The PEI was found to decrease the mutual influences of the components of the binary Ag(I)-Cu(II) system (Fig. 3, Table 3) and ternary Pb(II)-Cu(II)-Cd(II) system (Fig. 4, Table 3) at the electrode surface. Therefore, the anodic peak heights of the components increased in the presence of PEI. (Fig. 4). The different complex stabilities of Ag(I), Pb(II), Cd(II) and Cu(II) with PEI allowed Ag(I), Pb(II) or Cd(II) to be determined in the presence of an excess of Cu(II) (Table 3).

Conclusion

The water-soluble polymers PEI and TU-PEI diminish the interactions of the components of the Cd(II)-Pb(II)-Cu(II) and Ag(I)-Cu(II) systems at the carbon-paste electrode surface and reduce the influence of Cu(II) on the anodic peak heights of Cd(II) and Pb(II) in the ternary system and on the anodic peak height of Ag(I) in the binary system. It is therefore possible to determine Ag(I), Pb(II) and Cd(II) in aqueous solutions of PEI in the presence of larger excesses of Cu(II) than when PEI is absent from the solution.

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Fresenius J Anal Chem (1998) 361:313–318 – © Springer-Verlag 1998

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Chromatographic determination of phenylarsenic compounds

Received: 17 July 1997 / Accepted: 9 October 1997

Abstract Gas chromatographic (GC) and liquid chromatographic methods for the investigation of phenylarsenic compounds are presented. With gas chromatography using an electron capture detector (ECD), the chemical warfare agents PFIFFIKUS, CLARK I and CLARK II can be detected. After derivatization with mercaptans and dimercaptans the sum of diphenylarsenic compounds resp. phenylarsenic and phenylarsonic compounds can be detected as the mercapto resp. dimercapto derivatives. High performance liquid chromatography (HPLC) analysis may be used for the detection of triphenylarsenic compounds and ADAMSITE.

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1 Introduction

Phenylarsenic compounds as chemical warfare agents were produced in large amounts during the world wars I and II. After World War II the production sites and filling plants were destroyed and the chemical warfare agents were sunk in the North Sea and the Baltic Sea or deposited in the production sites and filling plants [1]. Residues of these chemical warfare agents are still present and contaminate soil and water.

The most important phenylarsenic compounds, which were used as chemical warfare agents, were:

- Diphenylarsine chloride (Ph_2AsCl), called CLARK I
- Diphenylarsine cyanide (Ph_2AsCN), called CLARK II
- Phenarsazine chloride ($Ph_2As(NH_2)Cl$), called ADAMSITE
- Phenylarsine dichloride (Ph_2AsCl_2), called PFIFFIKUS and
- arsine oil, a technical mixture of arsenic(III) chloride, phenylarsine dichloride, diphenylarsine chloride and triphenylarsine [2].

CLARK I, CLARK II and ADAMSITE are strong irritants, which are called “sternutators”. Toxic effects of these compounds occur from concentrations in air of approx. 0.1 mg/m^3 on. PFIFFIKUS is toxic by inhalation (irritant) and by skin contact [2].

In water, soils and sediments the phenylarsenic compounds can be metabolized via hydrolysis and oxidation [2, 3]. In Fig. 1 the main reactions of the compounds and their metabolites are given.

A chromatographic determination of some phenylarsenic compounds was achieved mainly with hyphenated techniques. These utilized GC or HPLC and element specific detectors like photooxidation-hydride-atomic absorption spectrometry (AAS) [4], inductively coupled plasma (ICP) with atomic emission spectrometry (AES) [5–8] or, more recently, mass spectrometry (MS) [9–11]. For phenylarsonic acid, ion chromatography [12, 13] and capillary electrophoresis (CE) [14] were described as additional separation methods. The matrices studied include river-water [13], sediments [11], oil-shale [7, 15], incineration effluents [6] and marine organisms [9]. However, very few chromatographic methods were described for the separation of the sternutators themselves rather than their possible metabo-

