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Supercritical fluid extraction of chemical warfare agent simulants from soil

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ABSTRACT

Chemical warfare agent simulants are efficiently recovered from 2-ppm spikes in 1 g of Rocky Mountain Arsenal Standard Soil using methanol–carbon dioxide (5:95) at 300 atm for 2 min at 60°C. Recoveries (n = 3) were 79 ± 23% for dimethylmethylphosphonate, 93 ± 14% for 2-chloroethylethyl sulfide, 92 ± 13% for diisopropylfluorophosphate and 95 ± 17% for diisopropylmethylphosphonate. Recoveries are higher than, but less precise than those achieved from a 5-min ultrasonic micro-scale extraction using methanol. Much less laboratory waste is generated than the current standard organic solvent extraction method (33 g of soil shaken with 100 ml of chloroform).

INTRODUCTION

Current standard methods [1] for extracting agents bis(2-chloroethyl)sulfide (HD) and O-isopropylmethylphosphonofluoridate (GB) or O-ethyl-S-2-(diisopropylaminoethyl)methylphosphononothioate (VX) from soil involve shaking 33 g samples with 100 ml of chloroform. Although the method is simple and straightforward, the mass of toxic waste is considerable, and the sensitivity of the final analytical methods is limited by the solid:liquid ratio if the solvent is not concentrated.

Supercritical fluid extraction (SFE) appears to offer a good alternate to solvent extraction in this application. Carbon dioxide and nitrous oxide have been used [2–8] in both off- and on-line interfacing with gas chromatography (GC) to achieve highly efficient recoveries and sensitive analyses of many low polarity organic compounds from soil, sediment, diesel exhaust and air particulates, using small masses of sample and short extraction times. Recoveries for many solutes have been superior to those achieved using soxhlet or ultrasonic solvent extraction [2,7]. Binary supercritical fluids [3,4,6] can be used to improve extraction recoveries from sorptive matrices. This paper reports the successful recovery and analysis of chemical warfare agent simulants from soil using SFE followed by off-line GC.

EXPERIMENTAL

Equipment

SFE was performed using two commercially available devices. A Suprex SFC/200A supercritical fluid chromatograph was used for most of the work. The column was replaced with a Brownlee high-performance liquid chromatography (HPLC) guard column or a Keystone Scientific SFE vessel (nominal volume of *ca.* 0.5 ml) holding *ca.* 1 g of soil. The UV detector was replaced with a high pressure shut-off valve and a *ca.* 30 cm length of 25 μm I.D. fused-silica tubing from SGE was attached to the valve outlet for a restrictor. The experiments with 10 g of soil were performed using an ISCO System 1200, a *ca.* 30 cm length of 50 μm I.D. fused-silica tubing, and a 5-ml extraction cell.

Off-line gas chromatographic analysis of the simulants was conducted on two instruments. The initial work was done on a Perkin-Elmer Model 3920 using a 30 m × 0.53 mm I.D. × 1.5 μm film thickness DB-5 fused-silica capillary column with a 7 ml/min flow-rate of helium. The column oven was temperature programmed from 70°C (after a 4 min isothermal hold) to 150°C at 8°C/min with the injector and flame ionization detector held at *ca.* 120°C and 200°C, respectively. A 3-μl volume was injected slowly using the solvent flush technique, and quantitation was performed by the method of internal standards using a Maxima chromatography data system on an IBM XT personal computer. Later work used a Varian Model 3400 gas chromatograph equipped with the same column and a 1:1 split of the column effluent to flame photometric (P mode) and electron-capture detectors. The column oven temperature program was 70°C (2 min isothermal hold) to 130°C at 4°C/min. The injector was held at 200°C and the detectors were maintained at 220°C. A 1-μl injection was made using the solvent flush technique, and quantitation was conducted by the method of internal standards using either a Maxima chromatography data system or a Model 4400 Varian integrator.

