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Determination of organoarsenicals in the environment by solid-phase microextraction–gas chromatography–mass spectrometry

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Abstract

The development of a method for the analysis of organoarsenic compounds that combines dithiol derivatization with solid-phase microextraction (SPME) sample preparation and gas chromatography–mass spectrometry (GC–MS) is described. Optimization focused on a SPME–GC–MS procedure for determination of 2-chlorovinylarsonous acid (CVAA), the primary decomposition product of the chemical warfare agent known as Lewisite. Two other organoarsenic compounds of environmental interest, dimethylarsinic acid and phenylarsonic acid, were also studied. A series of dithiol compounds was examined for derivatization of the arsenicals, and the best results were obtained either with 1,3-propanedithiol or 1,2-ethanedithiol. The derivatization procedure, fiber type, and extraction time were optimized. For CVAA, calibration curves were linear over three orders of magnitude and limits-of-detection were $<6\cdot10^{-9}$ *M* in solution, the latter a more than 400× improvement compared to conventional solvent extraction GC–MS methods. A precision of <10% R.S.D. was typical for the SPME–GC–MS procedure. The method was applied to a series of water samples and soil/sediment extracts, as well as to aged soil samples that had been contaminated with Lewisite.

Keywords: Soil; Warfare agents; Organoarsenic compounds; Chlorovinylarsonous acid; Arsenic

1. Introduction

The determination of the chemical forms of arsenic in the environment is critical because of the different toxicities of arsenic species. The widespread use of inorganic and organic arsenic compounds in agriculture and industry results in significant anthropogenic input of this element into the environment [1]. Therefore, numerous studies have focused on the development of analytical methods for speciation of a variety of chemical forms of arsenic [2]. In this work, we focus on the development of a method for the determination of Lewisite decomposition products. Lewisite (*trans*-dichloro-2-chlorovinyl arsine) was developed for use as a chemical weapon in World War I. In the environment, Lewisite in contact with water quickly hydrolyzes to form 2-chlorovinylarsonous acid (CVAA) and then dehydrates to form 2-chlorovinylarsenious oxide (CVAO) [3]. The presence of CVAA or CVAO in the environment is therefore a positive indication of Lewisite contamination. The determination of traces of Lewisite and its decomposition products is crucial to support efforts in the remediation of contaminated sites at many military installations and the verification of arms control agreements.

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Because CVAA is essentially nonvolatile and Lewisite is thermally labile, chemical derivatization is used to enable gas chromatographic analysis. The derivatization with dithiols to form stable and volatile cyclic arsodithio compounds has been demonstrated [4,5]. High-performance liquid chromatography (HPLC) with electrochemical or ultraviolet detection with sub-micromolar limits-of-detection (LODs) have been demonstrated for CVAA [6]. However, the HPLC-based detection approaches provide limited qualitative information. Gas chromatography with mass spectrometric detection (GC–MS) is the preferred technique for compound identification and confirmation. The derivatization of CVAA with dithiols in aqueous solution is followed by solvent extraction of the product to introduce it to the GC. We endeavored, however, to replace this step by solid-phase microextraction (SPME). The characteristic preconcentration effect of SPME has the potential to significantly improve the LOD compared to the solvent extraction method.

SPME is a modern extraction technique which combines sampling, extraction, concentration and sample introduction into a single step [7]. This solvent-free, simple, and inexpensive extraction technique has found numerous applications in environmental analysis since its development earlier this decade by Pawliszyn and co-workers at the University of Waterloo. Analyte derivatization combined with SPME for GC analysis is used mainly for polar analytes to enhance their detectability and to improve chromatographic resolution [8]. The derivatization of polar analytes combined with SPME was used for phenols [9], amines [10], organic acids [11], steroids [12] and fatty acids [13]. SPME can also be used to enable the GC analysis of nonvolatile organometallic analytes. For example, Gorecki and Pawliszyn used the tetraethylborate derivatization for the SPME–GC–MS determination of inorganic lead [14]. Other applications of tetraethylborate derivatization combined with SPME extraction include the simultaneous determination of organomercury, -tin, and -lead [15] methyltin compounds [16], methylmercury and inorganic mercury [17].

Recently, SPME was successfully used for the determination of nerve agents in natural water samples at ultra-trace levels [18]. In this paper, the development and optimization of a SPME–GC–MS procedure for CVAA determination using derivatization with dithiols is described. Also, the application of the dithiol derivatization for simultaneous determination of other inorganic and organoarsenic compounds is discussed.

2. Materials and methods

2.1. Instrumentation

A Star 3400 CX gas chromatograph equipped with a 1077 split/splitless injector coupled to a Saturn 4D ion trap MS system (Varian Associates, Sunnyvale, CA, USA) was used. The automatic gain control (AGC) of the ion trap MS system was used throughout this study. A 30 m×0.25 mm, 0.25 μm film thickness, DB-5MS column (J&W Scientific, Folsom, CA, USA) and ultrahigh purity (99.999%) helium carrier gas (AGA, Hammond, IN, USA) with gas linear velocity of 28 cm/s (measured at 300°C column temperature) were used in all experiments.

