Talanta 101 (2012) 524–529

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Analysis of arsenic species in fish after derivatization by GC–MS

Janine Richter*, Susanne Lischka, Christian Piechotta

BAM Federal Institute for Materials Research and Testing, Department of Analytical Chemistry; Reference Materials, Organic Environmental Analysis, Richard-Willstaetter-Straße 11, 12489 Berlin, Germany

ARTICLE INFO

Article history:
Received 3 July 2012
Received in revised form
26 September 2012
Accepted 6 October 2012
Available online 12 October 2012

Keywords:
Arsenic species analysis
Monomethylarsonate
Dimethylarsenate
Derivatization
Gas chromatography
Mass spectrometry

ABSTRACT

The derivatization of organoarsenic compounds by different reagents like thioglycolates or dithiols and the subsequent analysis by GC–MS as a molecular specific technique was investigated and described. The possible derivatization reagents methyl- and ethylthioglycolate (TGM and TGE), 1,3-propane- and 1,5-pentanedithiol (PDT and PeDT), which transfer the polar and nonvolatile analytes dimethylarsenate (DMA), monomethylarsonate (MMA), arsenite and arsenate into volatile compounds, were evaluated. The application for real samples like fish material was also studied.

In addition the gas chromatographic separation and resolution was optimized and experiments were carried out to determine the highest derivatization rates. Derivatization reagents were evaluated in terms of quantity and stability of the formed chemical species.

All derivatization products were characterized by mass spectrometry in order to identify the separated arsenic species.

The most efficient conversion of DMA and MMA was observed by using ethylthioglycolate as derivatization agent. Finally, the derivatization procedure and the GC–MS-method were validated to determine linearity, precision, selectivity, analytical limiting values and recoveries. For the proposed method a limit of detection (LOD) of 5.8 pg for DMA and 14.0 pg for MMA was found. The accuracy was established by comparing the mean value measured for DMA in the certified reference material BCR-627 (tuna fish) with the certified one.

MMA was not quantified in marine samples due to its low content. In shrimp samples DMA was not detectable. For codfish a DMA-content of 0.20 ± 0.004 mg kg^{-1}, for "Surströmming" an amount of 0.38 ± 0.02 mg kg^{-1} and for herring, which showed the highest amount of DMA, a content of 1.15 ± 0.03 mg kg^{-1} was determined.

1. Introduction

Different species of arsenic have been comprehensively investigated [1]. Natural and anthropogenic occurring arsenic species show a wide chemical variety. The main components in sediments and sea water are arsenite (As(III)), arsenate (As(V)), monomethylarsonate (MMA) and dimethylarsenate (DMA). Arsenate is incorporated in many marine organisms like algae, mussels and fish and is transformed into organic molecules as DMA und MMA. Almost 100% of the arsenic content is accumulated by fish as arsenobetaine [2,3]. The reason for the bioaccumulation is the structural similarity of the arsenobetaine and the osmolyte glycinbetaine, which adjusts the salinity in fish. Therefore, sea water fish contains more arsenic than their freshwater relatives [1]. The overall concentration of arsenic in marine organisms varies from 1 to 100 mg kg^{-1} [3]. It is assumed that the main arsenic uptake by humans in Europe results from the consumption of fish and shellfish [4]. The different arsenic species vary widely in toxicity. In contrast to the usual behavior the organometallic arsenic species are less toxic than the inorganic forms [5]. Therefore, it is necessary to develop new and improved methods for the species analysis to selectively determine the different compounds and in low concentrations [4,6].

The analysis of arsenic species using liquid chromatography coupled to inductively coupled plasma mass spectrometer (ICP-MS) is an unique technique, due to its high sensitivity. Detection limits between 0.006–0.015 μg L^{-1} for the different species can be obtained by LC-ICP-MS [7]. But this method offers a couple of disadvantages and limitations [8]. No structural elucidation is obtained by using ICP-MS. Due to the lack of reference substances unknown species can't be characterized and coeluting compounds can't be detected and identified [9]. Furthermore the risk of misinterpretation is given because matrix-depending shifts in retention time are possible. An alternative and well-known method is the analysis by hydride generation absorption spectroscopy (HG-AAS) [10]. It was used for the arsenic speciation in

* Corresponding author.
E-mail address: janine.richter@bam.de (J. Richter).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.10.021

drinking water, food and other environmental samples [11]. Therefore, in this method the arsenic compounds are reduced by sodium borohydride [12–14]. The volatile arsines are separated from the liquid residue to achieve an increased sensitivity and the isolation from the matrix. Bioorganoarsenicals as arsenobetaine, arsenocholine and arsenosugars couldn't be detected using HG-AAS, because the formation of volatile hydrides is not possible [3].

