methods are available for the determination of total arsenic in water. The most common of these methods include: atomic absorption spectroscopic method coupled with hydride generation atomic absorption spectrometry (HG-AAS) [7–11], electrothermal atomic absorption spectrometry (ET-AAS) [12–15], silver diethyldithiocarbamate method (SDDC) [16], inductively coupled plasma with mass spectrometry (ICP-MS) [17–19], inductively coupled plasma with atomic emission spectrometry (ICP-AES) [20–23], anodic stripping voltammetry (ASV) [24] and hyphenated techniques involving chromatography [25,26], capillary zone electrophoresis coupled with element-specific detectors such as inductively coupled plasma emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS) [27–30].

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The most widely accepted technique for the analysis of total arsenic at trace level is HG-AAS [31]. This method is characterized by detection limit below 0.001 mg L^{-1}. HG is a chemical derivatization process that produces volatile hydrides upon chemical treatment of a sample with reducing agent, typically sodium tetrahydroborate [32]. The determination of As by HG in sample solutions containing various inorganic and organic species is challenging. Several organoarsenic compounds do not form volatile hydride under sodium tetrahydroborate treatment or are converted with very low efficiencies. The hydride generation method for determination of arsine after the reduction of arsenic(V), was presented by Bundaleska et al. [33]. However, this technique does not identify other arsenic species, that is, which do not form volatile hydrides after reduction. For example, arsenobetaine, the major form of arsenic in marine animals, does not form methylated arsine after $NaBH_4$ reduction [33], but it has been reported that alkali-digested arsenobetaine form trimethylarsine. Schmeisser et al. [34] presented that hydride generation efficiency in case of arsenosugars found in biological samples depend on the type of hydride generation system and is influenced by the concentration of HCl and $NaBH_4$. For the four arsenosugars investigated by them, the hydride generation efficiencies were approximately 21%–28% or 4%–6% depending on HG system. Also, Marschner et al. [35] investigated hydride generation from arsenosugars in batch and flow injection mode. Its efficiency was found higher in H_2SO_4 medium than in HCl and higher in the batch mode than in the flow injection mode. The arsenosugars studied yielded HG efficiencies in the range 13%–30%. Marschner et al. [36] in other work characterized demethylation of MMAA, DMAA and trimethylarsine oxide (TMAO) during the reaction with $NaBH_4$ under analytical conditions in the presence of HCl, $HClO_4$ and H_2SO_4. They also concluded that extent of demethylation strongly depends on concentration of the acid and $NaBH_4$. The limited operating range of the HG-AAS method is particularly problematic when analyzing samples from areas with high and varying concentrations of arsenic in water.

The limitation of the HG-AAS detector to non-hydride active species can be eliminated by making the experimental scheme more complex, by addition an digestion unit between the separation unit and the detector for speciation analysis of organoarsenicals [31,37]. Several papers have described using coupling HPLC-HG-AAS method for speciation analysis of organoarsenic form. The quantitative analysis in this case is based on the external standard method, which limits the influence of hydride formation efficiency on determination result, but only affects the determination and detection limit. One major limitation in the coupling technique of the HPLC-HG-AAS system is that arsenobetaine, arsenocholine, tetramethylarsonium ion and most of arsenosugars do not form volatile hydrides [38–40]. In case of MMAA and DMAA was described experimental setup consisting of a flow injection hydride generator coupled to an atomic fluorescence spectrometer optimized in order to generation arsanes from MMAA, and DMAA with 100% efficiency with the use of HCl and $NaBH_4$ as a reagents by Marschner et al. [41]. This method was used for speciation analysis with high-performance liquid chromatography (HPLC) technique. Hydride generation-cryotrapping-gas chromatography-atomic absorption spectrometry (HG-CT-AAS) was applied for arsenic speciation analysis in an injectable drug, N-methylglucamine antimonate by Moraes et al. [37]. The method employs generation of substituted hydrides and selective hydride generation, which makes possible an analysis of arsenites and arsenates and their mono-, di-, and trimethyl substituted species.

