Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Chromatography A, 992 (2003) 1–9
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Detection of VX contamination in soil through solid-phase microextraction sampling and gas chromatography/mass spectrometry of the VX degradation product bis(diisopropylaminoethyl)disulfide

Gary L. Hook[a], Gregory Kimm[b], David Koch[a], Paul B. Savage[c], Bangwei Ding[c], Philip A. Smith[a,*]

[a]*Uniformed Services University of the Health Sciences, Department of Preventive Medicine and Biometrics, Bethesda, MD 20814-4799, USA*
[b]*US Army Command and General Staff College, Fort Leavenworth, KS, USA*
[c]*Brigham Young University, Department of Chemistry and Biochemistry, Provo, UT, USA*

Received 11 November 2002; received in revised form 30 January 2003; accepted 31 January 2003

Abstract

A solid-phase microextraction (SPME) and gas chromatography–mass spectrometry (GC–MS) sampling and analysis method was developed for bis(diisopropylaminoethyl)disulfide (a degradation product of the nerve agent VX) in soil. A 30-min sampling time with a polydimethylsiloxane-coated fiber and high temperature alkaline hydrolysis allowed detection with 1.0 μg of VX spiked per g of agricultural soil. The method was successfully used in the field with portable GC–MS instrumentation. This method is relatively rapid (less than 1 h), avoids the use of complex preparation steps, and enhances analyst safety through limited use of solvents and decontamination of the soil before sampling.

Keywords: Solid-phase microextraction; Field analysis; Warfare agents; VX; Bis(diisopropylaminoethyl)disulfide

1. Introduction

The chemical warfare agent (CWA) *O*-ethyl *S*-(2-diisopropylaminoethyl) methylphosphonothiolate (VX) is an organophosphorus nerve agent. With a lowest lethal dose (LDLO) of 70 μg/kg [1], VX is arguably one of the most toxic chemical warfare agents (CWAs), and its low vapor pressure allows it to be somewhat persistent in the environment. There is a need for rapid, reliable, and relatively simple field detection methods for persistent chemical warfare agents such as VX, when they exist as soil contaminants. An ideal field method will be rapid, safe for the analyst, and will provide orthogonal data, even at trace contamination levels, giving a high degree of certainty regarding analyte identity.

A number of chromatographic methods have been developed for identification of CWAs in soil using a variety of detectors [2–5]. Interest in development of field sampling and analysis methods has grown in

*Corresponding author. Tel.: +1-301-295-0391; fax: +1-301-295-9298.
E-mail address: psmith@usuhs.mil (P.A. Smith).

0021-9673/03/$ – see front matter
doi:10.1016/S0021-9673(03)00278-4

response to the demand for rapid field analysis in both the civilian and military communities [6–9] and fieldable gas chromatography–mass spectrometry (GC–MS) equipment is available. Using such instrumentation, data may be obtained that are of near equal quality to those produced in the laboratory, considering the instrument's sensitivity and usefulness of the resulting mass spectra. However, a major drawback to field GC–MS continues to be traditional sampling and sample preparation methods that require solvent extraction. Thermal desorption methods are available that bypass solvent use, but additional equipment and more complicated analysis procedures result when these are used, and they may not be easily adaptable to analysis of soil samples.

Solid-phase microextraction (SPME) has been used widely for environmental sampling and a thorough review of SPME background and methodologies is readily available [10,11]. SPME has been used for sampling and detection of CWAs in air and water [12–15]. SPME methods for detecting CWAs or their degradation products on soil have been developed for use with analytical methods such as GC–MS [16–18] and GC with flame photometric detection [18].

The usefulness of gas phase SPME coupled to GC–MS for field analysis of unknown chemicals in complex environmental matrices has been demonstrated [19]. Field sampling/analysis using gas-phase SPME with GC–MS analysis has included detection of CS riot control agent and thermal degradation products [20], and detection of VX as a clothing contaminant [21].

