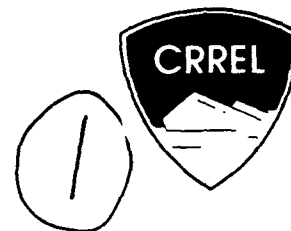AD-A282 338

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Evaluation of the Use of Supercritical Fluids for the Extraction of Explosives and Their Degradation Products from Soil

Philip G. Thorne
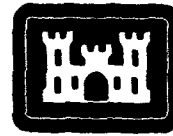
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Abstract

The use of supercritical fluids to extract explosives and degradation products from soil was compared to SW846 Method 8330, which uses a sonic bath with acetonitrile as a solvent. Pure CO_2 and CO_2 with additional organic solvents were tried under various conditions of time, temperature and pressure. No conditions were found that extracted all of the analytes tested—TNT, TNB, RDX and HMX—with efficiency equal to the standard method. Since the time and solvent usage was greater using supercritical fluids than with solvent extraction, these fluids cannot be recommended as an alternative to acetonitrile.

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US Army Corps of Engineers
Cold Regions Research &
Engineering Laboratory

Evaluation of the Use of Supercritical Fluids for the Extraction of Explosives and Their Degradation Products from Soil

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PREFACE

CONTENTS

ILLUSTRATIONS

TABLES

Evaluation of the Use of Supercritical Fluids for the Extraction of Explosives and Their Degradation Products from Soil

PHILIP G. THORNE

INTRODUCTION AND OBJECTIVE

The U. S. military is faced with the serious challenge of identifying and remediating sites that have been contaminated with explosive compounds, manufacturing by-products and degradation products. Since early in this century, explosives have been deposited in the environment as wastewater from manufacturing and load-and-pack operations and as residues from burning or detonation of off-specification and out-of-date munitions. The facilities where these operations have occurred or continue to occur include arsenals, depots, ordnance disposal areas and artillery and bombing ranges. Within these installations, field screening methods (Jenkins and Walsh 1992, Myers et al., in press) can be used to delineate the boundaries of contaminated areas. Once an area is found to be contaminated, it is vital to identify and quantitate all possible compounds.

The accepted analytical method for explosives, SW846 Method 8330, requires that the analytes be extracted from solid matrices by 18-hour sonication with acetonitrile (ACN) and analyzed by liquid chromatography. These extraction conditions have been proven to be efficient, precise and robust (Jenkins and Grant 1987, Jenkins 1989, Walsh et al. 1993). However, the time and organic solvent requirements are a disadvantage. The objective of this study was to compare the extraction efficiency, specificity, method reproducibility and time and solvent requirements of supercritical fluid extraction (SFE) with 18-hour sonic extraction with ACN.

SUPERCRITICAL FLUID EXTRACTION

The term "supercritical fluid" is used to describe a state of a substance that lies above a critical temperature and pressure. Figure 1 is a phase diagram for CO_2. At the gas/liquid interface, increasing temperature reduces fluid density via thermal expansion, while increasing pressure increases gas density via compression. At the "critical point" of 31°C and 73 atmospheres (atm), the liquid and gas densities converge and the resulting phase shares the attributes of both a liquid and a gas. Thus, the supercritical fluid can be dense enough to solvate organic analytes while having a high diffusivity that promotes rapid mass transport (Clifford 1993). Since solvation and transport are the necessary conditions for extraction, it follows that supercritical CO_2 would be a potential solvent. The fact that CO_2 is cheap and nontoxic is a major advantage.