The aim of the study is to demonstrate the impact of organoarsenic compounds with a different molecular structure on the total arsenic determination result in water samples according to standard ISO procedure [8] by HG-AAS, without the parameter optimization to reach 100% yield and speciation. Detailed studies of the hydride generation technique have revealed several problems in the direct (without speciation analysis) quantitative determination of total arsenic in environmental samples. This problem is particularly evident in the case of samples containing inorganic and organic forms of arsenic on different oxidation states [42]. It is well known that most organoarsenic compound like arsenobetaine, is a non-hydride forming As species, and also in HG-AAS technique the efficiency of arsine production is dependent on the acidity of the solution and the concentration of $NaBH_4$ [36,43,44]. The ISO standard is widely used in environmental monitoring to determine total arsenic in water samples. The study is intended to illustrate that lack of knowledge of the exact qualitative composition of compounds containing arsenic in the structure (organic compounds of arsenic) has a significant impact on the overall result of the analysis. Investigations in literature were made in most cases for the methylated As species (MMAA, DMAA and TMAO) and arsenosugars, but there is no information about the behaviour of other organoarsenic compound which have different molecular structure. The evaluation of using HG-AAS technique according the standardized procedure for the determination of total arsenic present in organoarsenic compounds in this work was carried out for three compounds with significantly different molecule structure, physicochemical properties, and occurred in different types of environmental samples. The DMAA found in copper ore mine waters and surface water, phenylarsonic acid present in the effluent from non-ferrous metals, and *p*-arsanilic acid used as, a veterinary feed additive to promote growth and prevent or treat dysentery in poultry and swine, were chosen for further investigations [45]. Arsenic occurs in the (V) oxidation state in those compounds.

2. Experimental

2.1. Reagents

The following compounds were used as a model substances with organic arsenic: *p*-arsanilic acid (PAA, Sigma-Aldrich, USA), phenylarsonic acid (PA, Acros Organics, Belgium), dimethylarsinic acid (cacodylic acid) (DMAA, Sigma-Aldrich, USA) and a mixture of these three substances in deionised water. The structure of organoarsenic compounds are given in Fig. 1. All reagents used were of analytical reagent grade.

Suitable working solutions were prepared by diluting the stock solutions with concentrations given in Table 1.

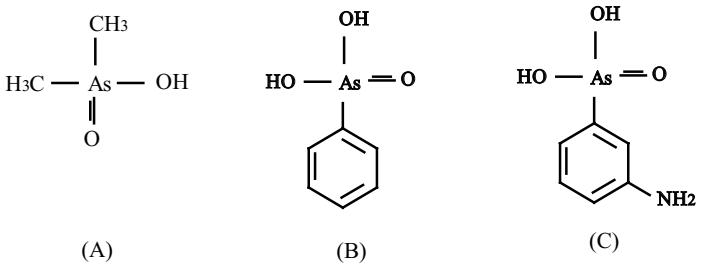

Fig. 1. Structure of organoarsenic compounds (A) dimethylarsinic acid, (B) phenylarsonic acid, and (C) *p*-arsanilic acid.

Table 1
Concentrations of selected organoarsenic compounds in stock solutions

Compound	Concentration of compounds in stock solution, mg L^{-1}	Concentration of As in stock solution, mg As L^{-1}
DMAA	94.23	51.25
PA	64.36	23.89
PAA	56.75	19.61
Mixture consist of:		54.34
DMAA	58.35	31.71
PA	31.57	11.72
PAA	31.57	10.91

2.2. Methods

Arsenic was determined by hydride generation method (HG-AAS) according to common procedure such as ISO 17378-2:2014 [8]. Prior the determination arsenic in samples was reduced from As(V) to As(III) form by consecutively addition of concentrated chloric acid (I) and pre-reducing agent (II). For better reduction of organic arsenic the samples were left standing overnight in the room temperature. The concentration of reducing agent ($NaBH_4$) used in flow injection analysis (FIAS) module was 0.2% for Series A and increased up to 0.5% for Series B. Arsenic hydride was separated in FIAS module and was transferred with argon stream to the quartz cell where was atomized in the temperature of 900°C.