The SPME holder for manual sampling and SPME fibers were obtained from Supelco (Bellefonte, PA, USA). A laboratory hot plate/stirrer Model PC-162 (Corning, New York, USA) with stirring speed of 6 units and PTFE-coated stir bars [Fisher Micro Bar, 1.5 mm diameter; 8 mm long from Fisher Scientific (Pittsburgh, PA, USA)] were used to stir the samples for the SPME experiments. The samples, usually 2.5 ml of an aqueous solution, were placed in 4-ml clear glass vials with a PTFE silicone septum (Supelco) for the extraction step.

2.2. Reagents

The stock solution of the *trans*-2-chlorovinyl arsonous acid (CVAA) was prepared from solid 2-chlorovinyl arsonous oxide (CVAO) by dissolving it in 10 m*M* HCl (Optima grade, Fisher Scientific). Nanomolar level solutions of CVAA were prepared shortly before use. The following derivatization reagents, obtained from Aldrich (Milwaukee, WI, USA), were used as received without further purification: 1,2-ethanedithiol (EDT, 90+%), 1,3-propanedithiol (PDT, 99%), 1,4-butanedithiol (BDT, 97%), toluene-3,4-dithiol (TDT, 90%), methyl thioglycolate (TGM, 95%), and 2,3-dimercapto-1-

propanol (BAL, 95%). Dimethylarsinic acid (DMA, 98%) and phenylarsonic acid (PhAs, 97%) were also obtained from Aldrich. High-purity deionized (18 MΩ) water (Barnstead NanoPure, Dubuque, IA, USA) was used for the preparation of all solutions.

2.3. GC–MS program and other parameters

The injection port was kept at 225°C for the syringe injection and at 250°C for the SPME desorption. The transfer line between the GC and MS was kept at 200°C for all experiments. The GC temperature program was identical for syringe injections and SPME, except for the SPME desorption step. The column temperature was held for 1.5 min for syringe injections or 5 min for SPME desorptions at 45°C, then programmed at 20°C/min to 165°C, followed by 8°C/min to 210°C and finally 50°C/min to 300°C, where it was held for 5 min. Mass spectra were obtained by scanning from m/z 35 to 400 with a 0.7-s scan time. A splitless injection was performed for both the syringe and SPME sample introduction.

2.4. Solvent extraction procedure

A 2.5-ml volume of CVAA standard prepared in 10 m*M* HCl was placed in a 4-ml vial, to which 1 μl of the neat derivatizing reagent was added using a GC syringe. The contents of the vial were mixed for 1 min, and 1 ml of toluene was added to extract the derivatization product. After 1 min of mixing, 1 μl of the toluene extract was injected into the GC–MS system.

2.5. SPME procedure

In the SPME procedure, a 2.5-ml aliquot of the CVAA solution in 10 m*M* HCl or extract was placed in a 4-ml glass vial and an aliquot of the neat derivatizing reagent (1 μl if not mentioned otherwise) was added using a GC syringe. The content of the vial was mixed for 1 min by stirring the solution with a stir bar and then the SPME fiber was placed in the solution with continued solution stirring for a predetermined time. The SPME sampling was done directly from the solution at room temperature. After sampling, the fiber was withdrawn into the needle and transferred to the GC injector. The sample was desorbed in the GC injector for 5 min at 250°C.

3. Results and discussion

3.1. Solvent extraction of CVAA-EDT

We initially examined the CVAA derivatization procedure developed by Fowler et al. [4] in which the cyclic disulfide 2-(2-chlorovinyl)-1,3,2-dithiarsenoline (referred hereafter as CVAA-EDT) is formed by reaction with EDT. We constructed calibration curves for the range of CVAA concentrations from $5.9 \cdot 10^{-6}$ to $2.3 \cdot 10^{-4}$ *M* (1 to 40 mg/l). A linear response with a correlation coefficient (r^2) equal to 0.999 for the peak area was observed. The reconstructed ion current (RIC) chromatograms were used to evaluate the peak areas. The LOD was $4.7 \cdot 10^{-6}$ *M* of CVAA in aqueous solution ($S/N > 3$ unless otherwise noted). The relatively low sensitivity of this method and the necessity of using an organic solvent led to our interest in SPME. The reported LOD for the solvent extraction method could be lowered if a higher ratio of the aqueous to organic phase were used in the extraction step to increase the preconcentration factor of the extraction procedure.