The functional groups of the toxicologic relevant arsenic species in fish can also be derivatized into volatile compounds to enable the analysis by GC–EI–MS. Furthermore the GC–EI–MS technique offers high chromatographic separation efficiency and a distinct structural analysis.

Arsenic containing fish is a complex matrix, which makes it necessary to extract the compounds of interest before derivatization and detection respectively. A very useful technique to separate the arsenic species from the non polar lipids and fatty acids or other matrix components is the pressurized liquid extraction (PLE) combined with a polar extracting agent like a water–methanol-mixture. The PLE uses the advantages of solvent extraction under increased pressure and temperature conditions. Comparable results can be achieved only by using a soxhlet apparatus as a time consuming continuous solid liquid extraction method [15].

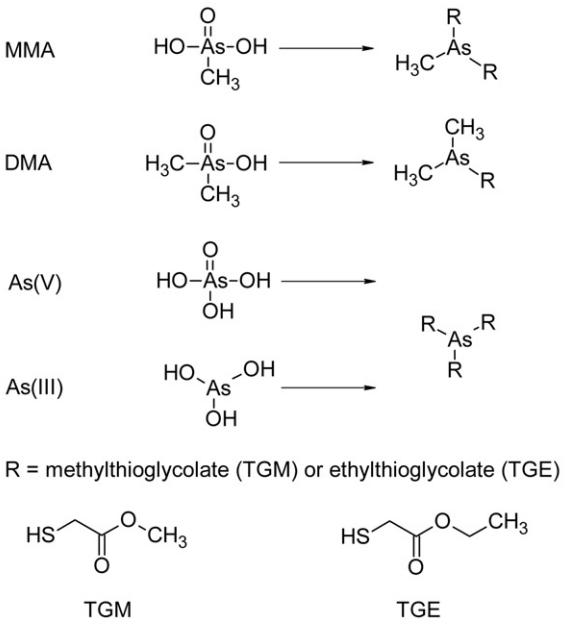

Fig. 1. Reactions of organoarsenicals and inorganic arsenic species with thioglycolates TGM and TGE.

Most of the arsenic species in fish are polar compounds and exist in a partial ionic form. For gas chromatographic analysis these species have to be converted into volatile and thermal stable compounds [6]. Based on the high thiophilic character of arsenic, derivatization reagents generating strong bonds within sulfuric compounds like thiols and dithiols should be utilized to obtain stable thioethers [16]. In the literature it is reported that the best results of derivatization and analysis are achieved by using methylthioglycolate (TGM) and 1,3-propanedithiol (PDT) [17].

One of the apparently most promising and moreover efficient derivatization method is the reaction of arsenic species with TGM. It is possible to convert the alkylated organometallic forms DMA and MMA simultaneously with the inorganic As(III) and As(V) into volatile sulfur derivatives [18,19]. It was proven that the TGM-derivatives show decomposition under thermal stress at high temperatures [20]. To avoid these degradation processes and to get more stable arsenic derivatives ethylthioglycolate was evaluated as a derivatization agent. The reaction pathways are shown in Fig. 1. First of all the strong reducing agents TGM and TGE transfer the pentavalent oxidized species into a trivalent reduced state and the reducing agent itself will be oxidized and forms a disulfide. Afterwards, further TGM or TGE react with the reduced arsenic compound to thioarsinate [21]. The reaction of inorganic arsenic compounds is not selective, which means that As(III) and As(V) react with TGM or TGE to the same derivative.

Instead of thiols, dithiols like 1,3-propanedithiol and 1,5-pentanedithiol can be used to transform the arsenic species DMA and MMA into a cyclic thioacetal which represents a more stable compound [22]. A separation of DMA- and MMA-PDT seems to be very difficult, because the retention times of the transformed species are very similar [23]. Therefore, 1,5-pentanedithiol was also investigated as a derivatizing agent to improve the separation in consequence of the structurally different products. The reactions of DMA and MMA with PDT and PeDT are substitution reactions under the elimination of water, Fig. 2.