Reagents

The simulants were purchased from the indicated vendors and were used as received: chloroethylethyl sulfide (CES), diisopropylfluorophosphate (DIFP), triethyl phosphate (TEP), and diethylaminoethanethiol hydrochloride (DEAT·HCl) all were from Aldrich (Milwaukee, WI, USA), and the dimethylmethyl phosphonate (DMMP) and diisopropylmethyl phosphonate (DIMP) were from Alfa (Danvers, MA, USA). The free base of DEAT was prepared by dissolving DEAT·HCl in water at pH 11, extracting with diethyl ether, and evaporating the solvent. Solvents were Burdick & Jackson distilled in glass grade from American Scientific Labs. (Atlanta, GA, USA). The SFC-grade carbon dioxide and methanol–carbon dioxide (5:95) were obtained from Scott Specialty Gases (Plumsteadville, PA, USA).

Caution: The DIFP simulant is highly toxic and is an acetylcholinesterase inhibitor. The CES can cause burns.

SFE

The SFE procedure consisted of weighing *ca.* 1 g of Rocky Mountain Arsenal Standard Soil into an extraction cell, and injecting a known volume of simulant spiking solution into the soil *ca.* 2 cm from the inlet end, assembling the cell and letting the sample set for 15 min at room temperature. The cell was installed in the apparatus and allowed to warm up to operating temperature. The inlet valve was opened to admit supercritical fluid to the cell, and the outlet valve was then opened to begin the collection of the extract. In early work, the fused-silica restrictor tubing was dipped into a vial containing 3 ml of methanol and TEP internal standard, while later, the volume of methanol was 2 ml and the TEP was added after the SFE was completed. The extractions were conducted at 60°C and 300 atm (unless otherwise listed). The vial containing the collecting solution was placed in a beaker of water at room temperature to prevent ice formation when extractions were carried out longer than 5 min.

RESULTS AND DISCUSSION

This study used simulants which have structural features similar to the actual agents but which lack the very high toxicity of the latter. DMMP was the simulant for agent VX, DIFP and DIMP modelled agent GB, and CES was used in place of HD. In addition, DEAT·HCl, a byproduct from VX manufacture, also was tested. All of the simulants can be separated and determined in a single GC run, as shown by the bottom chromatogram in Fig. 1. Low ppm solution concentrations can be determined using the flame ionization detector, and sub-ppm concentrations with the combination of flame photometric (P-mode) and electron-capture detectors.

It was found that pressures around 300 atm are needed to extract low-ppm concentrations of agent simulants from 1-g samples of soil. As shown in Table I, straight supercritical carbon dioxide at 60°C and 300 atm can easily extract the CES from soil in 5 min, but it is not able to efficiently extract the phosphonates and fluorophosphate even at higher extraction pressures or longer extraction times. Experiments in which supercritical carbon dioxide was bubbled through methanol spiked with the simulants showed that the latter were not volatilized from the collection solution by the decompressing supercritical fluid. DIMP has been recovered from water [8] in unknown yield using supercritical carbon dioxide. For soil, a 5% methanol