3.2. Solid-phase microextraction of CVAA-EDT

We applied SPME to the determination of dithiol-derivatized CVAA and examined fiber coatings, extraction time profiles, and calibration models. In the process of selecting a coating for the fiber, the polarity and volatility of the analyte were considered as well as the coating thickness [8]. We examined three fiber types: 100-μm thick poly(dimethylsiloxane) (PDMS), 85-μm poly(acrylate) (PA), and 65-μm poly(ethylene glycol)–poly(divinylbenzene) (Carbowax–DVB). The selection of these fibers was dictated by limited information in the literature about the volatility and polarity of the derivatization products. Although fibers of diverse properties were tested, the signal obtained did not differ significantly among them. The signal for the Carbowax–DVB fiber was ~10% lower than that obtained with the PDMS fiber and the response obtained with the PA

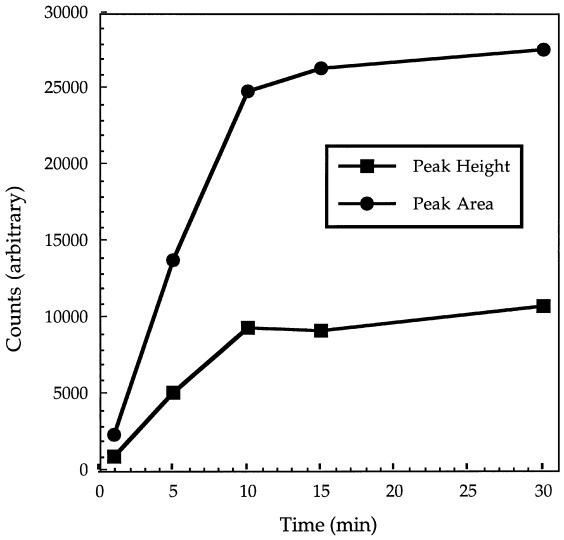

Fig. 1. Extraction time profile for CVAA-EDT.

fiber was ~40% higher than that obtained for the PDMS fiber. However, the PDMS fiber was selected for further optimization because of its ruggedness and reliability compared to the other fibers. An extraction time profile was obtained with a 100-μm PDMS fiber for $5.9 \cdot 10^{-7}$ *M* (100 μg/l) CVAA in 10 m*M* HCl using 1 μl of neat EDT for derivatization (Fig. 1). The steady state signal was reached after a 10-min equilibration time. Calibration curves were constructed with the 100-μm PDMS fiber for CVAA (1 μl of neat EDT for derivatization and 10-min equilibration time) ranging from $5.9 \cdot 10^{-8}$ *M* to $5.9 \cdot 10^{-4}$ *M* (10 μg/l to 10 mg/l). The peak areas for CVAA-EDT based on the reconstructed ion chromatograms were linear ($r^2 = 0.999$) over four orders of magnitude of CVAA concentration (results not shown). The LOD for CVAA was $1.2 \cdot 10^{-8}$ *M* (2 μg/l) in aqueous solution, a factor of 400 improvement compared to the solvent extraction GC–MS procedure described above. The precision (relative standard deviation, R.S.D.) was 8.1% (peak area, $n = 7$) for a $5.9 \cdot 10^{-7}$ *M* (100 μg/l) CVAA standard and 1 μl EDT.

We studied the performance of SPME for the determination of CVAA by applying the method to several environmental matrices (waters, soils and sediments). Natural water samples were acidified with 10 m*M* HCl while soil and sediment extracts were obtained by extraction of a 1-g sample with 10 m*M* HCl for 1 h. The extraction of soil samples with 10 m*M* hydrochloric acid has been reported to recover CVAA from solid matrices [19]. The extracts

Table 1
Recoveries (%) of fortified CVAA from aqueous matrices and soil/sediment extracts

Matrix	Based on peak height	Based on peak area
Tap water, Argonne	109	109
Ground water; Paducah, KY; acidified with 0.3 *M* HNO_3	85	89
River water; Satila River, GA; filtered with 0.45-μm filter	95	96
Sea water; Burlington, WA; filtered with 0.45-μm filter	135	129
Montana soil (SRM 2710), NIST	80	73
Reference soil SO−3, CASS	102	98
Reference stream sediment (STSD-4), CASS	113	106
Reference lake sediment (LKSD-2), CASS	83	75
Buffalo river sediment (SRM 2704), NIST	110	114

were filtered with 0.45-μm PTFE syringe filters and a 2.5-ml aliquot of the extract was fortified with $5.9 \cdot 10^{-7}$ *M* of CVAA. The percent recoveries of the CVAA-EDT using the SPME procedure with 1 μl EDT derivatization are presented in Table 1. The signal obtained for CVAA spiked into the matrix is compared with that of the CVAA standard in 10 m*M* HCl (both at $5.9 \cdot 10^{-7}$ *M*). The recoveries obtained for water samples were ≥90%. Significantly, the recovery for river water which contained a substantial amount of organic material was close to 100%. However, the recoveries from seawater were >100% which indicates that the partition coefficient of the CVAA-EDT is modified by the presence of high concentrations of inorganic salts in the matrix. The recoveries of CVAA from the soil and sediment extracts were ~100%. However, the lake sediment and the Montana soil recoveries were only ~80%. Because the pH of these extracts was not adjusted to 2 before fortifying the extract with the organoarsenical, we attribute the lower than expected signals to the change in pH of the (basic) extract. To ensure the quality of the data, a CVAA standard ($5.9 \cdot 10^{-7}$ *M*) was analyzed after each sample (R.S.D.=9.3%).