The lipophilic reaction products of both derivatization methods are extracted with a nonpolar organic solvent by liquid–liquid extraction. As a side effect the polar matrix can be eliminated as well. Alternatively a combination of the selected derivatization strategies and the use of solid phase micro extraction are possible and should result in better limits of detection [13,17,23].

The aim of our work was to evaluate the most effective derivatizing agent and to optimize the gas chromatographic separation efficiency. Experiments to find the optimal derivatization reagent quantity and to evaluate stability of the chemical species were performed. All derivatization products were analytical characterized by mass spectrometry.

The application, respectively the detection, of the methylated species DMA and MMA in real samples like fish and shellfish material was performed and the accuracy of the optimized analysis method was proven with a certified reference material.

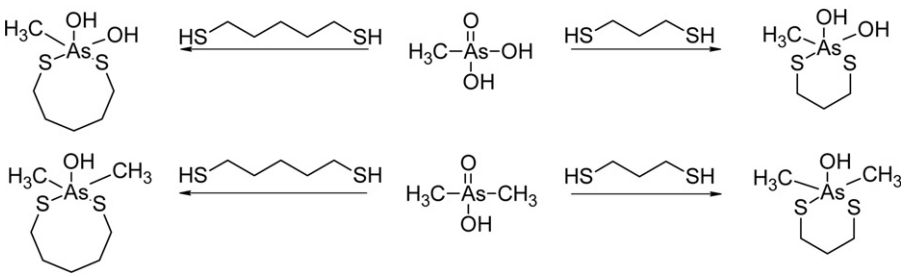

Fig. 2. Reactions of the organoarsenicals MMA (above) and DMA (below) with 1,3-propanedithiol (PDT, right reaction course) and 1,5-pentanedithiol (PeDT, left reaction course).

2. Experimental

2.1. Chemicals and standards

Water (18 MΩ) was prepared using a Milli-Q filtration system (Millipore, Billerica, MA, USA). All glassware were cleaned by using 10% (v/v) nitric acid (Merck KGaA, Darmstadt, Germany), which was followed by multiple rinsing with ultrapure water.

Stock solutions were prepared from standard substances sodium arsenite (Sigma-Aldrich, Steinheim, Germany), sodium arsenate (Arsenic ICP Standard, 1000 mg L^{-1}Merck KGaA, Darmstadt, Germany), monomethylarsonic acid (MMA) (Supelco, Sigma-Aldrich, Steinheim, Germany) and dimethylarsinic acid (DMA) (Merck KGaA, Darmstadt, Germany). All aqueous standards (1 mg L^{-1}) were made by using ultrapure water and stored at 4 °C for not more than two weeks. As internal standard (IS) hexachlorobenzene (99%, Sigma-Aldrich, Steinheim, Germany) dissolved in cyclohexane was applied.

As dispersant for pressurized liquid extraction finely ground quartz sand (< 125 μm Carl Roth GmbH + Co.KG, Karslruhe, Germany) and as the filling material sea sand purest (Merck KGaA, Darmstadt, Germany) were used. The derivatization reagents for MMA, DMA, and As(III) and As(V) were methylthioglycolate (TGM) (Merck-Schuchardt, Hohenbrunn, Germany), ethylthioglycolate (TGE) (Merck-Schuchardt, Hohenbrunn, Germany), 1,3-propanedithiol (PDT) (Sigma-Aldrich, Steinheim, Germany) and 1,5-pentanedithiol (PeDT) (Merck-Schuchardt, Hohenbrunn, Germany).

The marine fish and shellfish samples used in the study were commercial available frozen filets. The Surströmming is a commercial available Swedish tin. The certified reference material tuna fish tissue BCR-627 was purchased from the JRC-IRMM (Geel, Belgium).

2.2. Instrumentation

Organoarsenicals were determined by using a CP-3800 (Agilent) gas chromatograph coupled to a 1200 L Quadrupole MS/MS (Bruker) mass spectrometer. The software MS-Workstation (Thermo Fischer, Schwerte, Germany) was used for data acquisition and analysis. A 60 m CP-SIL 8 CB capillary GC column (Agilent) with 0.25 mm i.d. and 0.39 μm film thickness was used in the experiments. Helium was carrier gas and a gas flow of 1 mL min^{-1} was applied. The temperature of the transferline was adjusted to 280 °C. The injection of the derivatized species was done in splitless injection mode. The Electron impact (EI) mass spectra were obtained by using 70 eV. The arsenic species were investigated by using a scanning mode with a mass range from m/z = 50 to 350 amu to identify clearly each analyte by mass spectra and retention time. Afterwards for quantification SIM (single ion monitoring) mode was used. Therefore the Quantifier ions m/z = 209 ± 0.5 amu for DMA and m/z = 313 ± 0.5 amu for MMA were applied. Additionally the m/z 181 and 209 ± 0.5 amu were used as Qualifier ions. A scan time of 0.2 s was applied for all SIM parameters.