With a low vapor pressure, detection of VX in soil using a field analytical method that relies on the analyte being in the gas phase presents a challenge. Heating a sample that contains VX could volatilize sufficient analyte to allow headspace SPME sampling. However sample degradation issues argue against this approach for detecting the intact VX molecule. Bis(diisopropylaminoethyl)disulfide [$(DES)_2$, Fig. 1] has been reported to be present in stored VX [22,23] and is an environmentally persistent degradation product of VX [24]. Small [24] reported $(DES)_2$ would be the likely surviving compound from VX contamination either after decomposition (without decontaminant) or from decontamination with a solution consisting of 70% diethylenetriamine, 28% methyl cellosolve, and 2% sodium hydroxide. If this compound could be reliably produced from VX-contaminated material, and if it were stable enough to allow SPME sampling (possibly at elevated temperatures that would hasten its formation) it could serve as a useful marker for VX contamination.

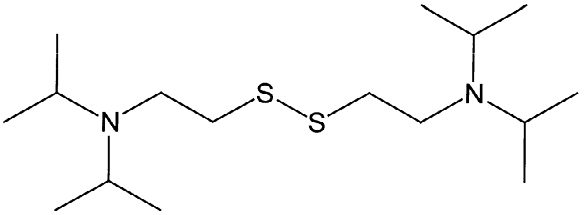

Fig. 1. Bis(diisopropylaminoethyl)disulfide $(DES)_2$.

This effort evaluates the use of headspace SPME with analysis by GC–MS as a relatively safe detection method for VX contamination on soil by identifying the presence of the degradation product $(DES)_2$ following high temperature alkaline hydrolysis of VX. In order to use SPME for detection of this analyte, sampling temperatures, fiber selectivity issues, and the kinetics of analyte loading onto the SPME fiber were studied. In addition to the study of these points, quantitative detection issues for $(DES)_2$ were evaluated in the laboratory using VX-spiked agricultural soil. Finally, the method was used in a field setting with VX-spiked soil. In addition to the potential usefulness of this method for soil with intact VX, it could also be useful in sampling for degraded VX in which $(DES)_2$ is already present.

From a safety perspective, the SPME methods discussed here avoid traditional solvent extraction, have a small logistical footprint, and sampling occurs from within a sealed system where the VX-contaminated soil has been at least partially decontaminated.

2. Materials and methods

2.1. Materials

VX (95% purity) was obtained from the US Army Edgewood Chemical Biological Center (Aberdeen Proving Grounds, MD, USA). For the laboratory work, the VX was diluted in chloroform to 0.9

mg/ml and was handled at that concentration. VX (97% purity) was obtained from Defence Research and Development Canada—Suffield (Medicine Hat, Canada) for the field studies. Standards for 2-(diisopropylamino)ethanethiol, bis(diisopropylaminoethyl)sulfide and $(DES)_2$ were synthesized. Bis-(diisopropylaminoethyl)sulfide was produced by reacting 2-(diisopropylamino)ethyl chloride hydrochloride (Aldrich, Milwaukee, WI, USA) with two equivalents of potassium thioacetate in acetonitrile. The resulting thioacetate was purified and reacted with ammonia in methanol to generate 2-(diisopropylamino)ethanethiol, which was coupled with 2-(diisopropylamino)ethyl chloride hydrochloride in acetonitrile with potassium carbonate. $(DES)_2$ was produced by exposing a sample of 2-(diisopropylamino)ethanethiol to atmospheric oxygen for 12 h, yielding the corresponding disulfide. The disulfide was distinguishable from the thiol and the sulfide by thin layer chromatography, ^1H nuclear magnetic resonance (NMR) spectroscopy and GC–MS with 70 eV electron impact (EI) and ammonia chemical ionization (CI) detection. An analytical standard for 2-(diisopropylamino)ethanethiol was obtained by adding $NaBH_4$ in methanol to reduce $(DES)_2$ back to the thiol compound. For retention time and mass spectrum comparisons, liquid injections were made for each standard.

All SPME fibers and holders used in this study are commercially available from Supelco (Bellefonte, PA, USA). The following five fiber coatings were evaluated: 100 μm polydimethylsiloxane (PDMS), 85 μm polyacrylate (PA), 65 μm Carbowax–divinylbenzene (CW–DVB), 65 μm Carboxen–polydimethylsiloxane (CAR–PDMS,), and 65 μm polydimethylsiloxane–divinylbenzene (PDMS–DVB). Prior to use, each fiber was conditioned following the manufacturer's recommendations. Blank runs were completed a minimum of once daily before use of any fibers for sampling.