3.3. Derivatization of As (III), DMA, PhAs and CVAA

Because other thiols and dithiols have been reported in the literature as derivatizing agents for CVAA with solvent extraction [4,5,20], we investigated the optimal derivatizing agent. We broadened our study to include other species of arsenic, both inorganic and organic, to develop a SPME method which would allow the speciation of a range of arsenicals with a single derivatizing reagent. Dimethylarsinic acid (DMA), phenylarsonic acid (PhAs), CVAA, and inorganic arsenite were chosen. An aliquot of neat derivatization agent was added to 2.5 ml of a $5.9 \cdot 10^{-5}$ *M* solution of the target arsenic compound prepared in 10 m*M* HCl at room or elevated temperature. Extraction with 1 ml hexane was then performed and 1 μl of the extract was subjected to GC–MS analysis. Methyl thioglycolate (TGM) has been used as the derivatizing reagent mainly for monomethyl arsonic acid (MMA), DMA [20–24] and also inorganic arsenic [As(III)/As(V)] [20,24]. However, decomposition of derivatization products [especially for As(III)] in the GC injector was observed. In a comprehensive GC–MS study of military-derived arsenicals, Schoene et al., [20] used on-column injection to obtain signals for a series of arsenicals derivatized with TGM. We initially examined the TGM-based method but were unsuccessful — apparently because of the requirement in SPME to use a high injection port temperature (250°C) for the desorption of analytes from the fiber. We also investigated the use of 2,3-dimercapto-1-propanol (also known as 'British Anti-Lewisite' or BAL), which has been used for the derivatization of inorganic arsenicals for GC analysis [25–27]. The formation of stable derivatization products with BAL was also reported for MMA (but not DMA) [27], and PhAs in ethanol [28]. In our experiments, we obtained the signals for As(III) derivatized with BAL in either 10 m*M* or 2 *M* HCl, at room temperature and with the reaction mixture heated at 70°C for 30 min, and also for As(V) which is reduced to As(III) giving an identical reaction product to the As(III). The mass spectrum indicated the likely formation of 2-hydroxy-4-hydroxymethyl-1,3-dithio-2-arsacyclopentane with the reported intense fragment ions as reported in the literature [26,27]. Surprisingly, however, we did not observe a signal for CVAA or DMA. We observed a very small signal for PhAs-BAL that we based on the reported mass spectrum [28]. Thus, although BAL showed promise for derivatizing inorganic arsenicals, it was disappoint-

Table 2
Optimization of the conditions for reaction of dithiols with arsenicals using solvent extraction.

Conditions	Peak area (in thousands of counts/s)		
	DMA	CVAA	PhAs
10 μl EDT	53.5	163.4	253.4
10 μl PDT	74.5	197.6	924.1
10 μl BDT	16.2	43.5	ND
1 μl EDT	ND	209.8	49.1
1 μl PDT	ND	228.1	ND
10 μl EDT/heat	90.7		497.2
10 μl PDT/heat	139.6		146.8
10 μl BDT/heat	109.4		ND
10 μl TDT[a]/heat	ND	182.1	ND

[a] 0.25 g/ml solution in acetone.
ND, not detected.
Heat, sample heated for 1 h at 70°C.