2.3. Sample preparation and extraction

2.3.1. Fish tissues

The fish samples codfish, herring and shrimps were purchased as commercial available frozen food, were freeze dried, milled and then homogenized. The herring tissue was additionally treated with a dose of 8 kGy gamma radiation to inhibit microbial degradation. The resulting powders were bottled under argon atmosphere in 20 mL brown glass vials. The Surströmming a Swedish fermented fish delicacy, which could contain a high amount of DMA and/or MMA, was purchased in a tin, was minced and used without any additional sample preparation. All fish samples were stored at −29 °C. The certified reference material BCR-627 was stored at 4 °C.

2.3.2. Pressurized liquid extraction

An ASE 200 (Sionex, Sunnyvale, CA, USA) was used with 11 mL extraction cells. For the first layer and the top of cell filling a fiberglass filter was used. A mixture of fish material and quartz sand at a ratio of 1: 6 was homogenized and filled into the cell between two layers of sea sand. For the determination of recovery rates the samples were spiked with standard solutions of the analytes. PLE was carried out at a temperature of 60 °C, pressure of 80 bar and a 1:1 (v/v) mixture of methanol and ultrapure water as extracting agent. Five cycles of 2 min static extraction time were performed with a flush volume of 60% and pressurized nitrogen purge of 60 s. The extracts were collected in amber glass vials cleaned overnight with 10% nitric acid.

The extracts were concentrated to 1 mL by using rotary evaporator with a temperature controlled water bath maintained at 40 °C.

2.3.3. Derivatization, extraction procedure and GC–MS analysis

The aqueous samples (1 mL) with known amounts of DMA, MMA, As (III) and As (V) and the fish extracts were acidified using 10 μL of HCl to a pH value 2. Subsequently 25 μL TGM or TGE were added. The reaction vessels were closed and shaken intensively at least for 2 min. Afterwards 1 mL cyclohexane and 10 μl of a 1 μg mL^{-1}-hexachlorbenzene dissolved in cyclohexane were added. After two additional minutes of shaking 1 μL of the organic phase of the reaction mixture was directly analyzed by GC–MS. The fish containing samples were centrifuged additionally at 35,000 rpm for 30 min before injection.

For the analysis the injection port was kept at 250 °C. For chromatographic separation the following oven program was used: 65 °C (1 min) at 30 K min^{-1} to 110 °C (2 min), then at 20 K min^{-1} to 300 °C (held for 4 min).

For the reaction with the dithiols PDT and PeDT 2 mL of DMA and/or MMA containing solutions were mixed with 500 μL 5 M HCl. These solutions were heated to 70 °C and 2 μL PDT or PeDT were added. After five minutes reacting time the samples were cooled down to room temperature. 1 mL toluene was used to transfer the derivatized analytes to an organic phase by 2 min shaking. After the separation of the two phases, an aliquot of 1 μL was used for GC–MS analysis.

The injection port was heated to 250 °C and the starting column temperature was 45 °C, which was held for 5 min. At 20 °C min^{-1} the temperature was increased to 180 °C, followed by 5 °C min^{-1} to 260, held for 1 min, and finally by 30 °C min^{-1} to 290 °C, also held for 2 min.

For the evaluation of validation characteristics the area ratios from the analyte and the internal standard (IS) were used. These calculations were performed using HCB as an internal standard with the Qualifier Ion $m/z = 284$ [24]. The analytical limits were calculated according to German standard, DIN 32645 [25].