2.2. SPME sampling

2.2.1. Selection of optimal fiber

Selection of the optimal SPME fiber for sampling $(DES)_2$ from among those tested was accomplished by obtaining triplicate samples from 15-ml silanized vials (without soil) having open screw top closures fitted with polytetrafluoroethane (PTFE)-lined silicone septa. Each vial was spiked with 2.0 μl of a standard solution [0.96 mg $(DES)_2$/ml] with a 10 μl syringe (Hamilton, Reno, NV, USA). To ensure reproducible spiking, a solvent chase method was used in which 1.0 μl of chloroform was drawn into the syringe, followed by 1.0 μl of air, and then the measured aliquot of the $(DES)_2$ solution. The temperature of the vial sampled was maintained at 50 °C by placing the vial in a digitally controlled hot-block heater (Barnstead/Thermolyne, Dubuque, IA, USA). Each sample was allowed to equilibrate in the hot-block for 10.0 min after which the septum was pierced with the SPME fiber assembly and the fiber extended into the vial for a 30.0 min extraction period.

At the end of the extraction period, the SPME fiber was retracted into its protective sheath, removed from the vial and immediately introduced into the heated GC injection port. The fiber was then lowered into the midrange region of the heated injection port liner (0.75 mm I.D. deactivated glass, Supelco) and GC–MS analysis commenced. The fiber providing the greatest GC–MS peak areas was selected for further sampling and analysis optimization.

2.2.2. Selection of optimal temperature and sampling time

Another set of spiked vials was analyzed using the optimal fiber to determine the effect of temperature on extraction. The extractions were performed under the same set of conditions used previously, except the temperature of extraction was varied (25, 50, 75, or 100 °C). Finally, the fiber was exposed at the resulting optimal temperature selected over an increasing extraction time period to examine fiber uptake kinetics for $(DES)_2$.

2.2.3. Laboratory soil headspace SPME

Once the optimal extraction parameters from among those studied had been identified, SPME of $(DES)_2$ from VX-spiked soil was completed. The soil used was standard reference material (SRM) 2709, San Joaquin soil (National Institute of Standards and Technology, Gaithersburg, MD, USA). Soil samples were created by spiking 1.0 g SRM soil in silanized vials with 100 μl of VX solution (0.9

mg/ml chloroform) followed by mixing of the spiked soil within the vial using a vortex mixer for 30 s. Some of these soil samples were analyzed using headspace SPME at 50 °C and the method described by Hook et al. [21] in an attempt to directly detect the presence of intact VX. To the remainder of the soil samples, 500 μl of decontamination solution (equal parts of 2.5 *M* NaOH and methanol) was added followed by an additional 30 s of mixing. These vials were placed in a heating block at 100 °C for a 10.0 min temperature equilibration period prior to the 30.0 min extractions. In order to estimate the sensitivity of the method for detecting $(DES)_2$, additional vials with soil and VX were prepared and sampled in this way. However, the mass of VX added to these vials ranged from 0.5 to 203.0 μg/g.

2.2.4. Soil headspace SPME, field sampling/analysis

Field samples were prepared by placing 1.0 g of the SRM soil in each of three silanized vials followed by spiking each vial with 90.0 μg of VX in a laboratory setting, and sealing each vial with a screw-top closure and PTFE-lined septum. Field analysis was performed the following day after applying 500 μl of decontamination solution to each vial. The 10.0 min. temperature equilibration, 30.0 min extraction time, and 100 °C extraction parameters were used for these samples and all handling was completed in a portable fume hood equipped with an activated charcoal filtering system.

2.3. Statistical analysis

Experimental data were examined for differences between $(DES)_2$ GC–MS peak areas. The statistical test used for this determination was the analysis of variance (ANOVA), which was completed for each of the three data sets. This was followed by Tukey's post hoc comparison to evaluate the source of observed differences. To examine reproducibility, the laboratory samples were run in triplicate and relative standard deviation (RSD) values were calculated.

