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Determination of selected organoarsenic compounds by SPME/GC-MS in aquatic samples

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ABSTRACT

A gas chromatography with mass spectrometry was developed for the determination of selected organoarsenic compounds, for example, monomethylarsonic acid, dimethylarsinic acid, phenylarsonic acid, nitarsone and roxarsone, in aquatic environment. For the analysis by gas chromatography, analytes was derivatized with 1,3-propanedithiol. The cyclic dithiaarsenoline formed was extracted from the sample matrix by solid-phase microextraction (SPME). The extraction studies were carried out on different types of extraction fibers such as polyacrylate, polydimethylsiloxane-modified divinylbenzene, carboxenpolydimethylsiloxane, divinylbenzene carboxen polydimethylsiloxane under different conditions. The optimized SPME conditions employed a 65 μm polydimethylsiloxane divinylbenzene fiber, derivatization reaction temperature of 60°C and fiber equilibration time of 30 min. The method allows for the simultaneous determination of monomethylarsonic acid, dimethylarsenic acid, phenylarsonic acid, roxarsone and nitarsone. The repeatability of the analytical method is in the range from 0.78% to 3.23%, and the limits of determination ranging from 0.35 to 5.88 μg L^{-1}, depending on the compound. The method was applied to determine an organoarsenic compounds in mining water and wastewater from metallurgy of non-ferrous metals industry.

Keywords: Organoarsenic compounds; GC/MS; SPME; Water

1. Introduction

Arsenic is widely distributed in the environment, contaminated soils, sediments and sludge are the major source of arsenic contamination of the food chain, surface water, ground water and drinking water. Arsenic is cycling among different valence states and chemical species in environment. Depending on the redox potential of environment, arsenic exists in four oxidation states: –3, 0, 3 and 5 [1]. While the treatment and removal of As(III) and As(V) from drinking water have received extensive attention, the wide spread use and environmental threat of organoarsenic species have received much less attention [2–5]. Humans are exposed to naturally occurring and anthropogenic sources of As compounds in environment [6]. Health problems associated with exposure to arsenic continue to command world attention. The World Health Organization (WHO) and Environmental Protection Agency (EPA, USA) reduced limits of As in drinking water to 10 μg L^{-1} [6]. Environmental fate and behavior, bioavailability and toxicity of arsenic vary with the chemical form (species) in which arsenic exists. While inorganic arsenite and arsenate are highly toxic, organoarsenic acids are less toxic. Thus, assessments of environmental impact and human health risk strictly based on measurements of total element concentration are not reliable. It is important to identify and quantify individual chemical species of the element. Organic connection of arsenic may be present in surface waters by biological activity of aquatic

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organisms – for example, by methylation reaction by phytoplankton. Organoarsenic compounds (OA) typically exist in the pentavalent oxidation state and have been introduced into the environment through agricultural applications. Methylated arsenicals are widely used as herbicides, for example, for cotton farming. Phenylated arsenic compounds including 4-aminophenylarsenic acid (*p*-arsanilic acid; *p*-AsA), roxarsone, (3-hydroxy-3-nitrobenzenearsonic acid, ROX) nitarsone ((4-nitrophenyl)arsenic acid, NITR) and carbarsone ([4-(carbamoylamino)phenyl]arsonic acid, CARB) are commonly utilized in the broiler poultry industry as feed additives. The phenyl arsenic feed additives were reported to be inert in the environment, and was indicated that those nontoxic organoarsenic compounds may be converted into more mobile and toxic inorganic arsenic species [2]. To date numerous arsenic compounds have been identified in biological and environmental samples. The wells located in Bangladesh and Taiwan repeatedly had high arsenic concentrations of up to 2,500 mg L^{-1} [3]. Literature data indicate that in these waters are not only found inorganic but also organic compounds of arsenic, which are better absorbed in the waters to the trophic chain [4].