3. Results and discussion

3.1. Comparison of the derivatization reagents

The established derivatization strategy of DMA, MMA, As(III) and As(V) using TGM developed by Beckerman [18] and Mester [14] was critically investigated by GC–MS. Referring to these approaches the reaction of the target analytes with TGE was evaluated. The analytes could be separated from all sample components and detected in the lower ng mL^{-1}-range. The inorganic species were not detected with

the same sensitivity. Only by using concentrations in the μg mL^{-1} range the inorganic arsenic appeared in the chromatogram. By comparing the retention time and the specific m/z-ratios in mass spectra this peak could be clearly identified as $As(TG)_3$. The mass spectra for As(III) and As(V) TGE-derivatives were identical. The obtained mass spectra of the TGM-derivatives were equal to those which are already published [14,18,20]. The mass spectra of the recent TGE-derivatives were measured and corresponding fragment ions are summarized in Table 3. The analytical results for both derivatization procedures were compared concerning the sensitivity to find the most efficient derivatization agent. The results for DMA and MMA, obtained by the measurement in full scan are shown in Fig. 3. The application of TGE showed a better sensitivity and therefore a lower limit of detection for the quantification of DMA and MMA. Moreover, a higher precision was observed.

The derivatization procedure by using dithiols was also applied for DMA and MMA. Therefore the derivatization reagents 1,3-propane- and 1,5-pentanedithiol were selected. For the PDT reaction both organometalic derivatives could be detected and identified by mass spectrometry. The mass spectra were already presented by Szostek and Killelea [17,23]. The derivatization with PeDT enabled only the verification of DMA for a concentration of 300 ng mL^{-1}. The characteristic fragment ions of the mass spectrum are shown in Table 3. A MMA-PeDT signal was not obtained, because

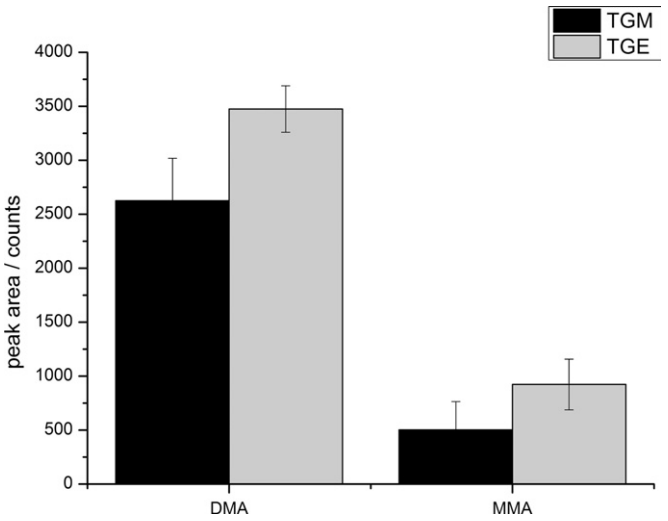

Fig. 3. Comparison of the peak areas for the determination of DMA and MMA with the derivatization reagents TGM and TGE.

the derivative might be not stable enough, or derivatization efficiency is not sufficient. Consequently, the PeDT derivatization method is not suitable for further application.

In conclusion the derivatization with TGE to detect DMA, MMA, As(III) and As(V) is the most suitable method. Therefore, this procedure was optimized, validated and applied for the analysis of the arsenic species of choice in real samples like fish and shrimps.

3.2. Optimization of derivatization and GC–MS-analysis

The reaction of the arsenic analytes with TGE and the contact of the derivatizing agent with air results in the formation of TGE-dimers. This compound and an excess of TGE could interact with the capillary GC column or affect the GC–MS system. To avoid these negative side effects, preferably the lowest possible amount of TGE should be used for derivatization. Therefore, various amounts of TGE were evaluated in aqueous samples and in the fish material herring to determine the optimal amount of derivatization agent. The use of 25 μL TGE provided the highest peak areas for DMA and MMA in herring and in aqueous solution, but especially for MMA the signal intensity was enhanced using this amount. Besides, a lower quantity of derivatization reagent leads to a minor measurement uncertainty considering a treble injection. An amount less than 25 μL TGE will deteriorate the detection limits.

Another parameter which should be optimized is the injection port temperature. It was reported that high temperatures could result in decomposition of the derivatized arsenic analyte [20]. The diminished sensitivity of inorganic arsenic detection obtained could be a direct consequence of this circumstance. The optimal injection port temperature was determined to 250 °C for fish samples. This value was used for validation and quantification experiments. No decomposition at this temperature was obtained for the DMA- and MMA-TGE. But As(III)- and As(V)–TGE derivatives showed a degradation, which could be not avoided by decreasing the injection temperature, but by using a different oven temperature. In this case a final column temperature below 220 °C should be chosen and held for at least 15 min.