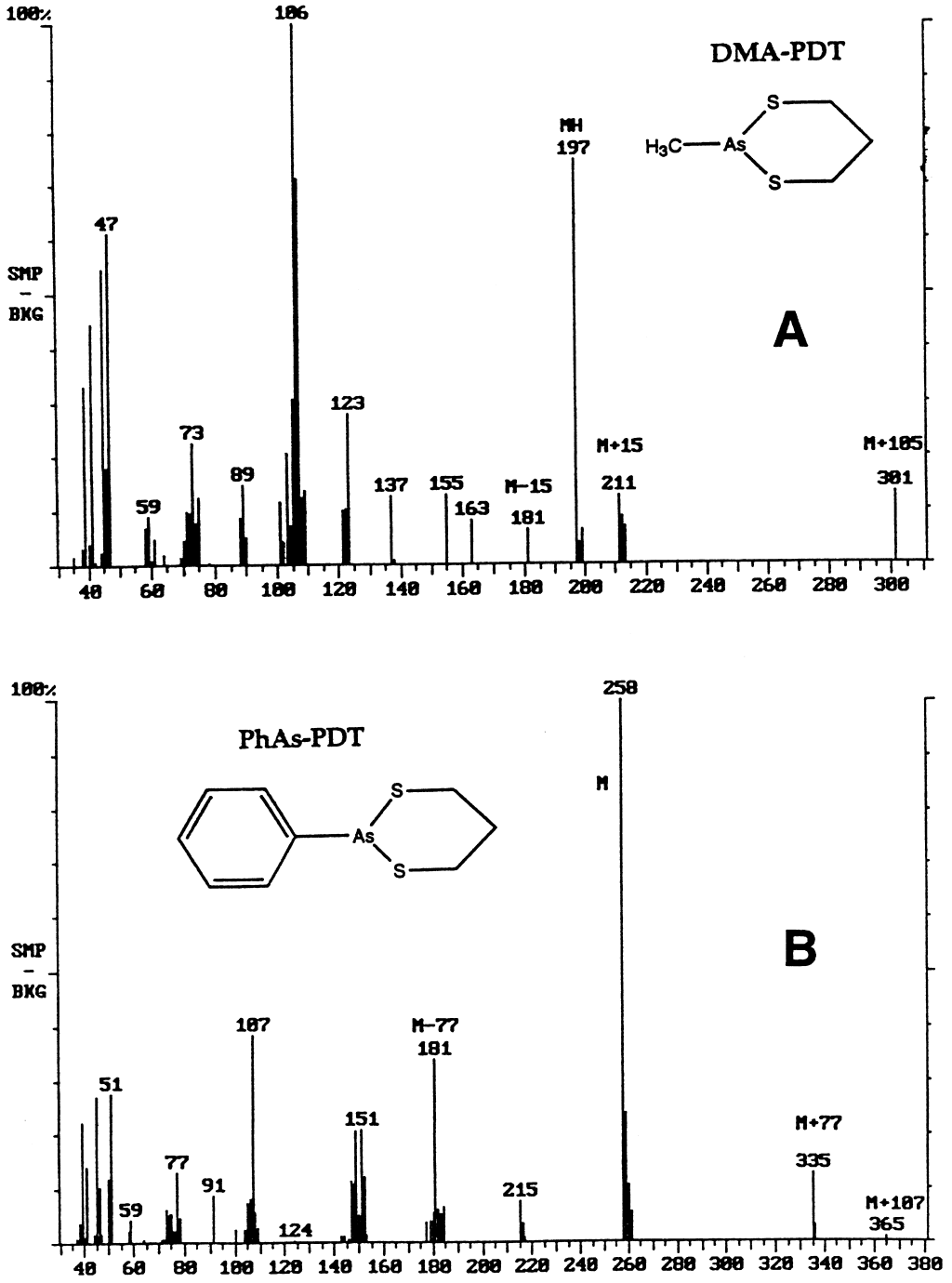

Fig. 2. Mass spectra of (A) DMA-PDT and (B) PhAs-PDT.

ing for the organoarsenicals that we were interested in studying.

We next turned our attention to the study of a series of dithiols: EDT, PDT, BDT, and TDT. Table 2 summarizes the results of these experiments for the target analytes. We obtained signals for approximately $5 \cdot 10^{-5}$ *M* (10 mg/l) of a given arsenical in 10 m*M* HCl with the solvent extraction of the derivatization product. Generally, the choice between EDT and PDT was difficult. Higher signals were obtained with 10 μl PDT at room temperature than with EDT; a signal for PhAs was not observed when using PDT. At elevated temperature PDT works better than EDT for DMA, but the opposite was true for PhAs. We did not observe a signal for PhAs with BDT or TDT; TDT derivatization also did not work for DMA. The limited solubility of TDT in water precludes its use in the SPME procedure. For further method optimization we chose PDT mainly because of the relatively low purity of commercial EDT. The SPME–GC–MS chromatograms of EDT contained many more signals resulting from contaminants than observed for PDT (results not shown).

The mass spectra that we observed for CVAA-EDT and the CVAA-PDT were identical to those described in the literature [4,5]. Intense molecular ions were present in the spectra at *m/z* 228 and 242, while loss of the chlorovinyl group (*m/z* 61) was obvious at *m/z* 167 and *m/z* 181 for CVAA-EDT and CVAA-PDT, respectively. Similar fragmentation patterns were observed for the CVAA-BDT (molecular ion *m/z* 256; chlorovinyl loss *m/z* 195) and CVAA-TDT (molecular ion *m/z* 290; chlorovinyl loss *m/z* 229). The mass spectra of DMA-PDT and PhAs-PDT are presented in Fig. 2. The reaction of PhAs with PDT gave the expected cyclic arsodithiol product. DMA, however, apparently reacts with PDT by the elimination of a methyl group to form the cyclic product. The *m/z* 197 ion indicates the protonated ion of the molecule shown in Fig. 2A. In both spectra the presence of self-chemical ionization processes occurring in the ion trap mass spectrometer is apparent (i.e., ions larger than M^+). The mass spectra obtained for DMA and PhAs with EDT indicated the formation of the same type of derivatives as described for PDT, with the same elimination of a methyl group in the case of DMA.