Nowadays, it is well established that total arsenic concentration provide no information about possible risks [5]. The determination of individual molecular species of arsenic is absolutely necessary for risk assessment. Knowledge about the chemical form of an element provides useful information on its bioavailability, transport and metabolism. Due to the fact that not all arsenic compounds can be easily reduced to volatile hydrides, various chromatographic separations have been utilized to examine all the arsenic compounds present in a sample [7]. Most of the arsenic compounds can be present in solution as neutral, anionic or cationic species, depending on pH. The most commonly used method for separating organoarsenic compounds is high-performance liquid chromatography (HPLC) [8–11]. To a lesser extent, gas chromatography and capillary electrophoresis are used. Before the separation, in order to enrich the retained compounds the microextraction to stationary phase and derivatization is applied, in which the test analytes are converted into compounds having a different volatility, polarity or hydrophilicity [12]. One of detection method of organoarsenic compounds is mass spectrometry with excitation in the inductively coupled plasma (ICP-MS). This technique is characterized by high sensitivity, low detection limit, good selectivity, simplicity and short time of analysis. Its disadvantage is the fact that no information is obtained about the structure of the tested compounds and the results of qualitative analysis are dependent on the availability of standards. In addition, the risk of elute other compounds can result in false results of the analysis (both qualitative and quantitative). The other technique for determination of organoarsenic compounds is mass spectrometry via electrospray ionization (ESI–MS), which is ideally suitable for non-volatile compounds and/or heat stable [13]. Two other techniques play an important role in organoarsenic compounds analysis, namely: atomic absorption spectrometry (AAS) and atomic fluorescence spectroscopy (AFS). Very often in analysis of inorganic form of arsenic, AFS and AAS are coupled with hydride generation (HGAFS, HGAAS) [14]. Sample concentration and extraction procedures consist of traditional approaches such as solid–liquid or liquid–liquid extraction, solid-phase extraction and solid-phase microextraction (SPME). Solid samples preparation generally includes milling, grinding, freeze-drying or sieving followed by some form of extraction. Leaching (solid–liquid extraction) or Soxhlet extraction is commonly practiced. Enhanced techniques such as pressurized liquid extraction, microwave-assisted extraction and supercritical fluid extraction have all been used in arsenic analysis [15]. Stationary phase microextraction is a novel extraction technique, which consists of both sampling and concentration. This technique can be easily automated and combined with HPLC [16]. In order to increase detection and improve the chromatographic separation prior to microextraction, the derivatization of analytes by dithiols, such as 1,2-ethanedithiol, 1,3-propanedithol, 1,4-butanedithiol, 2,3-dimercaptopropanole was carried out. Depending on the polarity and volatility of the derivatized product, different fibers were used: 100 mm polydimethylsiloxane (PDMS), 85 mm polyacrylate (PA) and 65 mm carbowax–polydivinylbenzene (Carbowax-DVB). Although the most intense and stable signals are obtained when using the PA but the best is the stationary phase of PDMS because of its low roughness and high strength compared with other fibers [16–18].

The purpose of this study was to develop a rapid and sensitive method for the determination of selected organoarsenic compounds, for example, monomethylarsonic acid, dimethylarsenic acid, phenylarsonic acid, roxarsone, nitarsone, carbarsone, in aquatic environment by using SPME/GC-MS. Methods were used to determine the selected organoarsenic acids in water and wastewater samples.

2. Experimental

2.1. Chemicals and reagents

Reference standards, monomethylarsonic acid (MMA; purity ≥ 97.5%), dimethylarsenic acid (DMA; purity ≥ 99%), *p*-arsanilic acid (*p*-AsA; purity > 99%), nitarsone (NITR; purity 99.6%), roxarsone (ROX; purity 99.9%), phenylarsonic acid (PAA purity 97%) was from Acros Organics (New Jersey, USA) and carbarsone (CARB; purity 99.7%) was from LGC Standards (USA). The derivatizating reagent for organoarsenic acids was 1,3-propanedithiol (PDT; purity 99%) purchased from Sigma-Aldrich (Steinheim, Germany). Hydrochloric acid and acetone were purchased from POCH (Gliwice, Poland). Water was HPLC-grade and obtained from J.T. Baker (Phillipsburg, USA).

2.2. Preparation of standard solutions

Stock solution of MMA, DMA, PAA, p-AsA, ROX, NITR, CARB selected from the organoarsenic compounds group was prepared in distilled water. The concentration of each compound in the stock solution was 0.8 mg mL^{-1}. A series of mixed standard solutions for SPME-GC/MS method, consisted of MMA, DMA, PAA, *p*-AsA, ROX, NITR and CARB (in concentrations from 0.019 to 60.8 μg mL^{-1}) were prepared from the stock solutions using HPLC-grade water acidified with 1 M HCl to pH about 2 as diluents. Six-point calibration curves were constructed in the same range.

2.3. GC-MS instrumentation

Gas chromatography (GC/MS) measurements were carried out on a PerkinElmer Clarus 500 system (Shelton, USA) which consisted of the following components: capillary column Elite-5MS (5% diphenyl, 95% dimethylpolysiloxane) of 30 m length × 0.25 mm ID with film thickness of 0.25 μm, (PerkinElmer, Shelton, USA), quadrupole ion trap mass spectrometer (50–650 *m*/*z* range), SPME apparatus (Supelco, Bellefonte, PDMS/DVB, USA).

For the SPME work, the injection port was 250°C for the fiber desorption step (splitless). The initial column temperature was 70°C, then programmed at 15°C min^{-1} to 230°C, and finally 2.5°C min^{-1} to 280°C, where it was held for 5 min. The transfer line between the GC and MS was maintained at 280°C. Quantitative analysis was performed using selected ion monitoring method, choosing two ions typical for this compound. Mass spectra were obtained by scanning from *m*/*z* 50 to 650 with 0.5 s scan time.