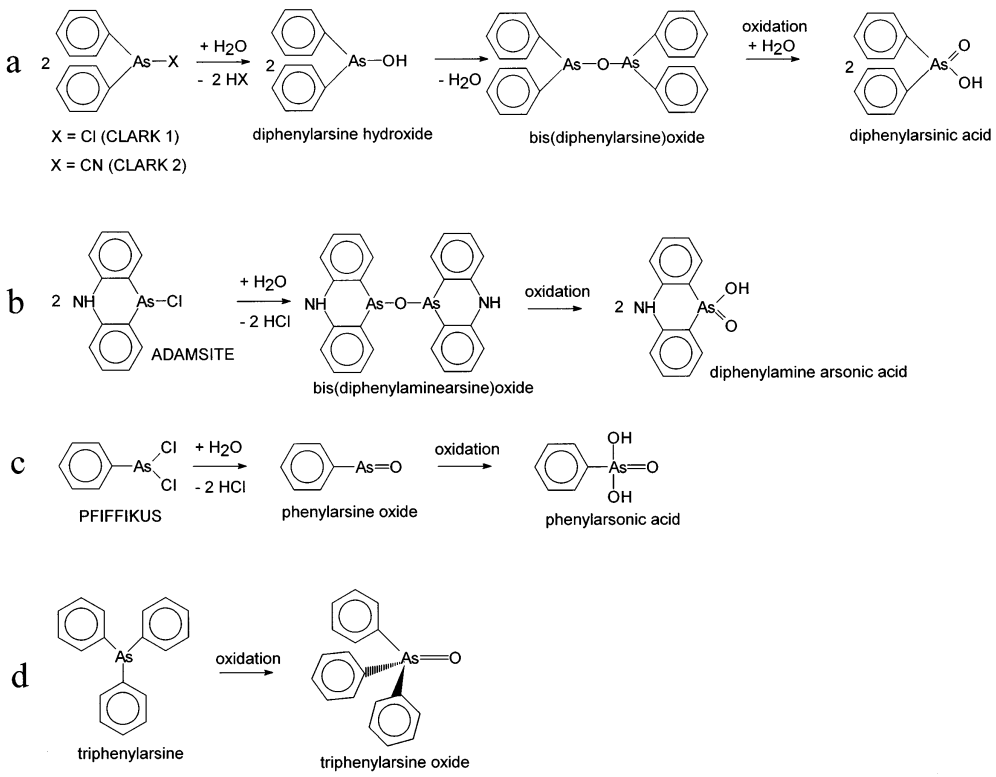

Fig. 1 a–d Scheme of hydrolysis and oxidation reactions of CLARK I and CLARK II (**a**), ADAMSITE (**b**), PFIFFIKUS (**c**) and triphenylarsine (**d**)

lites. In a thorough review of the chromatographic analysis of chemical warfare agents [16] of the analytes dealt with here, only ADAMSITE was mentioned at all. An environmental application can be found in [17]. Therein, ADAMSITE was studied in snow samples together with nerve agents. Other published methods were based on TLC [18] or gaschromatography without [19, 20] or after derivatization [21–23]. Thioglycolic acid methyl ester (TGM) was used as derivatization agent for some diphenylarsines and phenylarsines [21, 22]. ADAMSITE can be detected with GC/ECD after derivatization by bromination of the aromatic ring [23].

The aim of our study was to develop chromatographic methods for the separation of the phenylarsenic compounds presented in Fig. 1. We were especially interested in the possibility of derivatizing phenylarsenic compounds with mercaptans to yield derivatives, which can be sensitively detected with GC-ECD. The same reaction was already used vice versa for the separation of mercaptans after derivatization with phenylarsine oxide [24].

2 Experimental

2.1 Chemicals

The following chemicals were used: methanol p.a. (Merck, Darmstadt, Germany); acetone p.a. (Merck); t-butyl methyl ether p.a., 99.8% (Aldrich, Deisenhofen, Germany); diphenylarsine chloride [CAS No.: 712-48-1] (97%, with 3% impurity of diphenylarsine cyanide and 0.1% of triphenylarsine); diphenylarsine cyanide [CAS No.: 23525-22-6] without detectable impurities (GC, HPLC); phenarsazine chloride [CAS No.: 578-94-9] without detectable impurities (HPLC); phenylarsine dichloride [CAS No.: 696-28-6]; phenylarsine oxide [CAS No.: 637-03-6] (Aldrich); phenylarsonic acid [CAS No.: 98-05-5] 97% (Aldrich); triphenylarsine [CAS No.: 603-32-7] >98% (Aldrich); triphenylarsine oxide [CAS No.: 1153-05-5] 97% (Aldrich), thioglycolic acid methyl ester 95% (Aldrich); thioglycolic acid ethyl ester 97% (Aldrich); 1-ethanethiol 97% (Aldrich); 1-propanethiol 99% (Aldrich); 1,2-ethanedithiol 90% (Aldrich); 1,3-propanedithiol 99% (Aldrich).