The basic equipment required to conduct SFE is diagrammed in Figure 2. Liquid CO_2 is pumped from a cylinder into a heated chamber containing a sample. Supercritical temperature is maintained by the heater, while supercritical pressure is maintained by hydraulic back-pressure from an extremely small outlet called a restrictor. When the supercritical fluid and solvated analytes exit the restrictor, the CO_2 decompresses to a gas and deposits the analytes in the collection vessel, undiluted by extraction solvent. This easy elimination of solvent is another theoretical advantage of SFE compared to conventional solvent extraction.
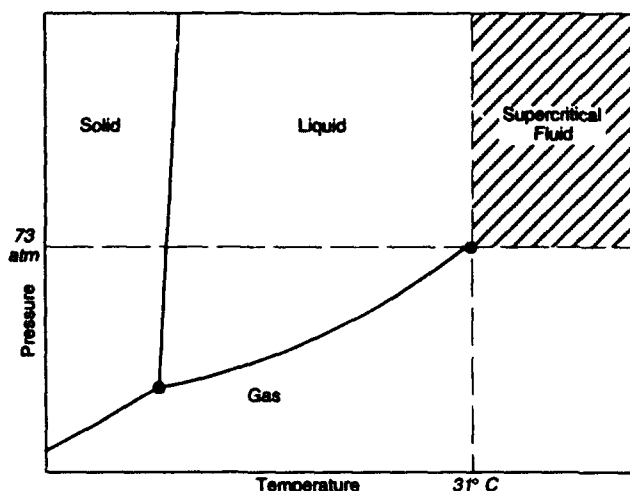
Figure 1. Phase diagram of CO_2.
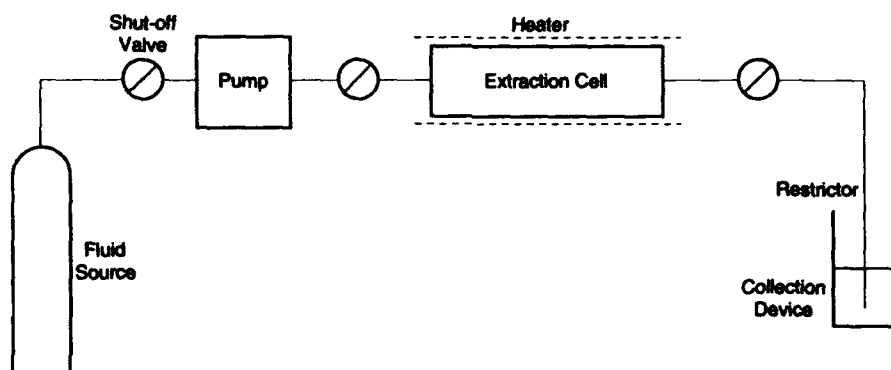
Figure 2. Design for a basic SFE apparatus. (After Hawthorne 1993.)

The advantages of extraction efficiency, speed, low solvent usage and highly concentrated analytes are being realized only for a few classes of compounds despite substantial research efforts. The U.S. Environmental Protection Agency has issued a Draft Method 3560, which uses SFE for total petroleum hydrocarbons. Other nonpolar organics such as polycyclic biphenyls and polychlorinated aromatic hydrocarbons have been successfully extracted from some matrices (Langenfeld et al. 1993); however, the procedures are not yet routine enough to be considered reliable. A recent survey (Stevenson 1993) has indicated that the low numbers of successful SFE applications and lack of regulatory approval for this technique may drive some manufacturers out of the field.

SFE OF EXPLOSIVES

To be successful, SFE must not only solvate and transport analytes but also disrupt any interactions between analytes and matrix that are stronger than the solvation energy. These three condi-

tions are each specific to both the analytes of interest and the matrix in which they are found.

The major munitions-related contaminants found in the soils at U.S. military facilities are TNT (2,4,6-trinitrotoluene), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and TNB (1,3,5-trinitrobenzene), the photodegradation product of TNT (Walsh et al. 1993). TNT and TNB are moderately polar nitroaromatics. RDX and HMX are highly polar nitramines.

The sorption mechanisms that bind explosives to soil particles are complex. Leggett (1985) studied the sorption of nitroaromatics and nitramines on clays and reported two types of binding. Nitramines appear to be nonspecifically and weakly bound by hydrophobic interaction with the bulk particles. Nitroaromatics also exhibit this weak bond, plus stronger hydrogen bonding and electrostatic interaction with specific sites on edges and plates of the clay matrix. These varying regimes of sorption help explain the environmental transport of RDX as compared to TNT. Although the aque-

2

ous solubility of RDX is less than that of TNT (42 mg/L vs. 130 mg/L), it has been found to migrate faster and farther as a solute in groundwater (Walsh et al. 1993).