2.4. Solid-phase micro extraction procedure

For the determination of organoarsenic compounds by GC/MS method, the sample was acidified to pH 2 with 1.0 M HCl. Next, a 5 mL portion of the sample was transferred into an 8 mL vial (clear vial, screw top with septa). The sample was then heated to 60°C and reacted with 1 μL of 1,3-propanedithiol for 15 min. The analytes were extracted from the sample matrix by SPME. The extraction studies were carried out on different types of extraction fibers such as 85 mm polyamide (PA Supelco, Bellefonte), 65 mm polydimethylsiloxane modified divinylbenzene (PDMA/DVB Supelco, Bellefonte), 65 mm carboxen polydimethylsiloxane (CAR/PDMS Supelco, Bellefonte), 65 mm divinylbenzene carboxen polydimethylsiloxane (DVB/CAR/PDMS Supelco, Bellefonte). Before first use, the fibers were conditioned in the injector of the gas chromatograph at 260°C in accordance with the supplier's instructions.

2.5. Real samples

The real water samples were collected daily in dark glass vessels and came from the mining industry, metallurgy of non-ferrous metals and chicken farms. The water samples were filtrated with 0.45°μm filters before SPME.

3. Results and discussion

Because of the non-volatile nature of organoarsenic compounds, it is not possible to analyze them without prior derivatization using gas chromatography. By using a reducing thiol, such as PDT, organoarsenic compounds are converted to their cyclic dithiaarsenolines [19,20]. Fig. 1 presents the scheme of net reaction for derivatization of PAA.

Those cyclic dithiaarsenolines can be extracted using SPME. Derivatization by PDT of solution containing MMA, DMA, PA, p-AsA, ROX, NITR, CARB was investigated.

1,3-propanedithiol (PDT) was chosen as the derivatizing reagent in view of the relatively high purity of the commercially available PDT. To prevent the protonation of the organoarsenic acid, aqueous standard solutions were acidified to pH of 2. To the prepared sample, derivatizing reagent was added and the reaction was carried out at 60°C. Extraction of the thiol derivatives of OA was made by SPME technique. Reaction derivatization according to the diagram in Fig. 1 takes place for MMA, DMA, PA, ROX and NITR. The signals observed in the chromatograms for standard solution were well-resolved peaks of MMA, DMA, PA, ROX and NITR (Fig. 2).

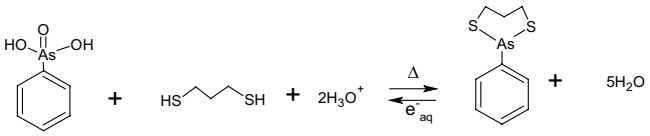

Fig. 1. Schemes of derivatization reaction of phenylarsonic acid.

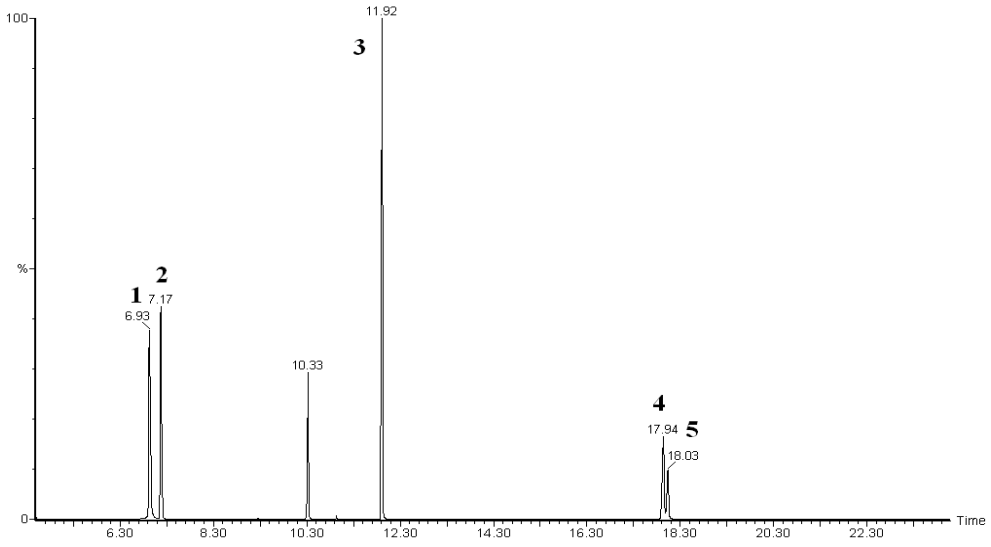

Fig. 2. Chromatogram of the mixture of selected thiol derivative of organoarsenic compounds: 1 – MMA, 2 – DMA, 3 – PAA, 4 – ROX, 5 – NITR (a standard solution 0.2 mg mL^{-1}).

p-AsA and CARB did not give any response in MS modes. Bednar et al. [19] indicates that amine group located on the aromatic ring retains an overall positive charge under pH 2. Although pH 2 is optimal for derivatization, presence of positive charged amino group reduces the derivatization efficiency.

Derivatization reaction of MMA, PAA, ROX, NITR with 1,3-propanedithiol gave the expected cyclical arsenic derivative. In this reaction, arsenic is reduced from (V) to (III) oxidation state. Basing on the mass spectrum of DMA and literature [20], it was unable to determine the exact structure of the thiol-derivatized reaction products of DMA. There are two possible reaction mechanisms. In the first case, assuming that there is a reduction of arsenic, the structure of the derivative of DMA indicates the identical product derivatization as in the case of monomethylarsonic acid (V). However, the mass spectra of the thiol derivatives MMA and DMA are significantly different from each other (Fig. 3).