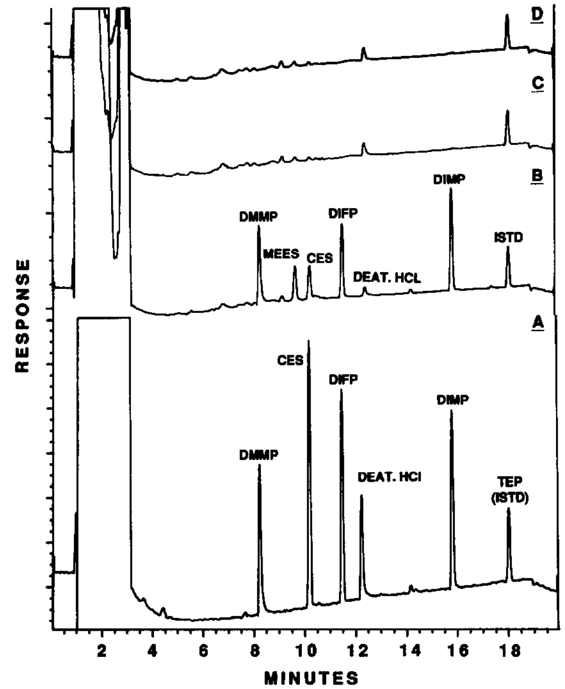

Fig. 1. Gas chromatographic analysis (flame ionization detection) of (A) simulant standard and (B) first 10 min SFE of spiked soil, (C) second 10 min SFE of soil, and (D) third 10 min SFE of soil. (Acronyms are defined in the Experimental section, and SFE conditions are listed in footnote *b* of Table II).

modifier is necessary in the carbon dioxide to recover all the simulants, and at 300 atm and 60°C, good recoveries are achieved in a 5 min SFE. Even low-polarity compounds such as five-ring polycyclic aromatic hydrocarbons and tetrachlorodibenzodioxin require methanol modifiers in their SFE from sorptive matrices [3,4,7].

The SFE recoveries are slightly higher but less reproducible than those achieved using a single ultrasonic solvent extraction (5 min) with methanol. The latter is probably better controlled at this stage of technology development, and non-uniformity of SFE flow may contribute [2] to the variability of the former. These SFE recoveries of simulants also are much higher but less precise than those reported [9] for sequential ultrasonic extractions with hexane and methylene chloride of triethylphosphate and agents GB, HD and GD (soman) spiked at 5 to 50 ppm in soil.

As shown in Fig. 1, a single SFE is sufficient for the simulants. In contrast, the agent manufacturing byproduct DEAT·HCl was recovered in low and irreproducible yield (typically 10% per extract fraction). This may be due to a low solubility of the compound in the supercritical fluid and/or strong sorption of the compound by the soil. Reaction of the amine with carbon dioxide to form a urea derivative also is possible [8], but is not consistent with the observed extraction behavior. Fig. 1 shows that while the simulants are extracted in the first 10 min fraction, DEAT·HCl continues to slowly extract in subsequent fractions. The free amine did not extract at all, suggesting that sorptive interactions with acidic sites on the soil may be the limiting factor. Nitrous oxide has been used successfully [8] to extract basic amines from soil, and may be useful

TABLE I

SFE RECOVERIES OF CHEMICAL WARFARE AGENT SIMULANTS FROM ROCKY MOUNTAIN ARSENAL SOIL

Fluid	Extraction[a]		Spike (ppm)	Replicates	Recovery (%), average ± S.D.			
	Pressure (atm)	Time (min)			DMMP	CES	DIFP	DIMP
CO_2	300	5	2	2	12	95	17	43
CO_2	300	12	2	1	9	90	ND[c]	15
CO_2	350	12	2	1	4	93	59	7
CO_2–CH_3OH	300	5	2	3	79 ± 23	93 ± 14	92 ± 13	98 ± 25
CO_2–CH_3OH	300	5	12	3	73 ± 9	ND	86 ± 10	95 ± 17
CH_3OH[b]	–	5	2	3	80 ± 3.5	85 ± 15	63 ± 4.2	87 ± 6.1

[a] SFE at 60°C using 25 μm I.D. restrictor and conditions shown. A 1-g amount of soil was extracted, and supercritical fluid was decompressed in 2 ml of methanol. Analysis by GC–flame photometric detection/electron-capture detection.

[b] Ultrasonic extraction of 1 g spiked soil with 2 ml of methanol for 5 min.

[c] ND = Not determined.

here. The DEAT·HCl also was not recovered (3%) from ultrasonic extraction using methanol.