Dual beam spectrometer AAS AAnalyst 400 (Perkin-Elmer, USA) equipped with S10 autosampler and Flow Injection Analysis module FIAS 100 with electrically heated quartz cell, was used for AAS detection. Data were processed with a computer and WinLab 32 for AA Ver. 7.0 software. Parameters of AAS Analyst 400 and hydride generation parameters are given in Tables 2 and 3.

Series of model solutions containing inorganic form of As(V) were prepared. Solutions were subjected to the presented above procedure. The obtained results became the basis for construction of the calibration curve. The concentrations of standards were, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 20.0, and 40.0 μg L^{-1} of As and blank. For each of the standard solutions at each concentration level analysis were performed three times. The method is characterized by limit of quantification (LOQ) of 0.27 μg As L^{-1} and the expanded uncertainty for $k = 2$ were 11%. The analytical precision was 12% (expressed as RSD%).

In order to demonstrate the effect of mineralization on the analysis results, the same solutions of selected organoarsenic compounds, was mineralized with a concentrated HNO_3 (V). A sample aliquot (50 mL) was boiling in a glass flask on electric plate with 5 mL of concentrated HNO_3 (V) until about 10 mL of solution was evaporated. The final volume of solution was set at 50 mL, and then quantitatively analyzed.

To determine the applicability of HG-AAS method for determination of As in selected organoarsenic compounds in water samples, the arsenic response factor (Ro) was adopted. Ro factor determines the percentage of determined total arsenic concentrations in relation to the total content of the element in the standard solutions, determined according to Eq. (1).

$$R_0 = \frac{\text{Determinated concentration of total As in standard solution}}{\text{Concentration of total As in standard solution}} \times 10 \quad (1)$$

3. Results and discussion

3.1. Compound structure influence on the arsenic response factor

The results in DMAA concentration determination indicates that only for the concentration above 10 μg As L^{-1}, the detector response was obtained at the level above the limit of quantification, which corresponds to the 18 μg L^{-1} of the analyte concentration. The investigations were carried out on the DMAA standard solutions, containing from 0.5 to 20.5 μg As L^{-1} in addition of 0.2% $NaBH_4$ (Table 4). No signal from the detector above

the limit of determination suggests, that for As in DMAA structure limit of quantification is above 9.5 μg L^{-1}. The Ro factor for this concentration was 10% (SD = 1.67%). A similar value of this factor equal to 9.4% (SD = 1.32%) was obtained in the analysis of a solution in a concentration of 20.5 μg As L^{-1}. The results demonstrate that the use of 0.2% of a reducing agent allows for determination about 10% of total As present in the form of DMAA in the solutions.

The high limit of quantification compared to other published results, in which the hydride generation efficiency is close to about 100%, is due to the use of a higher HCl concentration in accordance with the provisions of the ISO normative methodology. The results presented in the literature result from the optimization of the methodology for the determination of DMAA. Rüde and Puchelt [46] showed that at a high concentration of HCl, reduction of methyl derivatives of arsenic practically does not take place. DMAA species are converted not only to its corresponding hydride $(CH_3)_2AsH$, but also to other species like AsH_3 and CH_3AsH_2 [47,48]. Talami and Bostick [47] presented that the conversion to the noncorresponding hydride was pH dependent. This was confirmed by Musil et al. [49], DMAA is efficiently converted to the corresponding arsanes at lower HCl concentration, but with increasing concentration, the DMAA HG efficiency can be almost completely suppressed. Regmi et al. [50] explained the cleavage by formation of a analyte – borane complex which withdrew electron density from methylene making it more suitable to hydride attack. This indicates that arsenic determination based on the generation of substitutes arsanes in the HCl media could provide inaccurate results.