2.4. GC–MS methods

The fiber optimization, temperature and extraction time samples for $(DES)_2$ were analyzed immediately following collection using a 6890 series gas chromatograph and 5973 quadrupole mass-selective detector (Agilent Technologies, Wilmington, DE, USA). The GC system was fitted with an Agilent, HP-5MS, 30 m×0.25 mm I.D. column having a film thickness of 0.25 μm. Helium at 1 ml/min was used as the carrier gas. The oven was programmed to increase from 40 to 250 °C at 20 °C/min following a 2.00 min hold time at the initial temperature. Desorption of the SPME fiber samples was accomplished in the splitless injection mode for 2.00 min, followed by a 50 ml/min injector purge. The injector temperature was maintained at 250 °C throughout an analysis, and the mass spectrometer transfer line was kept at 270 °C. Electron impact ionization (GC–MS-EI) was used for most of these samples. Mass spectra were collected over the range of m/z 35–350 for GC–MS-EI, and chemical ionization (GC–MS-CI) analyses. GC–MS-CI operating conditions followed D'Agostino et al. [23] with anhydrous ammonia (99.99%, Aldrich) used as the CI reagent gas. Sample retention characteristics and mass spectra were stored using the Agilent Chemstation software package.

Due to VX handling constraints, laboratory SPME extraction samples of decontaminated VX on soil were analyzed using a different (but identically configured) GC–MS system with a J&W Scientific (Folsom, CA, USA) DB-5, 30 m×0.25 mm I.D. column having a film thickness of 0.25 μm. Operating parameters were as described above. Both GC–MS-EI and GC–MS-CI analyses were completed with this instrument.

GC–MS-CI with headspace SPME sampling of decontaminated VX provided molecular mass information for degradation products observed. Silanized vials were spiked with 45 μg of VX followed by application of 500 μl of decontamination solution. Extractions were performed using the same extraction conditions as before (100 °C, 10.0 min equilibration, 30.0 min extraction with PDMS fiber). GC–MS-CI was performed on the $(DES)_2$ and bis(diisopropylaminoethyl)sulfide standards by direct injection of dilute concentrations of each standard independently.

Field analyses were performed using a third GC–MS system (van mounted) of the same type used for laboratory samples with water electrolysis providing

high purity H_2 carrier gas. This instrument was fitted with an HP-5MS column (30 m×0.25 mm I.D., 0.25 μm film thickness) and operating parameters were identical to those used in laboratory GC–MS-EI analyses.

3. Results and discussion

3.1. Fiber selection

Table 1 provides the data obtained from fiber selection experiments. The PDMS, PA, and CW–DVB fibers were found to provide the greatest sensitivity and statistically they provided peak area responses that were indistinguishable. The fiber of choice for further work was the PDMS fiber as it provided good sensitivity and it has already been shown to be the optimal fiber for field sampling and analysis of intact VX [21].

3.2. Temperature and sampling time selection

Table 2 provides the data resulting from temperature optimization experiments. Apparently due to its low volatility, $(DES)_2$ could not be detected at room temperature. The GC–MS peak area responses obtained at 50, 75 and 100 °C were not statistically different. For further work, 100 °C was selected for use to maximize the $(DES)_2$ production rate during the degradation of VX on soil.

Fig. 2 presents the uptake curve obtained for $(DES)_2$. Statistically, the peak areas for the 20, 30, 45 and 60 min extractions were indistinguishable from each other yet different from the peak areas for 1 and 10 min.

Table 2
Optimal temperature selection, GC–MS-EI peak area counts for $(DES)_2$, 30.0 min extraction, PDMS fiber

Sample No.	25 °C	50 °C	75 °C	100 °C
1	ND*	$2.57\cdot10^8$	$2.78\cdot10^8$	$2.64\cdot10^8$
2	ND*	$2.83\cdot10^8$	$2.42\cdot10^8$	$2.49\cdot10^8$
3	ND*	$2.73\cdot10^8$	$2.84\cdot10^8$	$2.25\cdot10^8$
Mean	–	$2.71\cdot10^8$	$2.68\cdot10^8$	$2.46\cdot10^8$
SD	–	$1.29\cdot10^7$	$2.31\cdot10^7$	$1.94\cdot10^7$
RSD	–	4.77	8.60	7.90

* Non-detectable.

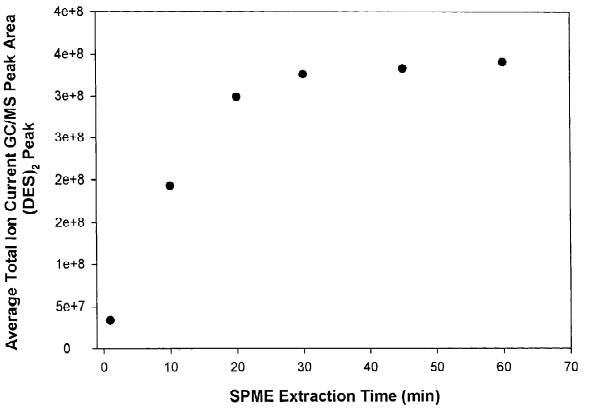

Fig. 2. GC–MS-EI total ion current peak area for $(DES)_2$ plotted against SPME sampling time (PDMS fiber, 100 °C).