Bis(diphenylarsine)oxide [UPAC: tetraphenyl diarsoxane, CAS No.: 2215-16-9] and diphenyl arsonic acid [UPAC: diphenyl arsinic acid, CAS No.: 4656-80-8] were not available as reference substances.

Stock solutions of the phenylarsenic compounds in t-butyl methyl ether were prepared in the concentration range of 0.5 mg/mL to 4.4 mg/mL. Stock solutions of the mercaptans in acetone were prepared in a concentration of 10.0 mg/mL

2.2 Derivatization and gas chromatographic equipment and conditions

All derivatizations were done at a temperature of 20° C in acetonic solution in 1.2 mL vials mixing 0.5 mL acetone, 20 µL phenylarsenic compound (stock solution) and 20 µL mercaptan (stock solution). The reactions are completed in 15 min.

For the separation of the derivatives an HP 5890 series II+ gas chromatograph (Hewlett Packard, Waldbronn, Germany) with HP 7673 autosampler and ECD were used. The temperatures of the injection block and the detector were 250° C and 300° C, respectively. The injection volume was 1 µL (split injection, split approx. 1 : 10). A (5%-phenyl)-methylpolysiloxane column, 30 m, 0.25 mm i.d., 0.25 mm d_f (DB-5 from J&W, Köln, Germany) was used. The carrier gas was nitrogen with a column headpressure of 100 kPa. The temperature of the column was 230° C. Data acquisition was accomplished with Gynkosoft, v. 5.32 (Gynkotek, Germering, Germany).

For identification of the derivates a GC/MS-system VG Trio 2 in the EI mode (70 eV) was used. The injection volume was 1 µL (splitless injection). A (5%-phenyl)-methylpolysiloxane column, 30 m, 0.25 mm i.d., 0.25 mm d_f (DB-5 from J & W, Köln, Germany) was used. The carrier gas was helium. The

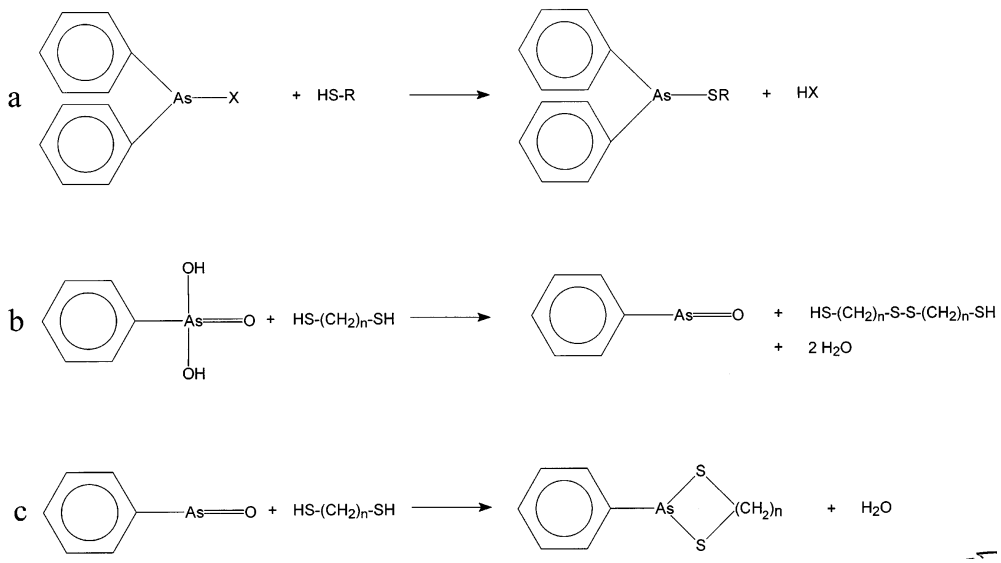

Fig. 2 a–c Scheme of the derivatization reactions; **a**: reaction of diphenylarsenic compounds with thiols and dithiols; **b**: reduction of phenylarsonic acid by dithiols; **c**: reaction of diphenylarsine oxide with dithiols

Table 1 Retention times (t_R) and limits of detection (LOD) of phenylarsine and diphenylarsine derivatives; abbr. see text