Table 2
AAS parameters

Parameter	Value
Wavelength, nm	193.7
As EDL Lamp Current, mA	400
Slit, nm	0.7
Data processing	Peak area
Integration time, s	15
Cell temperature, °C	900

Table 3
Arsenic hydride generation parameters

Parameter	Value
Acid (I)	2.5 mL of concentrated HCl
Pre-reducing agent (II)	2.5 mL of 5% (w/v) KI + 5% (w/v) ascorbic acid
Volume of the sample	20 mL + I + II
Time of reduction	Overnight in the ambient temperature
Carrier solution	10% (v/v) HCl
Reducing agent	Series A 0.2% $NaBH_4$ in 0.05% NaOH Series B 0.5% $NaBH_4$ in 0.05% NaOH
Carrier gas	Argon
Loop sample volume	500 μL

Marschner et al. [35] studies hydride generation form arsenosugars and found higher efficiency of HG in H_2SO_4 medium then in HCl in batch mode then in injection one. Also, investigations [36] shows that the extent of demethylation strongly depends on the concentration of acid and $NaBH_4$. The demethylation can be strongly suppressed in HCl medium by partial hydrolysis of $NaBH_4$ with optimal concentration of acid before it reacts with MMAA, DMAA, and TMAO.

In the case of phenylarsonic acid determination, under the same conditions signal linear dependence was obtained in a function of the concentration of arsenic present in the test compound with the regression coefficient (R^2) at 0.99 (Fig. 2).

Based on the standard deviation of a set of signals and the angle of the calibration curve the limit of quantification of PA was determined as 0.9 μg L^{-1}, which corresponding to a concentration equal to 0.3 μg As L^{-1}. The average coefficient Ro for PA was 76.1% (SD = 1.56%) and ranged from 73.7% to 77.8% (Table 5). There were no changes in the coefficient Ro in function of the concentration of arsenic in test solutions in the concentration range of 0.6 to 24 μg As L^{-1}. The results indicate that the use of HG-AAS allows to determining of 76% total arsenic contained in phenylarsonic acid molecules.

Results of measurements of *p*-arsanilic acid by HG-AAS obtained during the Series A showed a logarithmic relationship

Table 4
Relationships arsenic response factor (Ro) vs. concentration of DMAA and reducing agent (Series A - 0.2%; Series B - 0.5%)

Concentration of DMAA, μg L^{-1}	Concentration of As, μg As L^{-1}	Determined As, μg As L^{-1}	Ro, %	Determined As, μg As L^{-1}	Ro, %
		Series A		Series B	
0.94	0.51	n.d.	–	n.d.	–
1.88	1.02	n.d.	–	n.d.	–
3.77	2.05	n.d.	–	n.d.	–
9.42	5.12	n.d.	–	0.56	10.9
18.85	10.25	1.04	10.04	1.11	10.8
37.69	20.50	1.88	9.40	1.96	9.5

n.d. – below limit detection.

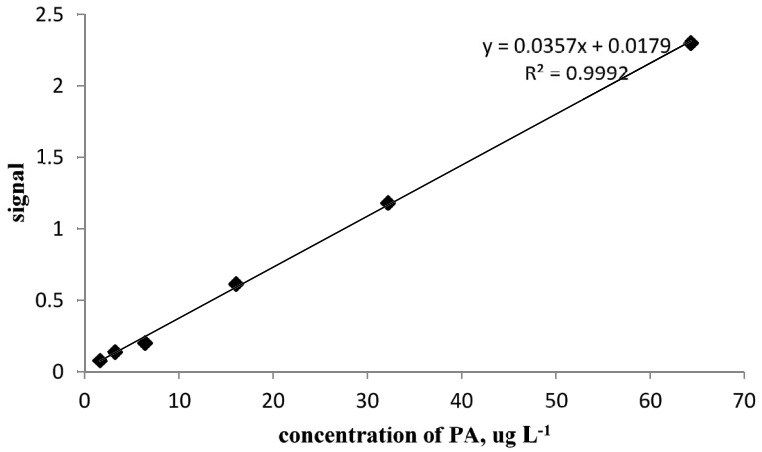

Fig. 2. Dependence of the signal in function of the concentration of PA.