Derivatization reaction eliminate methyl group and formed thiol - arsenic cyclic derivative and the ion *m*/*z* 197 suggests the presence of protonated molecular ion. According to a second possible mechanism, it is the reaction of the acid with a thiol, which possesses strong reducing properties, resulting in a trivalent methylarsine CH_3AsH_2. Only this compound undergoes cyclization with PDT to form the pentavalent form, a thiol derivative of dimethylarsinic acid $(CH_3)_2AsHS$-$S(CH_2)_3$. As a result of EI ionization, a fragmentation ion corresponding to *m*/*z* 197 such as $(CH_3)_2AsH + S\text{-}S(CH_2)_3$, is formed.

In Table 1, the retention times and characteristic ions with its intensities of investigated thiol derivative organoarsenic compounds are presented. In Fig. 4, a mass spectra of nitarsone thiol derivative is shown.

3.1. Optimization of SPME conditions

Several parameters, namely type of fiber, time and temperature of extraction and salt addition, were varied in order to find suitable conditions for the determination of OA in water samples. Isolation of the PDT-derivatized organoarsenicals from the water sample was made by the SPME. MMA, DMA, PAA, ROX and NITR were extracted from aqueous standard solutions at a concentration of 40 μg mL^{-1} each, sample volume was 5 mL and extraction took 30 min. The optimum temperature of the enrichment of analytes was chosen on the basis of four different stationary phases of fiber extraction, for example, PDMS/DVB, PA, CAR/PDMS, DVB/CAR/PDMS made in a range of ambient temperatures, 25°C, 60°C and 70°C, taking as a criterion the highest value of the signal area obtained during the chromatographic analysis. For every fiber, extraction was performed six times.

For extraction carried out at 25°C, the highest and most reproducible signals for the thiol acid derivatives MMA, DMA and PAA were obtained using fibers coated with PA (Fig. 5).

The fiber with the stationary phase DVB/CAR/PDMS showed similar to PA phase extraction efficiency of the thiol derivative of the MMA, but the extraction PAA and DMA derivative efficiency were much smaller. For all of the types of fibers, very low signals from the thiol derivatives ROX and NITR were obtained. In the case of CAR/PDMS only signals for MMA and DMA derivative were observed. The CAR/PDMS fibers are better to extract compounds with smaller molecular size and get progressively worse with increasing molecular mass of the analytes [21].

Fig. 6 shows the relationship between the average surface area of the analyte signal from the type of fiber used in the extraction process at 60°C.

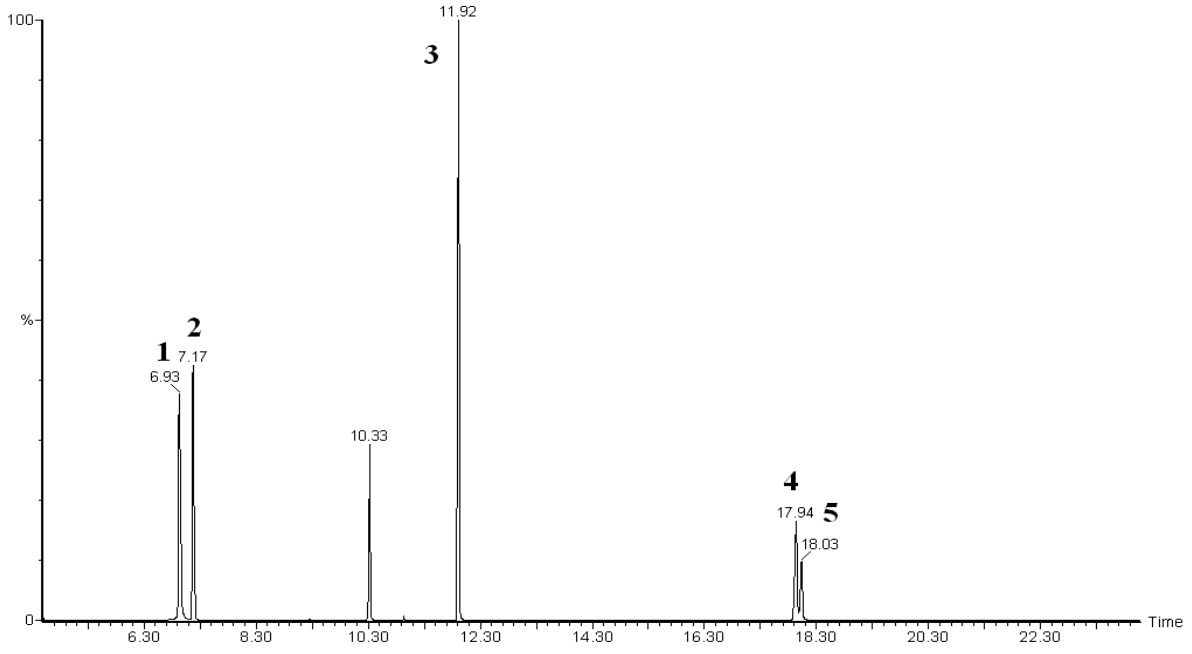

Fig. 2. Chromatogram of the mixture of selected thiol derivative of organoarsenic compounds: 1 – MMA, 2 – DMA, 3 – PAA, 4 – ROX, 5 – NITR (a standard solution 0.2 mg mL^{-1}).