Phenylarsenic compound	Mercaptan for deriv.	Derivative	t_R/min	LOD/ng
$PhAs\text{-}Cl_2$	–	–	2.70	4.0
$Ph_2As\text{-}Cl$	–	–	4.29	0.6
$Ph_2As\text{-}CN$	–	–	4.60	0.3
$Ph_2As\text{-}X$	EtSH	$Ph_2As\text{-}SEt$	5.85	0.6
$Ph_2As\text{-}X$	PrSH	$Ph_2As\text{-}SPr$	6.82	0.6
$Ph_2As\text{-}X$	TGM	$Ph_2As\text{-}SGM$	10.89	0.4
$Ph_2As\text{-}X$	TGE	$Ph_2As\text{-}SGE$	12.54	0.4
$Ph_2As\text{-}X$	$Et(SH)_2$	$Ph_2AsSEtSH$	12.29	0.6
$Ph_2As\text{-}X$	$Pr(SH)_2$	$Ph_2AsSPrSH$	15.65	0.9
PhAsO	$Et(SH)_2$	$PhAsS_2Et$	4.50	0.1
PhAsO	$Pr(SH)_2$	$PhAsS_2Pr$	5.53	0.2

temperature of the column was started at 40° C and was raised to 250° C at 10° C/min.

2.3 HPLC equipment and conditions

The HPLC equipment consisted of a gradient pump M-480, an on-line degasser GT-103, an autosampler GINA 50 and diode array detector UVD 340-S. Data acquisition was accomplished with Gynkosoft, v. 5.32 (all Gynkotek, Germering, Germany). The injection volume was set to 20 µL. For separation of the organoarsenic compounds two different systems were used. For the first one an RP-18 column (250 × 3 mm, NUCLEOSIL 120-5) with the following linear gradient was used: acetonitrile/water 50/50 (v/v) to acetonitrile 95/5 (v/v) in 22.5 min, then reequilibration for 15 min. The second one was carried out with a cyanopropyl column (250 × 3 mm, NUCLEOSIL CN 100-5) with an eluent gradient from acetonitrile/water 10/90 (v/v) to acetonitrile/water 70/30 (v/v) in 30 min and subsequently applying the starting eluent for 15 min.

3 Results and discussion

3.1 GC analysis

From the investigated phenylarsenic compounds only phenylarsine dichloride, diphenylarsine chloride and diphenylarsine cyanide and, in high concentrations (more than 200 ng/µL), triphenylarsine can be detected with gas chromatography using an ECD without derivatization.

Diphenylarsines

All mercaptans and dimercaptans react with diphenylarsines in forming stable diphenylarsine thioether (Fig. 2). The derivatives were identified using GC/MS and are given in Table 1. The derivatization reactions are nearly quantitative. The equilibrium concentrations of the mercapto derivatives are 90–98%, if the diphenylarsine concentrations are 100 ng/µL or lower.

When derivatizing diphenylarsines with more than one mercaptan or dimercaptan, the yields of the resulting diphenylarsine thioether are proportional to the molar ratio of the used mercaptans. Figure 3 shows the gas chromatographic separation of the six diphenylarsine derivatives at 230° C.

Phenylarsines

Phenylarsine oxide and dichloride form phenylarsine thioether with mercaptans. These products are not stable in acetonic solution. Therefore mercaptans cannot be used for the analytical detection of phenylarsines.

1,2-Ethanedithiol reacts with phenylarsine oxide and dichloride in forming the stable 2-phenyl-<1,3,2>dithiarsolane

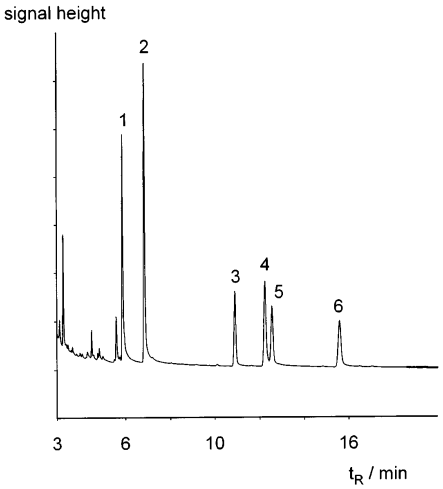

Fig. 3 Gas chromatogram of six diphenylarsine derivatives by using 400 ng Ph_2As-Cl; *1*: Ph_2As-SEt, *2*: Ph_2As-SPr, *3*: Ph_2As-SGM, *4*: Ph_2AsS_2Et, *5*: Ph_2As-SGE, *6*: Ph_2AsS_2Pr