The experiments with different dithiols and solvent extraction indicated that heating the reaction mixture could enhance the signal. Thus, the reaction time and temperature were optimized with the SPME procedure. Using a 100-μm PDMS fiber with 10-min deposition time, a mixture of DMA, CVAA, and PhAs at ~$5 \cdot 10^{-7}$ *M* (100 μg/l) in 10 m*M* HCl with 1 μl of PDT was heated at 70°C, then cooled to room temperature (approximately 25°C) for the

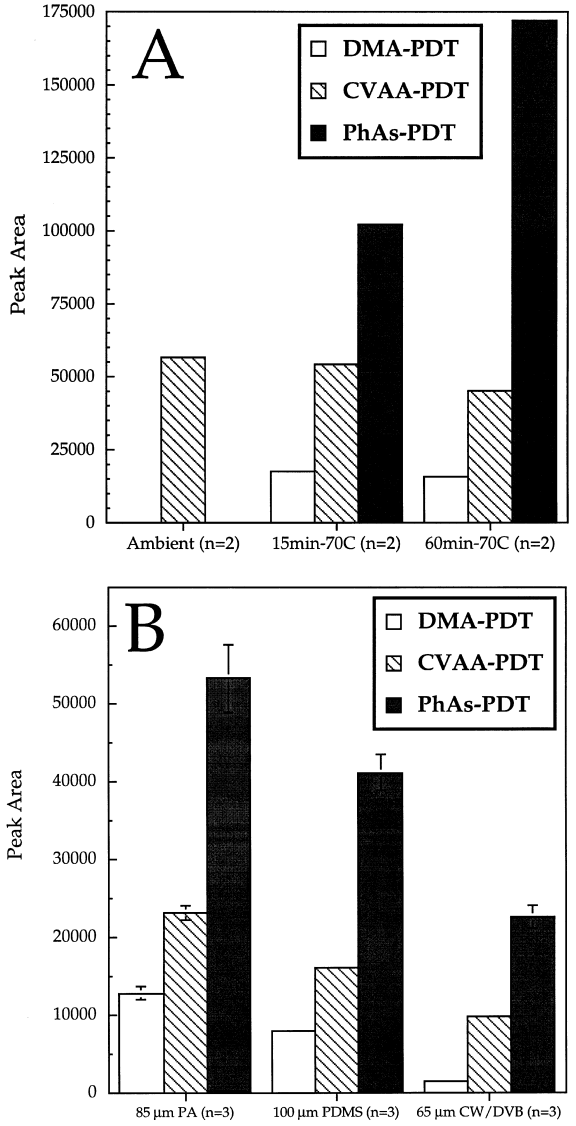

Fig. 3. Optimization of reaction conditions for (A) DMA, CVAA and PhAs with PDT and (B) fiber type. Error bars indicate one standard deviation ($n=3$).

SPME procedure. Fig. 3A presents the results of the optimization. If the mixture was not heated, the only signal observed was for CVAA. With heating the reaction mixture for 15 min at 70°C, the signals for DMA and PhAs appeared and the signal for the CVAA did not change appreciably. Extending the time of heating to 1 h improved the signal for PhAs in particular, but the signal for the CVAA decreased. The 15 min heating at 70°C was chosen as optimal, mainly because of time considerations.

Three different SPME fiber types were considered for optimization with respect to all three arsenicals with PDT derivatization and sample heating. The optimization was performed with ~$5\cdot10^{-7}$ *M* solution of each arsenical in 10 m*M* HCl with addition of 1 μl of PDT followed by heating of the sample for 15 min at 70°C, as presented in Fig. 3B. SPME sampling was performed from the sample cooled to room temperature. Similarly to the results obtained for the CVAA-EDT fiber optimization, the highest signals were obtained within the 65-μm PA fiber for all three arsenicals. However, the signals obtained with the other two fibers were not dramatically different from one another. The 65-μm PA fiber was thus used to perform the calibration. Calibration curves were constructed for DMA, CVAA, PhAs (results not shown); a representative chromatogram obtained for 100 μg/l of the arsenical mixture is shown in Fig. 4. The calibration was performed in the range from $5.9\cdot10^{-8}$ *M* (10 μg/l) to $5.9\cdot10^{-6}$ *M* (1 mg/l) (r^2=0.998). We observed a deviation from linearity in the calibration curve above $5.9\cdot10^{-6}$ *M*, apparently related to the concurrent appearance of a white precipitate in the sample solution and affecting the linearity for PhAs-PDT most significantly. The LODs for DMA, CVAA and PhAs were $1.2\cdot10^{-8}$ *M* (1.7 μg/l), $5.9\cdot10^{-9}$ *M* (1.0 μg/l) and $4.8\cdot10^{-9}$ *M* (0.97 μg/l), respectively (*S*/*N*=3). It is worth noting that the LOD obtained for CVAA is slightly lower than that obtained for the derivatization with EDT.