There is a two-fold interaction of explosives with the organic matrix that surrounds the mineral core of soils. For nitroaromatics, the extent of binding is highly variable and depends on the chemical composition of the organic fraction (Leggett 1991). Even without strong binding, the organic layer presents a diffusional barrier. Pawliszyn (1993) theorized that desorption rates from soils are additive. First the solvent must penetrate to binding sites, then transport analytes through the organic layer before reaching any bulk extraction fluid. Englehardt et al. (1991) found that the efficiency of SFE of explosives from soil was inversely related to soil organic content. This reduction could be caused by binding of explosives to soil organics or to reduced diffusion of supercritical fluid in and out of the matrix—or both.

SFE INSTRUMENTATION

Attempts by manufacturers to build routinely usable SFE instruments have resulted in a wide variety of hardware. The sample throughput capacity of these systems is largely determined by

pump and sample-cell design, while the flow restrictor and trapping system has the biggest effect on analyte recovery. A recent review (Lopez-Avila et al. 1992) compares and contrasts four of these instruments.

The primary selection criterion for an instrument to be used in this laboratory was sample throughput. The Dionex 703 was chosen because it has a reciprocating pump that delivers fluid continuously to eight cells simultaneously. This system is diagrammed in Figure 3.

The restrictor on the 703 is constructed of a fused silica capillary, encased in steel. This unit has a separate heating block. Heating the restrictor slightly above the extraction cell temperature reduces the risk of capillary blockage due to condensation of volatile analytes or crystallization of saturated solutions of soluble analytes. Ideally, supercritical conditions are maintained throughout the length of the capillary. At the restrictor exit, the CO_2 rapidly decompresses, resulting in adiabatic cooling that will freeze any water that was extracted from the sample. Thus, heating must be effective all the way to the restrictor tip.

Trapping the analytes from the decompressed supercritical fluid presents another challenge for manufacturers. The Dionex bubbles CO_2 and analytes through solvent that is chilled to 1°C. The
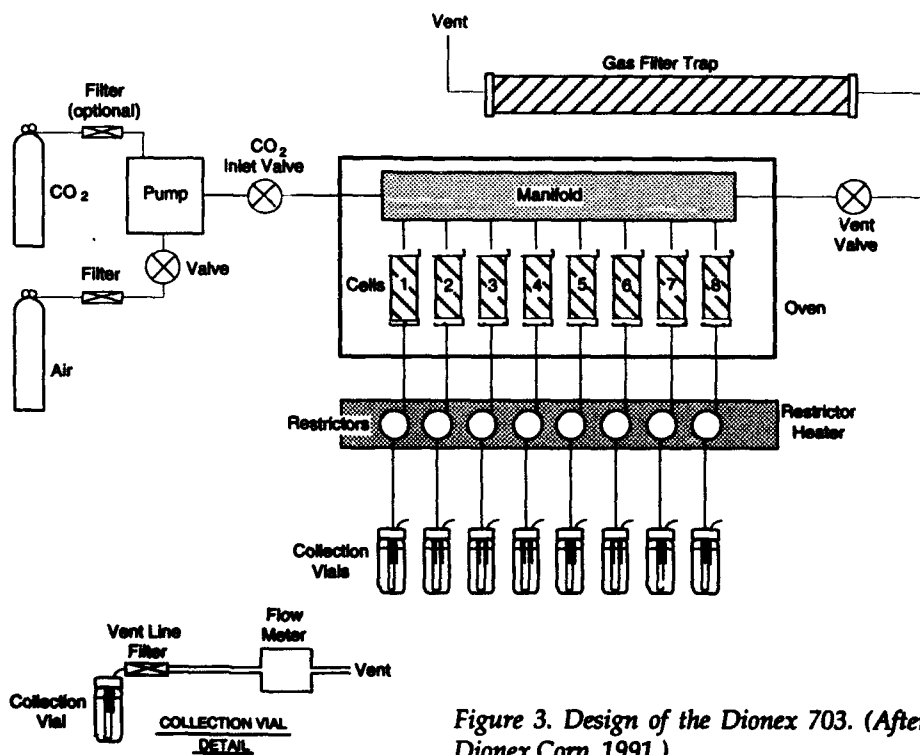

Figure 3. Design of the Dionex 703. (After Dionex Corp. 1991.)

3

heated restrictor is separated from the cold solvent by a glass tube within the collection vial. Although Dionex reports good recoveries from this restrictor-trap configuration (Porter et al. 1992), the design also includes a 0.45-μm filter in the vent line to prevent analytes that have "blown-by" the trap from being deposited in the vent lines and flow meters.