The results indicated that the increase in temperature across the tested range causes an increase of extraction efficiency for almost all OA tested compounds. It was also found that the temperature of 60°C guarantees a reproducible, high analytes signals. At temperatures above 60°C not clear increase in the peak area of the analyzed compounds were obtained and were characterized by high variability. The highest extraction efficiency at 60°C was observed for MMA and DMA acid derivatives for PA, CAR/PDMS and DVB/CAR/PDMS. Signals derived from the thiol derivative PAA, ROX and NITR were biggest and most reproducible when the extraction was conducted using the bipolar PDMS/DVB stationary phase. It is well-known that lower temperature favors the sorption to the fiber but in the case of thiol derivative OA temperature adsorption below 60°C probably lead to degradation of derivatives. These phenomena can explain the decrease of extraction efficiency for OA. Further studies using the SPME technique was carried out using the fiber coated by PDMS/DVB phase, and the extraction was carried out at 60°C.

SPME technique is an equilibrium technique, therefore, the extraction time significantly effects on its efficiency. To select the optimal value of this parameter, studies were conducted in terms of the extraction time from 10 to 30 min. As shown previously, extraction was carried out at 60°C. Different extraction time profiles were observed for the analytes on the tested coating (Fig. 7).

It is apparent that the signals obtained increased with increasing extraction time for PAA. Increased signals for NITR and ROX were observed after 20 min of extraction;

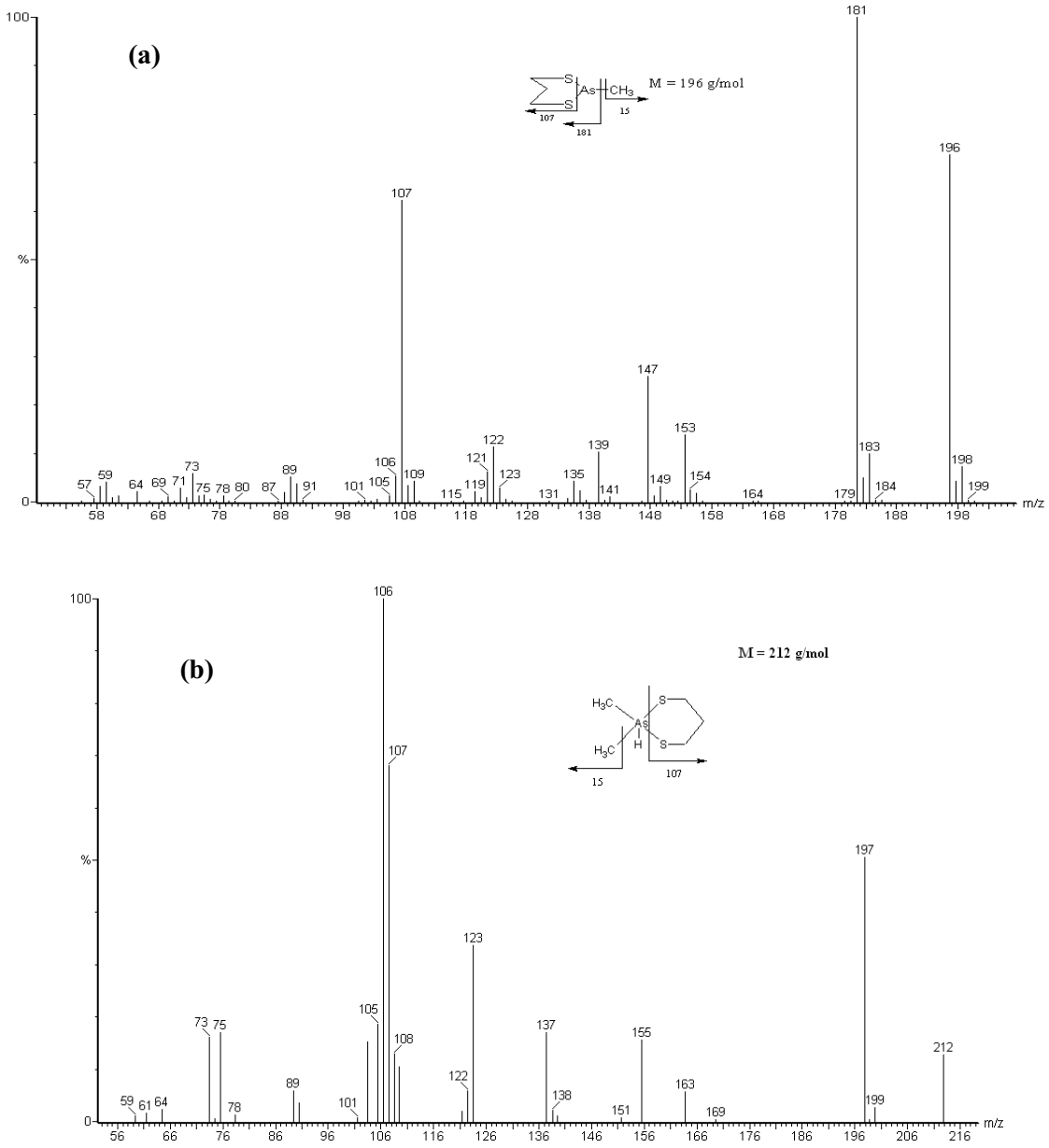

Fig. 3. Mass spectrums of a thiol derivative of (a) monomethylarsonic and (b) dimethylarsinic acid.