3.4. Analysis of authentic samples

The SPME–GC–MS method was tested on two authentic soil samples from a military installation. These samples required concentrated HCl to stabilize

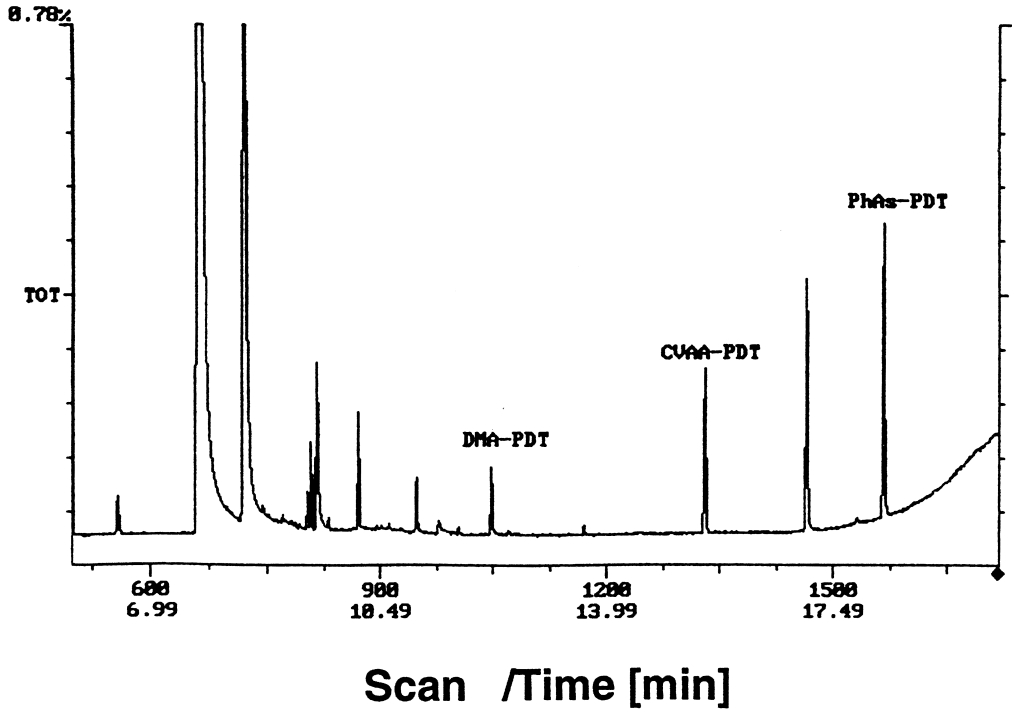

Fig. 4. Chromatogram for the PDT derivatives of DMA, CVAA, and PhAs, with each at a concentration of ~$5\cdot10^{-7}$ *M* (100 μg/l).