METHODS

Extractions were carried out using SFC-grade CO_2 or mixtures of CO_2 and organic solvent from Scott Specialty Gases. The capacity of the extraction cell, temperatures of cell and restrictor, pressure and extraction time were varied. Some experiments were run with various solvents added ("doped") to the sample before extraction. Various types and quantities of trapping solvent were tested in the collection vials.

Blank soils and analytes used for spikes were Standard Analytical Reference Materials from the U.S. Army Environmental Center. TNT, TNB, RDX and HMX were dissolved in acetonitrile and applied to dry soil. Extractions were run after solvent evaporation was complete. A field-contaminated soil from an ordnance burning ground at the Iowa Army Ammunition Plant in Middletown, Iowa, was used to test the results of the initial spike recovery tests. The explosives content of this soil has been well documented (Jenkins and Grant 1986, Jenkins and Walsh 1987).

Residual analytes remaining after SFE were extracted as described in Method 8330. One or two grams of sample were extracted into 10 mL of acetonitrile for 18 hours in a 20°C sonic bath. The samples were removed from the bath and allowed to settle. Aqueous calcium chloride (10 mL at 5 g/L) was added to the extract to flocculate suspended soil particles and the mixture allowed to settle. This was then filtered through a 0.5-μm Millex SR filter and stored at 4°C in the dark until analyzed.

Analyses of supercritical fluid extracts and residual acetonitrile extracts were performed as described in Method 8330. A 100-μL aliquot of extract/aqueous calcium chloride (50/50) was applied to a 25-cm × 4.6-cm (5-μm) LC–18 (Supelco) HPLC column. The analytes were eluted using 1.5 mL/min 1:1 (v/v) methanol/water and detected at 254 nm.

All solvents used for extraction, collection and elution were HPLC-grade from Alltech. Reagent-grade water was prepared using a Milli-Q Type 1 Reagent-Grade Water System (Millipore). Calcium chloride was Baker reagent-grade.

RESULTS

All of the initial experiments were done as time-course studies to determine the minimum possible extraction time. Extractions were interrupted every 15 or 30 minutes, and new collection vials were put in place. Most analytes were recovered in the first 30 minutes. However, for the most intractable analytes (HMX and RDX) runs up to 60 minutes seemed necessary. There was no detrimental effect on analytes already collected in vials, so the remaining trials were run for 60 minutes.

The first experiments were performed with pure CO_2 and spiked soils, using acetonitrile as a trapping solvent. Since the samples were only a few grams, extraction cells with 3-mL capacities and pressure ratings of 340 atm were used. CO_2 densities of 0.55–0.99 g/mL were achieved at temperatures from 25 to 150°C. Following SFE the samples were sonicated for 18 hours with ACN to remove residual analytes. This allowed a determination of extraction efficiency even if trapping efficiency was low. The results are summarized in Table 1.

Nitroaromatic recoveries were often low and vent filters became discolored. Flushing the filters with solvent removed considerable quantities of analytes, mostly TNT and TNB. Tests indicated that collection vials needed to contain 15 mL of solvent to minimize this problem. Even with this precaution it was necessary to flush the filters with collection solvent after each run to recover analyte "blowby." Various trapping solvents were tried, with methanol giving the best results.

Extraction efficiencies with pure CO_2 were so low that polar modifiers were tried. It was convenient for initial experiments to simply add liquid modifier ("doping") to the extraction cell before applying supercritical conditions. In this case, most of the modifier was rapidly removed by the CO_2, but the results were indicative. Based on these early tests, mixtures of CO_2 and appropriate solvents were purchased premixed and compressed

Table 1. Analyte recoveries using unmodified CO_2.

CO_2 density	Pressure	Oven temp (°C)	Extraction efficiency*			
			HMX	RDX	TNB	TNT
0.48	200	100	16	26	50	92
0.55	200	75	14	18	25	40
0.63	200	50	20	17	29	83
0.79	340	150	10	73	62	97
0.99	340	25	9	6	19	41

* Extraction efficiency = [(μg spike – μg sonic residual)/μg spike] × 100

4

Table 2. Analyte recoveries using polar modifiers.