3.3. Compound identification by GC–MS

Both GC–MS-CI and GC–MS-EI spectral and retention time matches were obtained for $(DES)_2$, 2-(diisopropylamino)ethanethiol, and bis(diisopropylaminoethyl)sulfide peaks using authentic stan-

Table 1
Optimal fiber selection, GC–MS-EI peak area counts for $(DES)_2$, 30 min extraction, 50 °C

Sample No.	PDMS	PA	CW–DVB	PDMS–DVB	CAR–PDMS
1	$2.57\cdot10^8$	$2.15\cdot10^8$	$2.40\cdot10^8$	$1.83\cdot10^8$	$6.57\cdot10^7$
2	$2.83\cdot10^8$	$2.56\cdot10^8$	$2.60\cdot10^8$	$1.39\cdot10^8$	$7.13\cdot10^7$
3	$2.73\cdot10^8$	$2.22\cdot10^8$	$2.55\cdot10^8$	$1.57\cdot10^8$	$6.13\cdot10^7$
Mean	$2.71\cdot10^8$	$2.31\cdot10^8$	$2.52\cdot10^8$	$1.61\cdot10^8$	$6.61\cdot10^7$
SD	$1.29\cdot10^7$	$2.19\cdot10^7$	$1.05\cdot10^7$	$2.17\cdot10^7$	$5.00\cdot10^6$
RSD	4.77	9.47	4.17	13.48	7.57

dards. Fig. 3 illustrates a GC–MS-CI total ion chromatogram from decontaminated VX. It is recognized that GC–MS-CI is not a method that would find use in typical field GC–MS analyses but its use here in the laboratory confirmed production of $(DES)_2$ from alkaline hydrolysis of VX, and simplified interpretation of laboratory generated data. The GC–MS-EI spectra of VX and its degradation products that contain the diisopropylaminoethyl functional group are dominated by the m/z 114 ion, and little unambiguous diagnostic information for these analytes is available from stable high mass ions. Degradation products for which standards were not available were thus identified based upon the pseudo-molecular and fragmentation ion data provided by GC–MS-CI, and by comparison to GC–MS-CI analyses performed by D'Agostino et. al. [23]. In order to examine field samples for the presence of $(DES)_2$, authentic standards of the disulfide compound should be analyzed ahead of time to obtain a retention time for this analyte, a relatively easy procedure if the $(DES)_2$ standard is available.

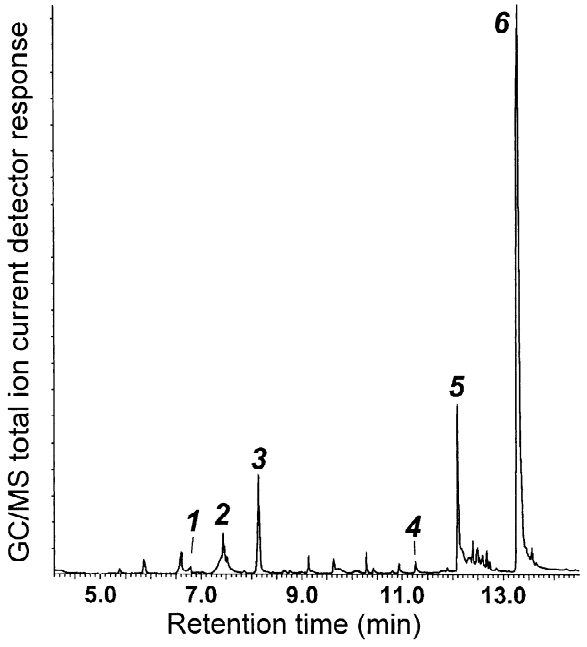

Fig. 3. Ammonia GC–MS-CI chromatogram of VX subjected to alkaline hydrolysis; Compound key for Figs. 3, 4a, 4b, and 6: 1=*O,S*-diethylmethylphosphonothiolate[1], 2=2-(diisopropylamino)ethanethiol[2], 3=2(diisopropylamino)ethyl methyl sulfide[1], 4=VX[2], 5=bis(diisopropylaminoethyl)sulfide[2], 6=bis(diisopropylaminoethyl)disulfide[2].