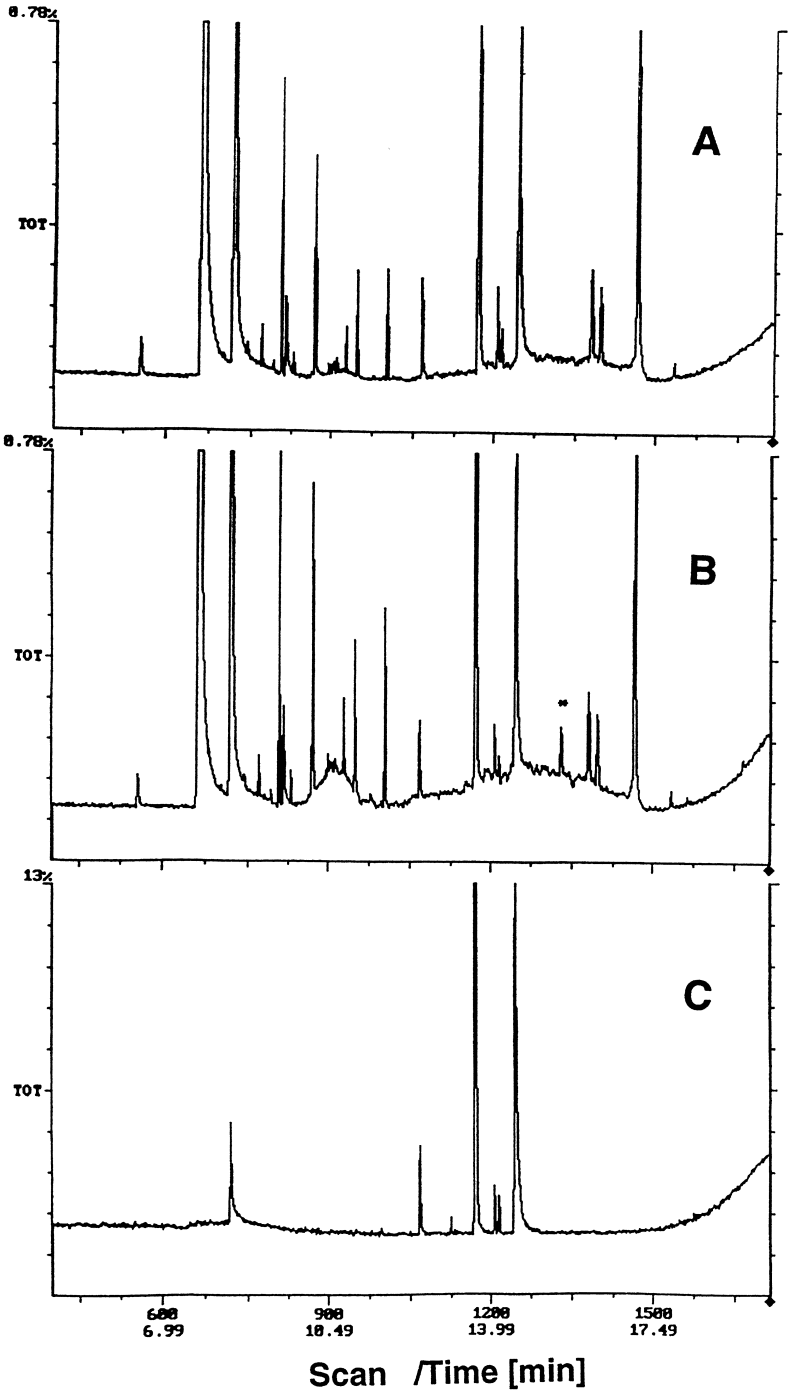

Fig. 5. Chromatograms of soil samples (A) S2 and (B) S1 with 1 μl PDT derivatization and of S1 (C) without PDT derivatization.

the pH of the extracting solution at 2 [29]. The 1-g samples were extracted with 10 ml of 10 m*M* HCl for 1 h; nearly 1 ml of HCl was necessary per gram of soil sample to keep the pH at 2. The filtered extracts were derivatized with EDT or PDT (1-, 5-, or 10-μl aliquots) and then subjected to SPME–GC–MS analysis. Losses of the derivatizing agent to side reactions with other non-CVAA components of soil extracts could be significant [29]. Problems with dithiol solubility in water were encountered when 10 μl of dithiol was used per 2.5 ml of the extract; small oily droplets of dithiol would form and adhere to the SPME fiber. Of the two samples, CVAA was detected as expected in the sample from a former storage location (S1). CVAA was not detected in the second sample, which was collected at a nearby uncontaminated location (S2); chromatograms for S2 and S1 are presented in Fig. 5A and B, respectively. The CVAA-PDT peak is marked with an asterisk in Fig. 5B. The presence of additional peaks that are not derived from PDT impurities (compare to Fig. 4) are apparent in Fig. 5A and B. SPME–GC–MS analysis of S1 was done without the addition of PDT to determine if these signals result from the derivatization step (Fig. 5C) which clearly indicates that the additional signals were not generated in the derivatization step. A good agreement of quantitative results for analysis of sample S1 using different amounts of EDT or PDT was obtained when the amount of dithiol used for analysis of the extract was the same as used to obtain the calibration. These quantitative results agree with those obtained by solvent extraction–GC–MS [29] and flow injection potentiometric stripping analysis [30]. Furthermore, the S2 (blank) sample extract was fortified with CVAA and the signal was recovered close to 100% of the expected value. We did not detect other organoarsenic compounds in these samples using PDT derivatization at an elevated temperature.

4. Conclusions

The research presented herein demonstrates that SPME can be successfully applied to GC–MS analysis of organoarsenic compounds when chemical derivatization with dithiols is used. The SPME–GC–MS procedure was optimized mainly with respect to the determination of CVAA. However, the method can be extended to other arsenicals by heating the sample during the derivatization process. The LOD for CVAA is improved by more than two orders of magnitude when SPME–GC–MS is used compared to conventional solvent extraction methods. A linear response was obtained for the arsenicals examined with the SPME–GC–MS procedure, and the precision was 5–10% R.S.D. The optimized method was successfully applied to the determination of CVAA in authentic samples. This method can further be extended to the determination of inorganic arsenicals simultaneously with organoarsenicals if two different dithiols are used for the derivatization (e.g., PDT and BAL). It would be worthwhile to examine the feasibility of extending this method to the determination of other organoarsenicals of interest to the United Nations in the implementation of arms control treaties.

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