Modifier	Pressure	Oven temp (°C)	% recovery* HMX	RDX	TNB	TNT
5% acetone	200	75	0	15	70	100
dACN	200	75	57	74	95	99
dACN	200	100	52	71	93	97
dACN	200	50	41	52	83	92
10% acetone	200	50	0	15	100	98
10% ACEdACN†	200	50	25	44	98	98
10% acetone	200	75	0	12	99	99
10% ACEdACN	200	75	27	59	100	100
5% ACN	500	50	91**	91**	92**	94**
5% ACN	600	31	100**	99**	96**	95**

* % recovery =[(µg SFE/(µg SFE + µg sonic residual)] × 100.
† d = doped; ACE = acetone.
** Sonic residuals were not determined [% recovery = (µg SFE/µg spike) × 100].

in cylinders. Acetone and acetonitrile were tried since these are effective solvents in traditional extractions of explosives residues (Jenkins and Grant 1987, Jenkins 1989). Various temperatures and pressures were tried. Generally recoveries were higher than with pure CO_2. However, with increasing material removed from the matrix, restrictor plugging became a major problem. It was also observed that analytes could be deposited in restrictors without plugging them entirely, thus presenting a potential for cross-contamination between extractions. Attention needed to be directed to the flow meters that monitor each cell during a run. Restrictors with reduced flow could then be removed and cleaned by solvent flushing.

Indications were that good recoveries might be possible for most of the analytes. Larger (10-mL) cells with 640-atm pressure ratings were used for the remainder of the trials. The manufacturer recommends filling any vacant cell volume with an inert packing to optimize the fluid flow. Cross et al. (1993) reported reduced recoveries when small samples were packed into large cells due to analyte loss onto the supposedly inert filler. This was not a problem in our studies using a locally acquired sand. The best recoveries from spiked soils were obtained by using 5% ACN-modified CO_2 at high pressures. The results are summarized in Table 2.

It is generally recognized that spiked soils do not bind analytes with the same strength as field-contaminated soils (Chiou and Shoup 1985, Burford et al. 1993), resulting in different extraction kinetics (Jenkins and Grant 1987). It was decided to take the best conditions developed for spikes and apply them to soil from a military burning ground. The soil was extracted sequentially for 30 minutes at increasing pressures, with temperature held constant. It was hoped that this gradient of conditions (an option with some commercial instruments) would extract the most labile compounds under gentle conditions and thus remove them from the more extreme conditions required by the most polar analytes. A further benefit would be the gradual removal of analytes from heavily contaminated soils, thus reducing the risk of restrictor plugging. These results are summarized in Table 3. The extraction conditions of 5% ACN-modified CO_2 at 600 atm with a 120°C oven and 125°C restrictor for 60 minutes, collected in 15 mL of methanol, quantitatively recovered TNT, TNB and RDX. Recovery of HMX was only 32%.

A series of replicate extractions was done to test the chosen conditions during routine operations.

Table 3. Results of pressure gradient experiments.

Pressure	Temp (°C)	Cumulative % recovery* HMX	RDX	TNB	TNT
200	40	4	3	28	33
300	40	8	9	56	39
400	40	52	75	88	94
500	40	58	82	92	96
600	40	62	87	94	96
200	80	5	40	49	95
300	80	9	58	83	98
400	80	12	70	96	99
500	80	15	87	98	99
600	80	18	94	99	100
200	120	13	31	56	99
300	120	19	45	92	99
400	120	23	69	97	99
500	120	27	89	98	100
600	120	32	99	99	100

* Cumulative % recovery = [(µg SFE/(µg SFE + µg residual)] × 100.

5

Table 4. Accuracy and precision of SFE compared to sonic extraction.

| | Amount extracted [(μg extracted)/g soil] | | | |
	HMX	RDX	TNB	TNT
5% ACN				
avg	19.70	54.17	71.85	770.63
sd (n = 8)	12.70	13.17	13.92	86.12
RSD (%)	64.45	24.32	19.37	11.18
5% ACN + doped ACN				
avg	14.60	52.92	83.64	690.00
sd (n = 6)	4.82	7.52	1.99	10.43
RSD (%)	33.00	14.21	2.38	1.51
Sonic alone				
avg	62.75	74.17	74.07	718.53
sd (n = 15)	24.21	21.24	10.70	70.24
RSD (%)	38.58	28.64	14.45	9.78