Table 1
Masses and ions intensities selected thiol derivative organoarsenic compounds

Compound	Retention time, min	Molar mass, g mol^{-1}	Thiol derivative molar mass, g mol^{-1}	Characteristic ions *m*/*z* with its intensities, %
MMA	7.28	139	196	107 (54%) 181 (100%) 196 (70%)
DMA	7.03	137	212	106 (100%) 107 (72%) 197 (68%)
PA	12.05	202	259	107 (85%) 149 (85%) 258 (100%)
ROX	18.05	263	320	107 (88%) 181 (60%) 319 (100%)
NITR	17.95	247	304	107 (93%) 181 (95%) 303 (100%)

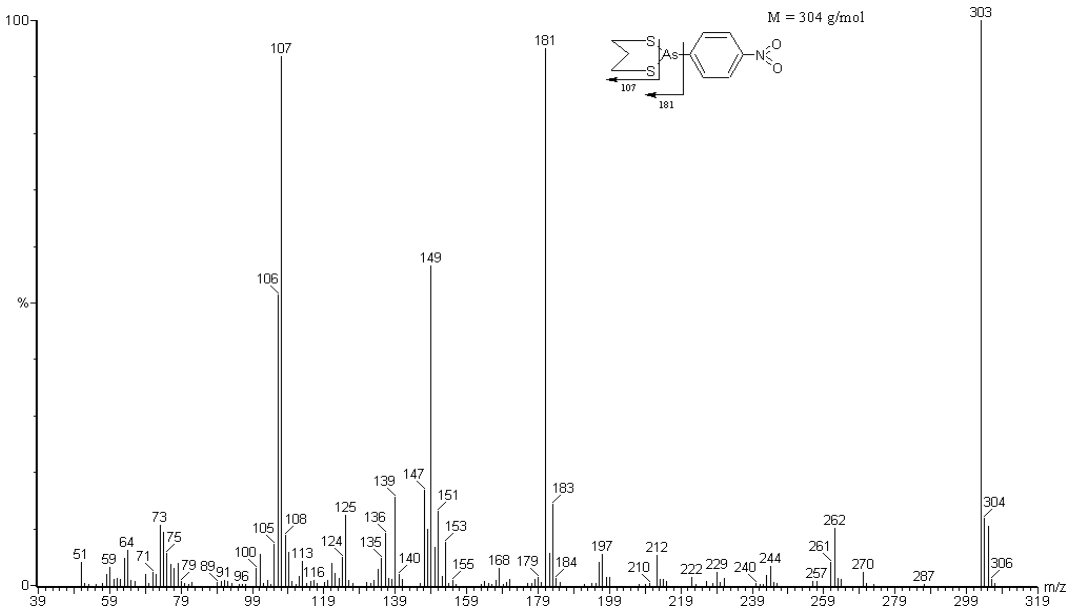

Fig. 4. Mass spectrums of a thiol derivative of nitarsone.

however, after 20 min of extraction, decreasing signal for MMA was noted. It was observed that the longest extraction time (30 min) provides to equilibration of the test compounds. The most effective extraction efficiency was obtained when the extraction was conducted using a PDMS/DVB stationary phase. A 65 μm PDMS/DVB SPME fiber was allowed to equilibrate with the sample for 30 min.

It is well known that sorption processes are affected by the ionic strength of the sample, which is adjusted by addition of salt [22]; however, in the case of less polar compounds such as thiol derivative of organoarsenic acid effects of salting is small [23].

3.2. Validation of the procedure PDMS/DVB – GC/MS

Calibration models for MMA, DMA, PA, ROX and NITR were constructed using standard concentrations in range 0.019 to 60.8 μg L^{-1} (n – 3 at each level). All calibration standards were extracted by SPME prior to GC–MS analysis. The linearity of the standard mixtures for six concentration

levels was relatively good in the whole range of tested concentrations and the correlation coefficient was above 0.99 (Table 2).

The limit of detection (LOD) were determined with the *S*/*N* = 3 method using consecutive dilution series. Detector signals, measured in arbitrary units (peak areas), were plotted vs. the amount of analyte injected, express in mass units (μg). The LOD and LOQ (three times LOD) were established using standard solutions at six concentration levels from 10.7 to 0.7 μg L^{-1}.