The internal standard was HCB, which was also used by Claussen [24] for arsenic species analysis. It only corrects effects of changes in detector performance. Effects of sample preparation and matrix influences are not corrected by HCB. To achieve such an adjustment a more structural and chemical similar compound like a ^{13}C-labeled DMA or MMA should be used. But those

Table 1
Analytical processes characteristics of DMA and MMA analysis using GC–MS method ($n=3$).

Analyte	*y*-intercept a	Slope b	R	LOD [ng mL^{-1}]	LOQ [ng mL^{-1}]	R.S.D [%]
DMA	0.028	0.02	0.9995	6	12	3.1
MMA	1.740	0.32	0.9969	14	28	3.5

Table 2
Arsenic compounds in certified reference material, real samples fish and shrimps obtained by GC–MS analysis (n=9).

	DMA [mg kg^{-1}]	MMA [mg kg^{-1}]
tuna crm	0.29 ± 0.01	< 0.1
codfish	0.20 ± 0.004	n.d.
Surströmming	0.38 ± 0.02	< 0.1
herring	1.15 ± 0.03	< 0.1
shrimps	n.d.	n.d.

(*n.d.—not detected*).

Table 3
Molecular fragment ions of obtained TGE- and PeDT-derivatives electron ionization mass spectra.

Derivative of analyt	Molecular fragment ions m/z	
DMA-TGE	208.8	$C_5H_{10}AsO_2S^+$
	180.8	$C_3H_4AsO_2S^+$
	106.9	AsS^+
MMA-TGE	312.7	$C_8H_{14}AsO_2S^+$
	208.8	$C_5H_{10}AsO_2S^+$
	180.8	$C_3H_4AsO_2S^+$
	107.0	AsS^+
As(V)–TGE	312.8	$C_8H_{14}AsO_2S^+$
	107.0	AsS^+
DMA-PeDT	224.7	$C_6H_{14}AsS_2^+$
	208.8	$C_5H_{10}AsS_2^+$
	106.8	AsS^+

standards are not commercially available. If ^{13}C–DMA and ^{13}C–MMA were used as IS, our experiments showed that a high-resolution mass analyzer will be needed for the analysis. Using deuterated compounds a H/D-exchange might be a risk.

The validation of the method and the quantification of the arsenic species were performed with the optimized parameters. Using an improved oven temperature program, described in the experimental part, DMA and MMA can be detected with excellent separation efficiency. Fig. 4 shows an example for the obtained chromatograms.

3.3. Analytical validation characteristics

The calibration was performed for DMA and MMA and the resulting linear fits are shown in Fig. 4. The analysis was done by using seven concentration levels containing DMA, MMA and IS HCB. All analytical parameters are summarized in Table 1. The method was selective and for both analytes a linear correlation was obtained at concentrations levels ranging from 50 to 300 ng mL^{-1}. Comparing the slopes of the linear regression MMA showed higher detection sensitivity than DMA. The determined correlation coefficients (R) proved the direct proportionality between the detected signal and analyte concentration in the sample, because R was close to one. Reproducibility measurements showed an acceptable relative standard deviation (R.S.D.) in the range of 0.5–5.3% for DMA and 0.8–5.7% for MMA. Detection (LOD) and quantification (LOQ) limits were calculated according to DIN 32645 [25] and by using a signal-to-noise ratio of three and ten respectively. The limits of detection were found to be 6 ng mL^{-1} for DMA and 14 ng mL^{-1} for MMA. Besides, the reliability of the analysis procedure was determined by recovery experiments. Therefore codfish samples were spiked with DMA and MMA in different concentrations (75–300 ng mL^{-1}) and analyzed. The recovery rates for DMA showed acceptable values between 100–130% and for MMA 60–70%. The disparate results could be caused by matrix effects in the fish samples and by a lower derivatization efficiency. Thus it was indicated that the fish matrix influences the derivatization of DMA and MMA by TGE. The accuracy of the optimized method was verified by the analysis of the certified reference material tuna tissue BCR-627 with a known DMA content of 2.0 ± 0.3 μmol kg^{-1}. The quantified mean value ($n=9$) was 2.07 ± 0.02 μmol kg^{-1}, which was in excellent alignment with the certified one. For MMA there is no reference material, which is equal or similar to the fish tissue, but the chemical behavior and the recovery from MMA are comparable with DMA.