Table 5
Relationships arsenic response factor (Ro) vs. concentration of PA and reducing agent (Series A - 0.2%; Series B - 0.5%)

Concentration of PA, µg L^{-1}	Concentration of As, µg As L^{-1}	Determined As, µg As L^{-1}	Ro, %	Determined As, µg As L^{-1}	Ro, %
		Series A		Series B	
1.61	0.59	0.44	73.7	0.45	76.3
3.22	1.19	0.90	75.6	0.93	78.2
6.43	2.39	1.86	77.8	1.86	77.8
16.08	5.97	4.62	77.4	4.62	77.4
32.16	11.90	9.15	76.9	9.27	77.9
64.32	23.90	17.95	75.1	18.66	78.1

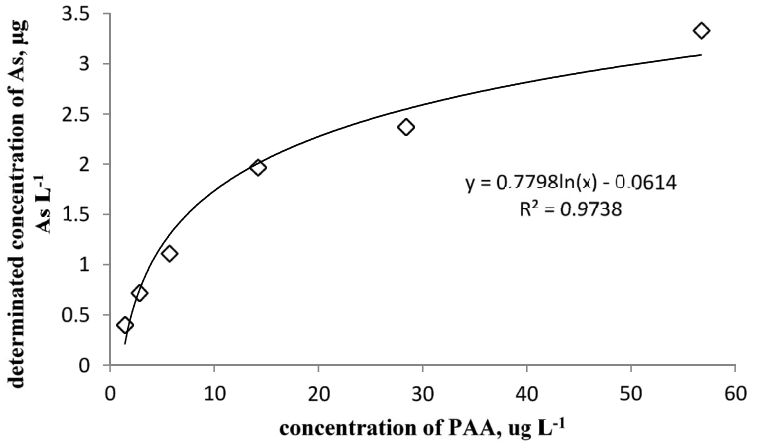

Fig. 3. Relationship of determined concentrations of arsenic contained in the PAA in function concentration of PAA.

between the concentration of PAA in the test solution, and the determined concentration of total arsenic (Table 6 and Fig. 3). Shown in Fig. 3 dependence indicates that the HG-AAS method for PAA do not fulfill the criteria of quantitative analysis. The Ro factor, in the case of *p*-arsanilic acid has increased in the range from 17.0% (SD = 0.4%) to 81.6% (SD = 0.6%) in function of PAA concentration decline in the solution (Fig. 4).

This phenomenon can be the result of increased concentration of amino groups in the test solutions. The amino groups will reduce the efficiency of the reduction of As(V) to As(III) or/and arsenic hydrogenation reaction, and may affect on the signal from the detector. Similar phenomenon was observed by Pohl and Zyrnicki [51], during arsenic determination in samples with high concentrations of heavy metals and nitrate. The results indicate that

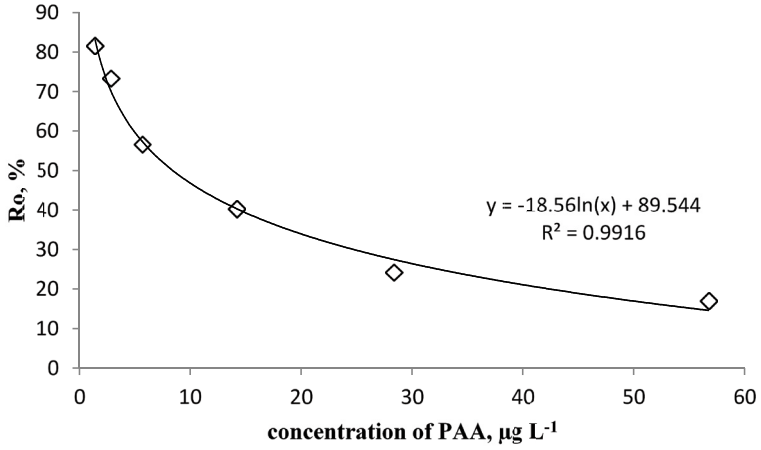

Fig. 4. Relationship of the Ro vs. concentration of PAA.