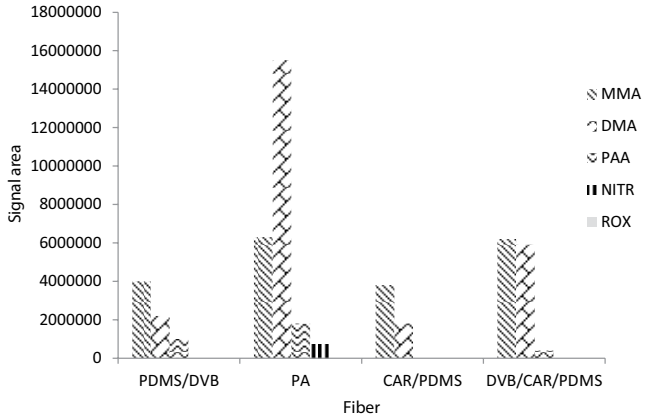

Fig. 5. Dependence of the signal area on the used type of fiber extraction at 25°C.

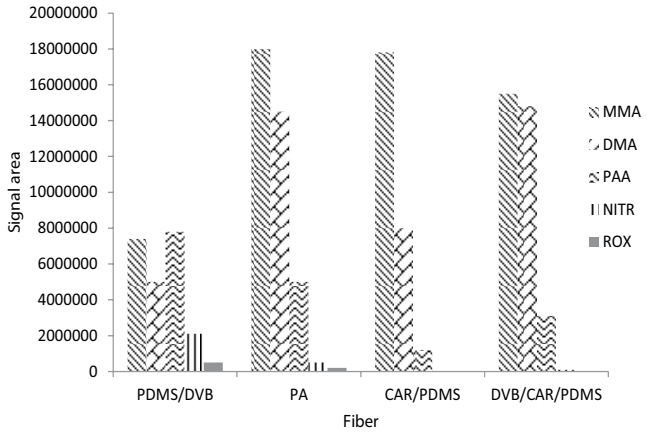

Fig. 6. Dependence of the signal area on the used type of fiber extraction at 60°C.

Intra-day precision and accuracy were evaluated by analyzing six replicates of water spiked with organoarsenic compounds at three concentration levels on the same day. Repeatability and intermediate precision of this method indicate a high repeatability, obtained coefficient of variation (CV) values were less than 3.3% (Table 3).

The evaluation of the inter-day precision and accuracy was made within a 5-d period at three concentration levels. The obtained CVs were lower than 3.5% for all analytes at the tested concentration levels. The determined accuracy parameters indicate that method fulfils the requirements for analytical methods and can be used to monitor concentrations of the organoarsenic compounds in water.

3.3. Analysis of the real water samples

Developed and validated procedures were used for the determination of organoarsenic compounds in mine waters, industrial waters, waters from sewage treatment plants and effluent from chicken farms. All samples were taken in 1.5-L glass containers. In order to remove solid particles, sample immediately after collection was filtered by microfilter (0.45 mm) and subjected to further analysis involving isolation, enrichment of analytes and quantitative analysis.

Analysis of the mine water from the mining regions of copper ore showed that it contains organoarsenic compounds such as monomethylarsonic acid and dimethylarsinic acid (Table 4). MMA concentration in the tested waters ranges within level below the limits of quantification to a 9.34 μg L^{-1} depending on the collection site. In mining waters occurs dimethylarsinic acid, the concentration of which is in the range from below the limit of quantification to 11.7 μg L^{-1}.

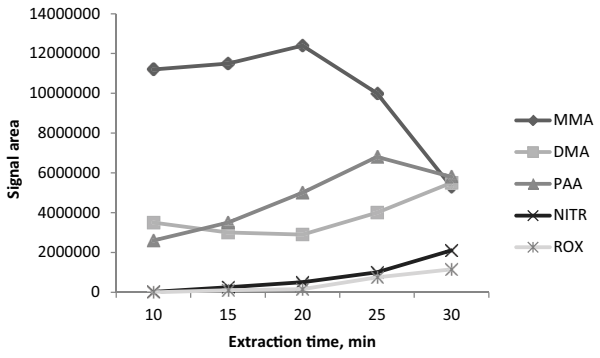

Fig. 7. Relationship signal area vs. extraction time for PDMS/DVB fibre at 600°C.

Table 2
Range of linearity, calibration curves and parameters of the LOD and LOQ of selected organoarsenic compounds

Compound	Linearity range μg L^{-1}	Calibration curve equation	R^2	LOD μg L^{-1}	LOQ μg L^{-1}
MMA	0.4–49.2	$y = 442{,}667x + 547{,}940$	0.994	0.12	0.35
DMA	0.8–60.8	$y = 627{,}856x + 725{,}055$	0.998	0.24	0.71
PA	0.6–43.0	$y = 454{,}558x + 133{,}281$	0.997	0.15	0.46
ROX	2.3–42.0	$y = 21{,}258x + 5{,}532$	0.999	1.50	4.51
NITR	2.9–48.8	$y = 48{,}340x - 988$	0.999	1.96	5.88