[1]Identification based upon apparent CI pseudo-molecular ion only.

[2]Identification based upon apparent CI pseudo-molecular ion, retention time and EI spectrum match with authentic standard.

3.4. Soil headspace SPME

Initial studies of soil spiked with VX (no alkaline hydrolysis) demonstrated that SPME–GC–MS was unable to reproducibly detect the presence of intact VX at 50 °C. Additional attempts to detect intact VX at 100 °C were also unsuccessful. Field analysis for $(DES)_2$ from the decontamination of VX-spiked soil was successful and total ion and extracted m/z 114 ion chromatograms are shown in Fig. 4. $(DES)_2$ is the predominant peak, consistent with laboratory analyses. Formation of $(DES)_2$ from hydroxide-catalyzed degradation of VX has been observed previously [25]. This process is proposed to occur via the pathway given in Fig. 5. At 100 °C with a 30.0 min extraction, $(DES)_2$ was detected with >3:1 signal-to-noise ratio down to a level of 1.0 μg of VX spiked to 1.0 g of the SRM soil (1 ppm). A linear response was observed from 1 to over 100 ppm VX soil concentration when plotting the logarithm of soil concentration against average GC–MS-EI $(DES)_2$ m/z 114 peak areas. A GC–MS-EI chromatogram (m/z 114 extracted ion trace) is shown for a 1 ppm laboratory sample in Fig. 6.

With the methods described here, $(DES)_2$ can be detected in soil from initially intact VX in less than 1 h. It may be possible to reduce this time by eliminating the 10.0 min equilibration period, although we did not explore this possibility. This method may have application in detecting the presence of VX in complex media other than soil. As shown in Fig. 4, the selection of the m/z 114 ion trace for detection of VX and its degradation products that contain the diisopropylaminoethyl functional group enhances the field analyst's ability to identify compounds of interest in an otherwise complex chromatogram. Owing to the variables related to different soil types, quantitation of VX soil contamination would be difficult using the methods investigated here. However, based upon the ortho-

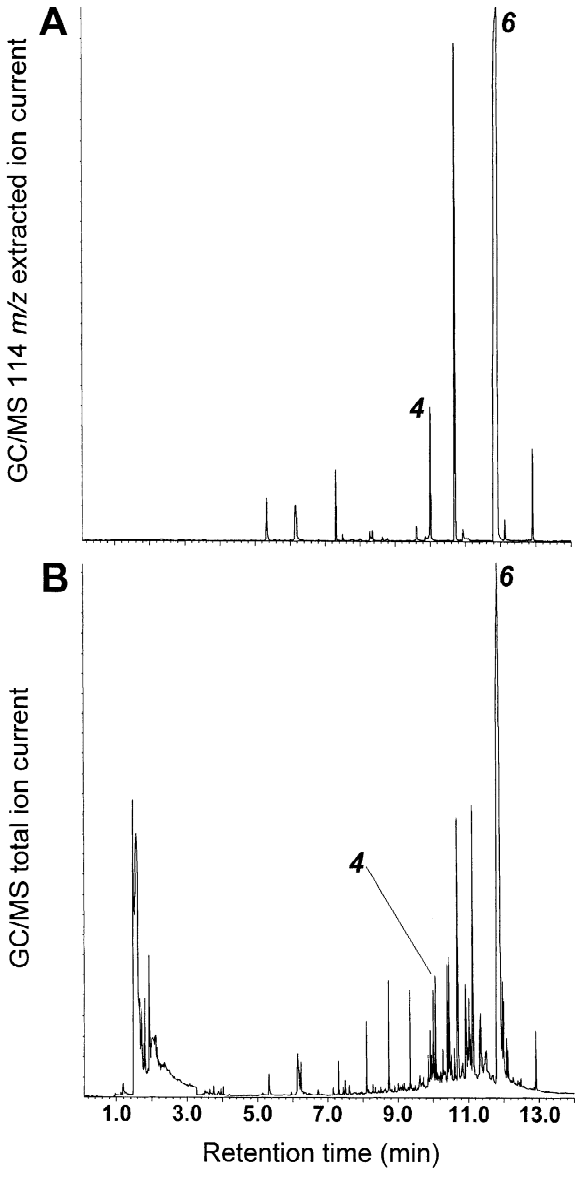

Fig. 4. (a) GC–MS-EI m/z 114 extracted ion trace from field analysis of 90.0 μg of VX spiked to SRM soil following alkaline hydrolysis, 10.0 min equilibration, and 30.0 min extraction with PDMS fiber at 100 °C. (b) Total ion chromatogram of same GC–MS data file as in (a).

gonal data produced by GC–MS-EI analysis, qualitative identification of $(DES)_2$ would be fairly unambiguous.