Table 6
Relationships arsenic response factor (Ro) vs. concentration of PAA and reducing agent (Series A - 0.2%; Series B - 0.5%)

Concentration of PAA, µg L^{-1}	Concentration of As, µg As L^{-1}	Determined As, µg As L^{-1}	Ro, %	Determined As, µg As L^{-1}	Ro, %
		Series A		Series B	
1.42	0.49	0.40	81.6	0.42	86.1
2.84	0.98	0.72	73.3	0.72	73.6
5.68	1.96	1.11	56.6	1.31	66.8
14.19	4.90	1.97	40.2	2.66	54.2
28.38	9.81	2.37	24.2	4.37	44.5
56.75	19.60	3.33	17.0	6.41	32.7

the structure of organoarsenic compound influence on the limit of quantification of arsenic, and the linearity of the analytical signal in function of the total As concentration. HG-AAS method applied for determining the concentration of *p*-arsanilic acid not fulfill the criteria posed for the analytical methods, therefore, it should not be applied to the determinations of total arsenic in samples which contains PAA acid. The investigations were also carried out on the mixture of previous organoarsenic acids (DMAA, PA, PAA) in composition given in Table 1, in concentration rage of 0.54 to 21.74 µg As L^{-1}. Signals were not obtained above the limit of quantification for 0.54 and 1.09 µg As L^{-1}. In other cases, the response factor was varied from 22.6% to 33.5% (Table 7). The expected concentration measured was calculated for the analyzed mixture of organoarsenic species taking into account the As contribution from individual species to the total As content (Table 7). In calculation were used the response factors (Ro) obtained for the individual species. In case of standard mixture with total As concentration of 10.87 µg As L^{-1} the As contribution was as follows: 6.34 µg As L^{-1} form DMAA, 2.34 µg As L^{-1} from PA and 2.18 µg As L^{-1} form PAA. The expected concentration measured should be <LOQ for DMAA (Table 4), 1.82 µg As L^{-1} for PA (assuming 77.8% Ro as presented in Table 5), and 1.23 µg As L^{-1} for PAA (assuming 56.6% Ro as presented in Table 6). The theoretical and measured values were different in case of concentrations up to 2.17 µg As L^{-1}. In the higher concentration levels the theoretical and measured values were statistically the same, when the uncertainty of the method was taking into account (u = 11%).

3.2. *Effect of $NaBH_4$ concentration on arsenic response factor (Ro)*

Wahed et al. [52] found that high concentrations of $NaBH_4$ and HCl adversely affected the signal to background ratio for arsenic. Concentrations of $NaBH_4$ above 1% caused background drifting and increased the flame. High concentrations of $NaBH_4$ showed negative absorbance because of high amounts of hydrogen produced from the reaction of $NaBH_4$ with HCl. Also, it is well-known that a number of organic compounds do not react with sodium tetrahydroborate these included arsenobetaine, trimethylated arsenic compounds and monomethylarsonic acid. To assess the impact of the reductant on arsenic response factor (Ro), study were carried out for the two concentrations of the reductant 0.2% $NaBH_4$ in 0.05% NaOH (Series A) and 0.5% $NaBH_4$ in 0.0% NaOH (Series B).

In the case of DMAA (Table 4) was found that increasing amount of reducing agent resulted in a lower limit of quantification of methods. It makes a possibility of determining Ro for the concentration of arsenic at 5 µg As L^{-1}, which corresponds to a concentration equal to 9.4 µg L^{-1} for DMAA. As in Series A, in samples with higher concentration of

Table 7
Relationships arsenic response factor (Ro) vs. concentration of organoarsenic compounds mixture (Table 1) and reducing agent (Series A - 0.2%; Series B - 0.5%), and theoretical concentration of As calculated basing on the results from experiments for single organoarsenic compounds, which should be determined. Uncertainty of the method u = 11% with k = 2

Concentration of As in mixture, µg As L^{-1}	Determined As, µg As L^{-1}	Ro, %	Theoretical concentration of As, µg As L^{-1}	Ro, %	Determined As, µg As L^{-1}	Ro, %	Theoretical concentration of As, µg As L^{-1}	Ro, %
	Series A				Series B			
0.54	n.d.	–	n.d.	–	n.d.	–	n.d.	–
1.09	n.d.	–	0.35	32.1	n.d.	–	0.36	33.0
2.17	0.49	22.6	0.70	32.2	0.38	17.5	0.73	33.6
5.43	1.82	33.5	1.68	30.9	1.48	27.2	1.71	31.5
10.87	3.26	30.0	3.05	28.1	3.26	30.0	3.28	30.2
21.74	6.67	30.6	6.65	30.6	7.85	36.1	7.36	33.8

n.d. – below limit detection.

reductant, Ro had a value in the range from 10.9% to 9.5% (SD = 0.9%).