Table 3
Precision and accuracy

Compound	Spiked μg mL^{-1}	Intra-day (n = 6)			Inter-day (n = 5)		
		Measured μg mL^{-1}	CV, %	RE, %	Measured μg mL^{-1}	CV, %	RE, %
	19.70	19.74	1.01	0.20	19.80	1.68	0.51
MMA	9.80	9.81	2.06	0.10	9.83	2.40	0.31
	1.90	1.94	1.59	2.10	1.95	2.12	2.63
	12.10	12.34	1.63	1.98	12.22	0.61	0.99
DMA	2.40	2.47	2.34	2.91	2.41	1.96	0.42
	0.50	0.51	1.26	2.0	0.52	0.31	4.00
	16.90	16.94	0.78	0.23	16.98	1.43	0.47
PAA	8.50	8.59	1.05	1.05	8.55	1.57	0.59
	1.70	1.75	1.71	2.94	1.78	1.24	4.71
	17.20	17.23	3.23	0.17	17.28	1.02	0.46
ROX	8.50	8.51	1.62	0.11	8.57	1.66	0.82
	1.70	1.79	2.82	5.29	1.71	1.07	0.58
	19.20	19.28	1.42	0.42	19.25	1.61	0.26
NITR	9.60	9.61	1.71	0.10	9.64	3.49	0.42
	1.90	1.93	1.26	1.57	1.96	2.12	3.15

CV – coefficient of variation, RE – relative error (measured concentration-spiked concentration/spiked concentration) × 100.

Table 4
Concentration of OA in mine water samples, μg L^{-1}

Sample	MMA	DMA	PAA	NITR	ROX
Mining water 1	> LOD < LOQ	> LOD < LOQ	No	No	No
Mining water 2	9.34 ± 0.28	10.06 ± 0.46	No	No	No
Mining water 3	3.81 ± 0.17	11.70 ± 0.35	No	No	No
Mining water 4	> LOD < LOQ	> LOD < LOQ	No	No	No
Technological water 1	22.08 ± 1.08	16.4 ± 2.36	> LOD < LOQ	No	No
Technological water 2	6.90 ± 0.31	> LOD < LOQ	No	No	No
Technological water 3	12.14 ± 0.55	11.5 ± 0.35	No	No	No
Technological water 4	> LOD < LOQ	> LOD < LOQ	No	No	No
Technological water 5	> LOD < LOQ	> LOD < LOQ	No	No	No
Industrial water 1	34.6 ± 1.7	72.6 ± 10.46	23.8 ± 2.54	No	No

No - below LOD.

Analysis of technological and industrial waters from copper mining industry showed the presence of compounds such as MMA, DMA and PAA (Table 4). MMA concentration in the tested samples ranged from below detection limit to 34.6 μg L^{-1} depending on origin and DMA acid which concentration is in the range from below the limit of quantification to 72.6 μg L^{-1}. Analysis by SPME-GC/MS methods showed the presence of PAA in "industrial water 1" sample at concentration 23.8 μg L^{-1}. In the analyzed water samples not were determined ROX and NITR at a level above the detection limit.

Five samples of wastewater and three effluent samples from chicken farms were analyzed. The effluents from farms were analyzed in particular for determination of OA compounds which are components of animal feed and metabolites of these compounds. Analysis of the effluents from chicken farms revealed that one sample contained DMA at a concentration of 9.6 μg L^{-1} and trace amount of MMA.

4. Conclusion

In this work were developed specific analytical procedures for speciation of organoarsenic compounds by using chromatographic techniques. Also were made their identification in liquid environmental and technological samples. Due to the lack of information on the bioavailability, changes in environment and toxicity, which depends on the oxidation state or structure of a molecule containing arsenic, arsenic compounds speciation, in particular, organoarsenic compounds, is being increasingly studied.

The use of gas chromatography preceded by derivatization of analytes using 1,3-propanedithiol and SPME by using

PDMS/DVB fiber allows for the simultaneous determination of MMA, DMA, PAA, ROX and NITR. The repeatability of the analytical method is in the range from 0.78% to 3.23%, and the limits of determination ranging from 0.35 to 5.88 μg L^{-1}, depending on the compound.

Analysis of real samples showed that mine waters contains organoarsenical acids such as MMA, DMA at concentrations of 10 μg L^{-1}. Industrial and technological water from mining technology are characterized by a content of organoarsenic compounds in concentration range of 6.9 to 72.6 μg L^{-1}. Trace amounts of MMA and DMA acids were also determined in the effluent from chicken farms.

Symbols

CARB	—	Carbarsone
CAR/PDMS	—	Carboxen polydimethylsiloxane
DMA	—	Dimethylarsenic acid
DVB/CAR/PDMS	—	Divinylbenzene carboxen polydimethylsiloxane
ESI–MS	—	Mass spectrometry with electrospray ionization
GC–MS	—	Gas chromatography with mass spectrometry
HCl	—	Hydrochloric acid
LOD	—	Limit of detection
LOQ	—	Limit of quantification
MMA	—	Monomethylarsonic acid
NITR	—	Nitarsone
OA	—	Organoarsenic compounds
PA	—	Polyacrylate
p-AsA	—	*p*-Arsanilic acid
PDMS/DVB	—	Polydimethylsiloxane/divinylbenzene
PDT	—	1,3-Propanedithiol
ROX	—	Roxarsone
SPME	—	Solid-phase microextraction

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