As a final word, analyst safety is important when using laboratory methods and instrumentation in the field to detect an analyte such as VX. This method promotes analyst safety by limiting the use of solvents to the small amount used for decontamination of the VX and generation of $(DES)_2$, and reduces exposure potential for the intact VX molecule. While the toxicity of $(DES)_2$ has not been well characterized in the literature, Munro et al. [26] reported an estimated reference dose (RfD) for $(DES)_2$ as 6.6 μg/kg/day. This is four orders of magnitude higher than the RfD for VX [27] therefore, $(DES)_2$ is anticipated to be of much lower toxicity than VX.

4. Conclusion

Orthogonal data were provided using a field expedient SPME–GC–MS sampling and analysis method to detect the presence of VX soil contamination. With the overall desire to develop a simple field sampling and analysis method, sample preparation was limited to addition of a small amount of alkaline methanol to silanized vials containing VX contaminated soil followed by heating at 100 °C during the 30 min passive SPME headspace sampling time. Analyst safety is enhanced by the alkaline hydrolysis of VX in the soil sample and the intent to determine the presence of VX through the identification of the resulting VX degradation product $(DES)_2$. As completed here, the presence of VX on soil was detectable through the use of the $(DES)_2$ marker at concentrations as low as 1.0 μg/g of soil (1 ppm, w/w). With a total sampling and analysis time of less than 1 h, high quality data for chemical identification is readily available. Even with the need for a heating block and decontamination solution, this method lends itself to field analysis as the complex sample preparation steps typically required for soil samples are avoided. In addition to enhanced analyst safety resulting from alkaline hydrolysis of VX in the sample, safety is further enhanced as SPME headspace sampling minimizes the potential for exposure to any contaminants present in the soil.

Acknowledgements

We are grateful to the US Army Medical Research

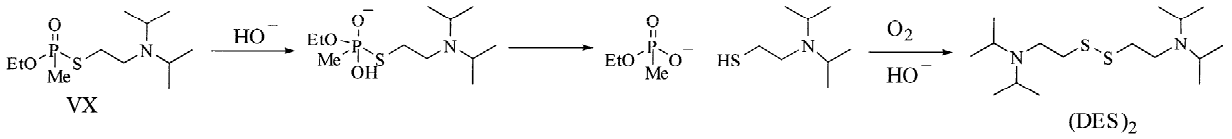

Fig. 5. Mechanism for formation of $(DES)_2$ from hydroxide-catalyzed degradation of VX.

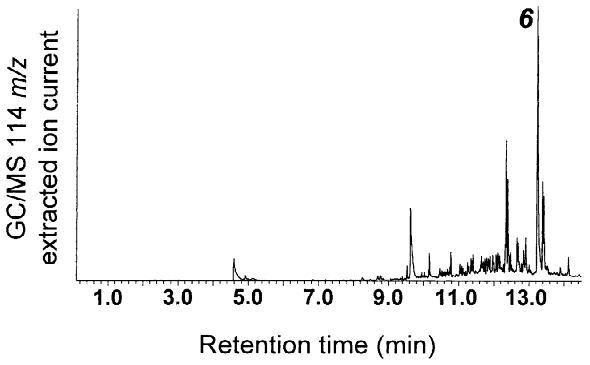

Fig. 6. GC–MS m/z 114 extracted ion trace from analysis of 1 ppm VX spike on SRM soil following alkaline hydrolysis, 10.0 min equilibration, and 30.0 min extraction with PDMS fiber at 100 °C. $(DES)_2$ was observed in total ion chromatograms in all samples where the VX soil concentration was 15 ppm (m/m) or greater.