Increasing the addition of a reducing agent (Series B) in the PA analysis resulted in a Ro slight increase, compared to Series A (Table 5). As in the case of Series A relationship of the analytical signal vs. arsenic concentration in the solution was linear.

Increase in reducing reagent addition caused a Ro increase in the whole range concentrations for PAA. The biggest Ro increase was observed for PAA concentrations of 14.19, 28.38 and 56.75 µg L^{-1} (Table 6). Fig. 5 compares the arsenic response factor (Ro) for the PAA determination in Series A and B.

In the case of determination of PAA, in Series B as in Series A, results shown no linear relationship between the concentration of PAA in the solution and signal.

Determination of total arsenic in the mixture of organoarsenic compounds showed that the increase in $NaBH_4$ addition resulted in changing of the arsenic response factor (Table 7). The higher addition of $NaBH_4$, cause the decrease of the Ro factor under concentrations 2.17 and 5.43 µg As L^{-1}, while at the concentration of 21.74 µg L^{-1} showed an increase of this parameter.

The results indicate an influence of the compound type on an arsenic response factor (Ro). The test organoarsenic compounds react with sodium tetrahydroborate, but the yield of the reaction is probably differentiated due to their structure. The highest response factors were found for phenylarsonic acid, the lowest for dimethylarsinic acid. The required oxidation state for hydride generation of arsenic is (III) and depending upon sample preparation, adjustment of the oxidation state is required. Low response factor in the case of DMAA may also result from the limited capacity of the reduction reaction leading to the formation of As(III). In the case of combined techniques HPLC-HG-AAS, when applied external standard method determination of DMAA is possible, but the detection limit of this compound is usually above 50 µg L^{-1}, which is not always satisfactory in the case of the analysis of arsenic compounds.

On the other hand a high response factor for the PA, and a linear relationship of the detector signal as a

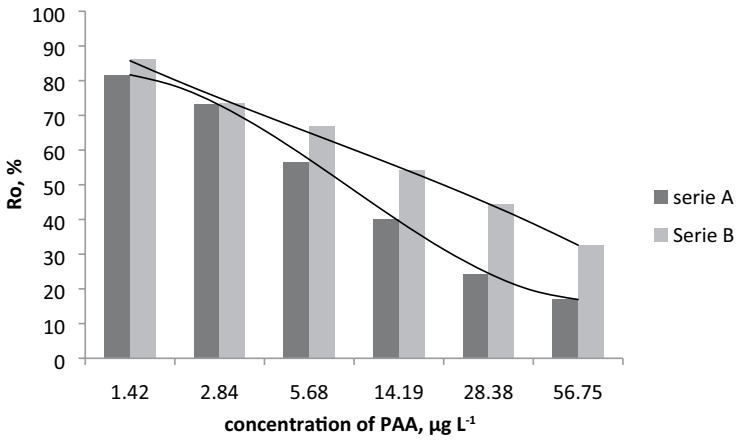

Fig. 5. Relationships of the Ro vs. concentration of PAA and concentration of $NaBH_4$ (Series A - 0.2% $NaBH_4$ in 0.05% NaOH; Series B - 0.5% $NaBH_4$ in 0.05% NaOH).

function of concentration indicates the technique can be used in speciation analysis of organoarsenic compounds. However, due to the non-linearity of the detector signal as a function of the concentration of *p*-arsanilic acid HG-AAS method should not be used for quantitative determinations.