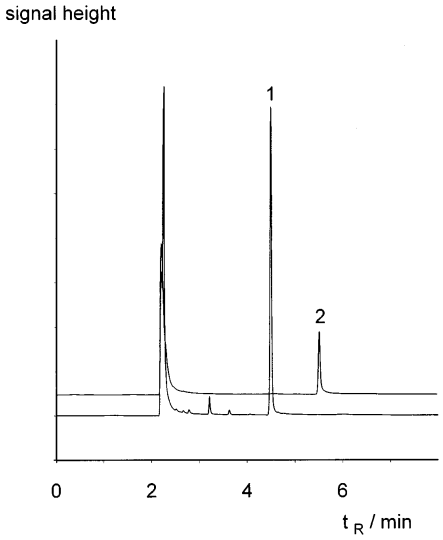

Fig. 4 Overlayed gas chromatograms of $PhAsS_2Et$ [1] and $PhAsS_2Pr$ [2], injected amounts: 40 ng

[CAS No.: 4669-53-8, $PhAsS_2Et$], 1,3-propanedithiol reacts with phenylarsine oxide and dichloride in generating the stable 2-phenyl-<1,3,2>dithiarsinane [CAS No.: 55883-62-0, $PhAsS_2Pr$]. Both reactions are quantitative. Phenylarsonic acid is reduced by 1,2-ethanedithiol and 1,3-propanedithiol to phenylarsine oxide. Therefore, the sum of the phenylarsenic compounds is determined after derivatization. The derivatives were identified by GC/MS. Since the reaction of phenylarsine oxide with a 1:1 molar mixture of 1,2-ethanedithiol and 1,3-propanedithiol yields 95% $PhAsS_2Et$ and only 5% $PhAsS_2Pr$, a chromatogram with both derivatives similar to the one in Fig. 3 cannot be given. Instead, Fig. 4 shows two overlayed gas chromatograms of these derivatives.

In Table 1 the retention times and limits of detection (LOD) of the investigated stable phenylarsenic and diphenylarsenic compounds are presented. The LOD were determined with the 3σ-method using a consecutive dilution series.

3.2 HPLC analysis

Table 2 gives the retention times and limits of detection for the HPLC separation for the six investigated phenylarsenic compounds with the two systems used. In Fig. 5 the separation achieved with the RP-18-system is shown, in Fig. 6 the corresponding result with the CN-column. In both figures separation of only five compounds is shown. The general elution order on both columns is, as one might expect, phenylarsenic < diphenylarsenic < triphenylarsenic compounds. Because the polarity of the investigated compounds differs remarkably, a rather steep gradient had to be used with both systems. In general, retention was stronger on the less polar RP-18-column.

CLARK I and CLARK II react with the water in the eluent by forming diphenylarsine hydroxide (Ph_2AsOH) and give only one peak. With both systems, phenylarsonic acid ($PhAsO(OH)_2$) is eluted near to or at the column dead time. For a stronger retention of this compound ion-pairing chromatography has to be used, but since the influence of an ion-pair reagent on the reactions of the phenylarsenic compounds is not known, this was not applied. In addition, separation of all six compounds was not possible with both systems. Phenylarsine oxide (PhAsO) and triphenylarsine (Ph_3As) are separated with both systems. With the RP-18 column is not possible to analyze Ph_3AsO. The retention time of the eluted peak differed remarkably from one chromatographic run to the next and sometimes no peak at all was detected, even when using measurement standards in high concentrations. Although there is no rational explanation for the behavior of Ph_3AsO at the moment, we tentatively suggest that irreversible binding to the column might have occured. With the CN column, Ph_2AsOH and $Ph_2As(NH_2)Cl$ were coeluted. All attempts to separate the overlapping peak pairs (using methanol as organic modifier or decreasing the slope of the gradient) did not improve the results in both systems, because peak broadening increased considerably as can already be seen in Fig. 6 (peak 1). Interactions of the diphenylarsenic compounds with the cyano group of the stationary phase might be responsible for this behavior. Because of the problems occuring with both columns, the choice of the column depends on the investigated substances. Interestingly the limits of detection achieved with the two systems differ remarkably and are always lower with the first separation system. They were determined with the 3σ-method using a consecutive dilution series.