3.4. Real sample analysis

For analyzing the fish and shrimp samples the arsenic species were extracted with PLE, derivatized and quantified by the optimized GC–MS method described in experimental part. The determined DMA and MMA contents in all samples are shown in Table 2. The shrimps neither contained DMA nor MMA. This confirms with results of Súner et al. [4]. For codfish the lowest content of DMA (0.20 ± 0.004 mg kg^{-1}) was found. Surströmming, which was subjected to organoarsenic producing fermentation process, contained more of this arsenic species (0.38 ± 0.02 mg kg^{-1}), but the highest DMA amounts were found in herring (1.15 ± 0.03 mg kg^{-1}). These results are common, because fish with a high fat content like herring usually show higher DMA amounts than fatless species like codfish [4].

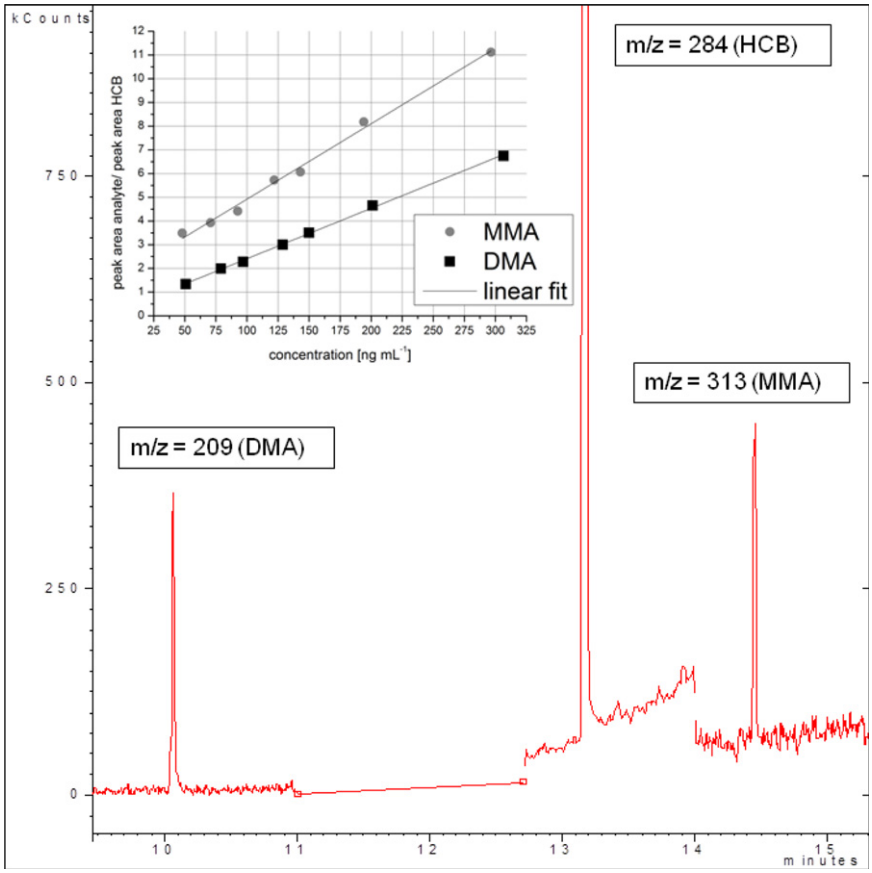

Fig. 4. Chromatogram (TIC) of DMA- and MMA-TGE analysis by GC–MS in SIM mode. MS calibration models of DMA and MMA in a concentration range of 50–300 ng mL^{-1} (insert).

The Quantification of MMA was not possible, because the contents were similar to the determined LOQ of the applied procedure. But in herring, Surströmming and the CRM tuna tissue MMA was detected.

4. Conclusions

The analysis of arsenic species with different derivatization methods was evaluated and the most effective derivatization reagent ethylthioglycolate was found. The derivatization procedure and the GC–MS method were optimized to identify and quantify simultaneously the derivatized compounds DMA, MMA, As(III) and As(V). The resulting method was fast, easy to perform and selective in detection of the various arsenic species. The method is linear in the concentration range from 50 to 300 ng mL^{-1}. The absolute calculated LOD was found to be for 5.8 pg for DMA and 14.0 pg for MMA. Agreeable values for recovery (60 − 130%) and precision (< 5%) were obtained. The trueness was established by verifying the reference value of DMA in the tuna fish reference material.