In early SFE development work two GC peaks were recovered for the CES, as shown in Fig. 1B. Relative retention data [10] would suggest 1,4-dithiolane as a candidate for the earlier-eluting peak, and this product has been identified [11] as a degradation product of pure CES. GC–mass spectrometry suggested that the new, earlier-eluting peak shown in Fig. 1 is a methyl ether derivative, possibly methoxyethylethylsulfide (MEES). Major *m/z* observed in the mass spectrum of the new peak were 120 (apparent M), 75, 58 and 45, *versus* 120 (M), 92, 61 and 46 in the spectrum for 1,4-dithiolane. The first step in the decomposition of CES has been postulated [11] as the formation of a reactive ethylene sulfonium ion via an S_N1 mechanism. MEES presumably could be formed by a nucleophilic attack on the ion by methanol (solvent for standards). The new product was observed in methylene chloride solvent extractions of the soil, but not when carbon dioxide–methanol was bubbled through a spiked solution of simulants in methanol (see Table II). It was not observed in the work reported in Table I where fresh spiking solutions were used. The controlling factors in its production have not yet been identified, but could include a catalytic effect from soil surfaces.

In earlier work with 25 μm I.D. fused-silica restrictor tubing, problems were encountered with tubing breakage at the point where the tubing dipped into the methanol collection solution. This was thought to result from ice crystal formation in the tubing. A small, *ca.* 10-mg layer of calcium chloride or sodium sulfate was placed in the downstream end of the extraction cell to trap water extracted from the soil. Tubing breakage was not solved, and, as listed in Table II, the recoveries of the phosphonates were reduced. However, the CES recovery was improved. With sodium sulfate, the production of the MEES also was increased such that the sum of the MEES and CES recoveries accounted for the CES spike. Sheathing the last 10 cm of the 25 μm I.D. tubing with 325 μm I.D. fused-silica tubing minimizes breakage. However, breakage has not been as much of a problem with the larger-bore 60 μm I.D. fused-silica tubing, and extraction recoveries appear to be equivalent.

Extraction of soil masses larger than 1 g is feasible. Experiments with 10 g masses of soil spiked at 2 ppm each simulant and extracted in the ISCO apparatus for 20 min yielded good recoveries: DMMP 70%, CES 81%, DIFP 103% and DIMP 110%. None of the simulants were detected in second and third 20-min SFE fractions. The lower recoveries of DMMP and CES could have resulted from purging out of the collecting solution with the greater flowrate of the 50 μm I.D. restrictor. Purging from the

TABLE II

EFFECTS OF RESTRICTOR AND DRYING AGENTS ON SFE OF SIMULANTS

Variable[b]	Replicates	Recovery[a] (%) average ± S.D.				
		DMMP	MEES[c]	CES	DIFP	DIMP
25 μm I.D. restrictor	3	96 ± 3.2	24 ± 11	28 ± 11	71 ± 19	97 ± 11
60 μm I.D. restrictor	1	103	29	27	75	93
$CaCl_2$[d]	2	5	27	40	94	14
Na_2SO_4[d]	1	51	40	60	101	57
Spiked CH_3OH[e]	1	98	0	96	92	103

[a] Recoveries from spiked Rocky Mountain Arsenal Standard Soil: DMMP = 32 ppm, CES = 10.6 ppm, DIFP = 10.7, DIMP = 16.2 ppm. Analysis by GC–flame ionization detection.

[b] SFE conditions: methanol–CO_2 (5:95) at 300 atm, 60°C, 10 min extraction of 1 g soil spiked as noted in footnote (*a*), and supercritical fluid decompressed in 3 ml of methanol.

[c] Methoxyethylethylsulfide recovery from spiked CES.

[d] 25 μm I.D. restrictor used, *ca.* 10 mg of drying agent packed in bottom of SFE cell.

[e] Supercritical CO_2–methanol bubbled through 3 ml of methanol spiked with simulants at concentrations equivalent to 100% recovery from soil.

collection solution was not tested with the larger bore restrictor tubing, but the flow-rate was obviously much greater than the *ca.* 200 ml/min gas flow-rate with the 25 μm restrictor. It is quite likely that detection limits may be lowered by an order of magnitude using the larger mass of soil.

CONCLUSIONS

The results of experiments with simulants suggest that SFE holds considerable promise for providing a rapid and efficient means of recovering chemical warfare agents from soil with less laboratory waste than current methods.

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