In Fig. 7 the UV spectra of the six compounds are compared. The UV spectra of all compounds except ADAMSITE

Table 2 Retention times (t_R) and limits of detection (LOD) for both HPLC systems (1: RP-18, 2: CN-column); abbr. see text

Substance	Peak No	t_R1/min	LOD1/ng	t_R2/min	LOD2/ng
Ph_2AsOH	1	6.0	7.5	13.3	52
$Ph_2As(NH_2)Cl$	2	4.5	8.5	15.2	140
Ph_3As	3	19.8	6.6	25.9	11.2
Ph_3AsO	4	not possible		16.5	4.6
$PhAsO(OH)_2$	5	1.8	34	1.9	n.d.
PhAsO	6	2.9	7.3	4.5	25.4

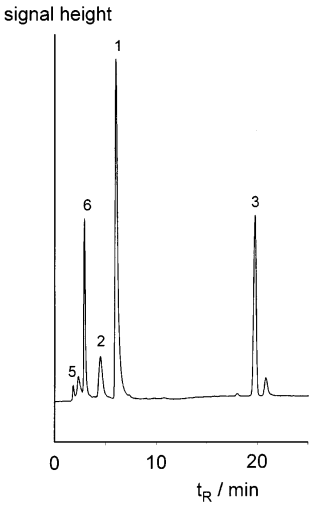

Fig. 5 HPLC chromatogram of five phenylarsenic compounds on an RP 18 column, injected amounts: 700 ng (CLARK I), 350 ng (all others). For peak identification see Table 2

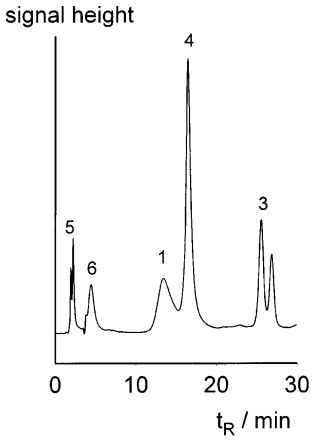

Fig. 6 HPLC chromatogram of five phenylarsenic compounds on a CN column, injected amounts: 1400 ng (CLARK I), 700 ng (all others). For peak identification see Table 2

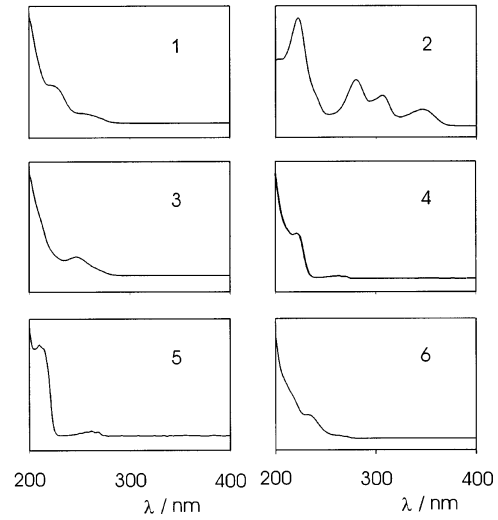

Fig. 7 Comparison of UV spectra of the six phenylarsenic compounds studied in HPLC. Numbers of spectra refer to the compound numbers in Table 2

are similar, but nevertheless they can still be used for peak identification. The very characteristic spectrum of ADAMSITE can be explained with the many mesomeric structures of the tricyclic compound. This causes a decrease in the energy gap between the HOMO and the LUMO, which subsequently leads to a bathochromic shift of the absorption bands.

3.3 Comparison of GC and HPLC analysis

Advantages of the GC/ECD analysis are 10 to 100 times lower detection limits, the shorter time needed for an analysis (less than 20 min compared to at least 35 min including equilibration time), the greater selectivity due to the derivatization and the possibility of easy confirming of results with the use of different derivatization reagents. With GC analysis the distinction between CLARK I and CLARK II is possible. After derivatization the phenylarsine compounds on the one hand and the diphenylarsine compounds on the other hand give only two derivatives, hence the sum of these compounds is determined.

Use of HPLC is necessary for the analysis of triphenylarsine compounds and ADAMSITE, which cannot be detected by GC/ECD. The distinction between As(III) and As(V) compounds, triphenylarsine and triphenylarsine oxide resp. phenylarsine oxide and phenylarsonic acid, is only possible with HPLC.