Institute for Chemical Defense, especially Dr. Thomas Logan and Mr. Austin Swift for providing the support to complete this work. Funding to accomplish this research was provided by the US Marine Corps Systems Command. The opinions or assertions contained herein are the private ones of the author and are not to be construed as official or reflecting the views of the United States Department of Defense or the Uniformed Services University of the Health Sciences.

References

[1] WHO Technical Report, Health Aspects of Chemical and Biological Weapons: Report of a World Health Organization Group of Consultants, World Health Organization, Geneva, 1970, p. 26;
WHO Technical Report, Health Aspects of Chemical and Biological Weapons: Report of a World Health Organization Group of Consultants, World Health Organization, Geneva, 1970, p. 40.
[2] E.W.J. Hooijschuur, C.E. Kientz, A.G. Hulst, Anal. Chem. 72 (2000) 1199.
[3] E.W.J. Hooijschuur, C.E. Kientz, U.A.Th. Brinkman, J. Chromatogr. A 928 (2001) 187.
[4] P.A. D'Agostino, L.R. Provost, J. Chromatogr. 589 (1992) 287.
[5] R.M. Black, R.J. Clarke, D.B. Cooper, R.W. Read, D. Utley, J. Chromatogr. 637 (1993) 71.
[6] L. Müller, in: J. Pawliszyn (Ed.), Applications of Solid Phase Microextraction, Royal Society of Chemistry, 1999, p. 269.
[7] H.B. Overton, H.P. Dharmasena, U. Ehrmann, K.R. Carney, Field Anal. Chem. Technol. 1 (2) (1996) 87.
[8] T. Gorecki, J. Pawliszyn, Field Anal. Chem. Technol. 1 (5) (1997) 227.
[9] Department of Defense, United States of America, DOD Instruction 6490.3, Implementation and Application of Joint Medical Surveillance For Deployments, Department of Defense, 7 August 1997.
[10] J. Pawliszyn (Ed.), Applications of Solid Phase Microextraction, Royal Society of Chemistry, 1999.
[11] S. Scheppers-Wiercinski (Ed.), Solid-Phase Microextraction: A Practical Guide, Marcel Dekker, New York, 1999.
[12] J.F. Schneider, A.S. Boparai, L.L. Reed, J. Chromatogr. Sci. 39 (2001) 420.
[13] P.A. Smith, M.V. Sheely, T.A. Kluchinsky Jr., J. Sep. Sci. 25 (2002) 917.
[14] H.A. Lakso, W.F. Ng, Anal. Chem. 69 (1997) 1866.
[15] M.T. Sng, W.F. Ng, J. Chromatogr. A 832 (1999) 173.
[16] G.L. Kimm, G.L. Hook, P.A. Smith, J. Chromatogr. A 971 (2002) 185.
[17] B. Szostek, J.H. Aldstadt, J. Chromatogr. A 807 (1998) 253.
[18] A. Alcaraz, S.S. Hulsey, R.E. Whipple, B.D. Andersen, in: M. Heyl, R. McGuire (Eds.), Analytical Chemistry Associated with the Destruction of Chemical Weapons, Kluwer, 1997, p. 65.
[19] G.L. Hook, G. Kimm, T. Hall, P.A. Smith, Trends Anal. Chem. 21 (2002) 534.
[20] P.A. Smith, T.A. Kluchinsky Jr., P.B. Savage, R.P. Erickson, A.P. Lee, K. Williams, M. Stevens, R.J. Thomas, AIHA J. 63 (2002) 284.
[21] G.L. Hook, G. Kimm, G. Betsinger, P.B. Savage, T. Logan, P.A. Smith, J. Separation Sci., submitted.
[22] D.K. Rohrbaugh, J. Chromatogr. A 809 (1998) 131.
[23] P.A. D'Agostino, L.R. Provost, J. Visentini, J. Chromatogr. 402 (1987) 221.
[24] M.J. Small, Technical Report 8208, US Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD, 1983.

[25] Y.C. Yang, J.A. Baker, J.R. Ward, Chem. Rev. 92 (1992) 1729.
[26] N.B. Munro, S.S. Talmage, G.D. Griffin, L.C. Waters, A.P. Watson, J.F. King, V. Hauschild, Environ. Health Perspect. 107 (1999) 933.
[27] Derivation of Health-Based Environmental Screening Levels for Chemical Warfare Agents: A Technical Evaluation, US Army Center for Health Promotion and Preventive Medicine, Aberdeen Proving Ground, MD, 1999.