3.3. Effect of mineralization on arsenic response factor (Ro)

In most of the analytical procedures for the determination of total arsenic, mineralization step is introduced for liquid samples, usually with nitric acid or sulphuric acid [53]. Therefore, studies were undertaken to evaluate the effect of mineralization on Ro. The studies were carried for the individual organoarsenic species (Table 8) and organoarsenic acid mixture having the composition shown in Table 1 and in concentration 10.87 μg As L^{-1}. The mineralization influence on the total arsenic determination by HG-AAS was carried out for the parameters for Series B, with higher concentration of $NaBH_4$. The results showed that the mineralization with nitric acid to a small extent influenced on the Ro increase (Tables 8 and 9). Average response factor for arsenic determinations of organoarsenic acid mixtures without mineralization was 29.2% (SD = 0.4%), while after sample mineralization obtained Ro was equal to 30.5% (SD = 0.5%). The difference in the values of Ro with and without mineralization was not statistically significant. The same situation was in case of sample of individual species (Table 8). It indicates that simple acid digestion performed in a hot plate with nitric acid was insufficient for mineralization of investigated organoarsenic compounds. Two main groups of mineralization methods for organic As compounds are reported in literature: wet with acid mixtures and microwave power and dry-washing method [54]. The different acid mixtures like HNO_3/HCl, HNO_3/H_2SO_4, $HNO_3/H_2SO_4/H_2O_2$, $HNO_3/HClO_4/KI$ were investigated for mineralization of As species. It can be concluded that the As recovery is dependent on the kind of samples.

Thus, classical analytical procedures for the determination of total arsenic including mineralization and quantitative determination by HG-AAS method, in case of samples containing different organoarsenic compounds, may influence on the correctness of the results.

4. Conclusion

The organoarsenic compounds show different behaviour in the hydride generation process in measurements of the total content of As in the sample. It was demonstrated that even at higher concentration of sodium tetrahydroborate, the response obtained from organoarsenic compounds is lower than that of inorganic species. Also, the percentage arsenic concentration determination by HG-AAS in relation to the total content of the element in the samples depends on the structure of organoarsenic compound. Many organometallic species cannot produce their hydrides by simple reduction. Thus the quantitative decomposition of these molecules to form hydride – forming species must be achieved before reduction. Even, mineralization of the samples containing organoarsenic compounds not in every case allows to quantitative analysis of total As with the required precision. The introduction of a photolytic process to produce simpler species which could generate hydrides by reduction appeared to be a good decomposition system.

Table 8
Relationships arsenic response factor (Ro) vs. concentration of organoarsenic species with mineralization step

	Concentration of organoarsenic compound, μg L^{-1}	Concentration of As, μg As L^{-1}	Determined As, μg As L^{-1}	Ro, %
DMAA	0.94	0.51	n.d.	–
	1.88	1.02	n.d.	–
	3.77	2.05	n.d.	–
	9.42	5.12	0.6	11.8
	18.85	10.25	1.18	11.6
	37.69	20.50	2.07	10.1
PA	1.61	0.59	0.45	76.7
	3.22	1.19	0.94	78.9
	6.43	2.39	1.87	78.2
	16.08	5.97	4.63	77.7
	32.16	11.91	9.36	78.6
	64.32	23.92	18.85	78.8
PAA	1.42	0.49	0.42	86.9
	2.84	0.98	0.73	74.5
	5.68	1.96	1.33	67.7
	14.19	4.90	2.70	55.1
	28.38	9.81	4.44	45.3
	56.75	19.60	6.57	33.5

n.d. – below limit detection.

Table 9
Result of an arsenic determination in model solutions containing organoarsenic compounds, a total arsenic concentration equal to 5.43 and 10.87 μg As L^{-1}, with and without mineralization

Parameter	Concentration of As, without mineralization, μg As L^{-1}	Concentration of As, with mineralization, μg As L^{-1}
Sample 1	3.26	3.37
Sample 2	3.22	3.37
Sample 3	3.19	3.32
Sample 4	1.56	1.62
Sample 5	1.54	1.62
Sample 6	1.59	1.68
Ro, %	29.2	30.5

Symbols

Ro	—	Arsenic response factor
MMAA	—	Monomethylarsonic acid
DMAA	—	Dimethylarsinic acid
PA	—	Phenylarsonic acid
PAA	—	*p*-arsanilic acid
TMAO	—	Trimethylarsine oxide

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