Therefore the choice of one particular separation method depends on the analytical problem that has to be solved.

4 Conclusions

For arsenic containing chemical warfare agents and their hydrolysis and oxidation products rather simple chromatographic methods are available, which might be applied to the analysis of soil and water samples. All stable mercapto and dimercapto derivatives can be used as reference compounds in the investigation of such samples by GC analysis. Most of these compounds cannot be detected with GC/ECD without derivatization. Our future efforts will concentrate on improving the separation with HPLC (e.g. temperature gradients, choice of columns), including a general investigation of the behaviour of phenylarsenic compounds on reversed-phase chromatographic columns. Besides, the use of an atomic emission detector in gas chromatography of the mercapto derivatives will be studied for comparison and the methods will be applied to the study of environmental matrices.

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Fresenius J Anal Chem (1998) 361:318–323 – © Springer-Verlag 1998

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In-situ methylation of strongly polar organic acids in natural waters supported by ion-pairing agents for headspace GC-MSD analysis

Received: 17 July 1997 / Revised: 29 September 1997 /
Accepted: 2 October 1997

Abstract Strongly polar organic substances like halogenated acetic acids have been analyzed in surface water and groundwater in the catchment area of the upper Elbe river in Saxony since 1992. Coming directly from anthropogenic sources like industry, agriculture and indirectly by rainfall, their concentrations can increase up to 100 µg/L in the aquatic environment of this catchment area. A new static headspace GC-MSD method without a manual pre-concentration step is presented to analyze the chlorinated acetic acids relevant to the Elbe river as their volatile methyl esters. Using an ion-pairing agent as modifier for the in-situ methylation of the analytes by dimethylsulfate, a minimal detection limit of 1 µg/L can be achieved. Problems like the thermal degradation of chlorinated acetic acids to halogenated hydrocarbons and changing reaction yields during the headspace methylation, could be effectively reduced. The method has been successfully applied to monitoring bank infiltrate, surface water, groundwater and water works pumped raw water according to health provision principles.

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Introduction

There is a widespread pollution of the aquatic environment by many anthropogenic organic substances in Central Europe due to their wide range of application in industry, agriculture and households and their biological persistence. Especially strongly polar organic compounds like synthetic amino acids (chelating agents EDTA, DTPA, NTA), aromatic sulfonic acids and halogenated carbon acids have become a subject of investigation in the past and for the next decade [1, 2].

Many of these substances appear in surface water of Central European rivers like Elbe, Rhine and Danube, in groundwater, river bank infiltrate and in drinking water [3]. Most of the haloacetic acids like mono-, di- and trichloroacetic acid (MCA, DCA, TCA) come from sources like chemical industries (semiproducts of chemical synthesis, solvents for polymers and detergents for metallic surfaces) or as metabolites from plant protection agents applied in agriculture. In 1992 chlorinated acetic acids were detected in Elbe river water up to a concentration of 70 µg/L [4], in tap and drinking water in the USA up to 160 µg/L in 1983/86 [5, 6]. By rainfall (degradation of halogenated hydrocarbons in the troposphere) or river bank infiltration these substances can reach the groundwater and can become a danger potential for drinking water treatment [7]. Because of the very high toxic and carcinogenic risks of some of these substances such as di- and trichloroacetic acid, a fast and exact analytical method for chloroacetic acids is needed to control their concentration, behavior and fate in surface, drinking and groundwater according to health provision principles [8].

Analytical methods of choice to detect halogenated acetic acids for levels less than 50 µg/L are gas chromatography with electron capture or mass selective detectors and sample preconcentration on solid phases or liquid-liquid extraction following diazomethane derivation [9–11]. Methyl esters of haloacetic acids are so much less soluble in water than free acids, giving headspace methods analytical possibilities. Using the method of static headspace and gas chromatography with dimethylsulfate (DMST) in-situ derivation [12], we have calculated detection limits for the haloacetic acids with an MSD of about 50 µg/L. That means, they are higher than the concentrations found in drinking and groundwater today. Main reasons of this situation are to be found in the equilibrium level of the distribution between liquid and gaseous phase for the micro pollutants (as their methyl esters), in the yields of the derivation reaction and in thermal instability of the analytes during the headspace procedure.