Different marine samples were investigated. MMA was detected, but not quantified in marine samples, because of its low content. No arsenic species could be detected in the shrimp samples. For codfish a DMA-content of 0.20 ± 0.004 mg kg^{-1}, for Surströmming a content of 0.38 ± 0.02 mg kg^{-1} and for herring, which showed the highest amount of DMA, a content of 1.15 ± 0.03 mg kg^{-1} was determined. Thus the method enables a practical way for the quantification of DMA and MMA in seawater fish species. The limits of detection might even be improved by solid phase micro extraction, because it was already shown that this extraction technique is applicable for the reported derivates [13,17]. Another possibility to get a more sensitive detection system might be the use of an atomic emission spectrometric detector, which is for arsenic and sulfur element specific [20,21].

References

[1] S. Ciardullo, F. Aureli, A. Raggi, F. Cubadda, Talanta 81 (2010) 213–221.
[2] R. Mukhopadhyay, B.P. Rosen, L.T. Phung, S. Silver, FEMS Microbiol, Ecol. 26 (2002) 311–325.
[3] M.C. Villa-Lojo, E. Alonso-Rodrı´guez, P. López-Mahı´a, S. Muniategui-Lorenzo, D. Prada-Rodrı´guez, Talanta 57 (2002) 741–750.
[4] M.A. Súñer, V. Devesa, M.J. Clemente, D. Vélez, R. Montoro, I. Urieta, M. Jalón, M.L. Macho, J. Agric. Food. Chem. 50 (2002) 924–932.
[5] A. Moreda-Pin˜eiro, E¨ Pen˜a,Va´zquez, P¨ Hermelo,Herbello, P¨ Bermejo, Barrera, J¨ Moreda,Pin˜eiro, E¨ Alonso,Rodrı´guez, S¨ Muniategui,Lorenzo, P¨n¨ Lo´pez,Mahi´a, D¨o¨ Prada,Rodrı´guez, Anal¨ Chem¨ 80 (2008) 9272–9278.
[6] R. Sur, H. Hajimiragha, J. Begerow, L. Dunemann, Chem. unserer Zeit. 37 (2003) 248–256.
[7] Y.-J. Hsieh, S.-J. Jiang, J. Agric. Food. Chem. 60 (2012) 2083–2089.
[8] M. Huang, Y.-t. Wang, P.C. Ho, J. Pharm. Biomed. Anal. 48 (2008) 1381–1391.
[9] Z. Mester, G. Vitányi, R. Morabito, P. Fodor, J. Chromatogr. A 832 (1999) 183–190.
[10] H. Haraguchi, A. Takatsu, Spectrochim. Acta, Part B 42 (1987) 235–241.
[11] H.M. Anawar, Talanta 88 (2012) 30–42.
[12] C.K. Jain, I. Ali, Water Res. 34 (2000) 4304–4312.
[13] Z. Mester, J. Pawliszyn, J. Chromatogr. A 873 (2000) 129–135.
[14] Z. Mester, G. Horváth, G. Vitányi, L. Lelik, P. Fodor, Rapid Commun. Mass Spectrom. 13 (1999) 350–353.
[15] B.E. Richter, B.A. Jones, J.L. Ezzell, N.L. Porter, N. Avdalovic, C. Pohl, Anal. Chem. 68 (1996) 1033–1039.
[16] A.R. Roerdink, J.H.Aldstadt Iii, J. Chromatogr. A 1057 (2004) 177–183.
[17] B. Szostek, J.H. Aldstadt, J. Chromatogr. A 807 (1998) 253–263.
[18] B. Beckermann, Anal. Chim. Acta 135 (1982) 77–84.
[19] N. Campillo, R. Peñalver, P. Viñas, I. López-García, M. Hernández-Córdoba, Talanta 77 (2008) 793–799.
[20] K. Schoene, J. Steinhanses, H.J. Bruckert, A. König, J. Chromatogr. A 605 (1992) 257–262.
[21] K. Dix, C.J. Cappon, T.Y. Toribara, J. Chromatogr. Sci. 25 (1987) 164–169.
[22] F.C. Knowles, A.A. Benson, Trends Biochem. Sci. 8 (1983) 178–180.
[23] D.R. Killelea, J.H.Aldstadt Iii, J. Chromatogr. A 918 (2001) 169–175.
[24] F.A. Claussen, J. Chromatogr. Sci. 35 (1997) 568–572.
[25] DIN 32645, Chemical analysis—Decision limit, detection limit and determination limit under repeatability conditions—terms, method, evaluation, Beuth Verlag GmbH, Berlin, 2008.