One series of samples also had 0.5 mL of ACN added to the cell before extracting with the 5% ACN-modified CO_2. This was one more attempt to increase the recovery of HMX and to see how this addition might affect the precision of the recoveries. The results are summarized in Table 4. The accuracy and precision of TNT and TNB recoveries were good compared to sonic extraction. The accuracy of the nitramine recoveries was poor, although the precision was reasonable considering the reported heterogeneity of this field-contaminated soil (Jenkins and Grant 1987). The addition of ACN to the extraction cell did improve the precision of recoveries compared to "undoped" 5% ACN or sonic extraction.

Finally, a short experiment was performed to test the effectiveness of water as an additional modifier. These tests were run on the same Iowa soil, with 5% ACN-modified CO_2 at 31°C and 600 atm with 0.5 mL water added to half the cells before extraction. The results are summarized in Table 5. Except for HMX, recoveries were excellent even at this low temperature; however, half of the water-doped cells became plugged. The soil had become densely packed against the outlet.

Table 5. Analyte recoveries using water as a modifier.

| | % recovery* | | | |
	HMX	RDX	TNB	TNT
Without water	2	13	32	90
	2	11	14	72
With water	31	99	99	100
	26	99	99	100

* % recovery = [(μg SFE/(μg SFE + μg residual)] × 100.

DISCUSSION

Desorption and solvation

Our results using pure CO_2 to extract explosives from soil are similar to those of Englehardt et al. (1991). Recoveries of all analytes were poor, with HMX and RDX being the worst. This result is predicted from the relation between elution behavior in C-18 liquid chromatography and SFE extraction efficiency (Englehardt et al. 1991, Clifford 1993, Englehardt and Haas 1993). The shorter the retention (or the lower the organic content of eluent required), the higher the supercritical fluid density required for extraction. In the case of the least retained explosives (HMX and RDX) the predicted density of CO_2 is over 1.0. Although our tests were ultimately run at 340 atm and 25°C, the resulting density of 0.99 was inadequate for quantitative extraction of any of the analytes.

Pure CO_2 is actually nonpolar as a supercritical fluid, although its large dipole produces some weak attraction for polar solutes (Clifford 1993). Adding polar solvent to the supercritical CO_2 is a possible solution to this problem (Bicking et al. 1993, Oosstdyk et al. 1993a, Pawliszyn 1993). Although the modifier actually reduces the already low solvating power of the CO_2 by reducing its density (Clifford 1993, Cross et al. 1993), the net effect of modifier addition should be increased recovery. These increases were easily realized for the nitroaromatics TNT and TNB, but the recoveries of the nitramines RDX and HMX were still low.

The moderate conditions used to extract nearly all the RDX using 20% (w/w) doped water indicate that the ideal extraction conditions may require very large polar solvent additions. Janicot et al. (1990) used 20% methanol for extractions.

As the modifier concentration increases, the extraction fluid may become near-critical (Clifford 1993). In this state the modifier exits as molecular clusters, driven deep into and out of the matrix by the mixture of gas and vapor. In effect, the CO_2 is used to dilute the solvent. Unfortunately the additional solvent may extract huge quantities of biological macromolecules such as proteins and humic substances, increasing the frequency of restrictor plugging and complicating the analysis of extracts (Cross et al. 1993, Snyder et al. 1993). In the case of HPLC-UV analyses as required by Method 8330, the plethora of highly uv-absorptive, poorly resolved compounds will likely interfere with the detection of explosives.

Englehardt and Haas (1993) suggested a presoak in organic modifier followed by evaporation before supercritical extraction. Apparently the

6

modifier moves analytes from deep within the matrix and deposits them on the surface of the soil particle, where the supercritical fluid need only solvate and flush them into the recovery vessel.

Both near-critical extraction and the solvent presoak method could be considered as hybrid solutions to the solubility limitations associated with the nitramines. The time required for these extractions would have to be very favorable to outweigh the increased use of solvent.

Further experiments could be done with water as the modifier. It appears that this would have to be added to the extraction gas, since the doped trials still did not recover all the HMX. Since water is present in variable amounts in different soils, the sensitivity of recovery to various percentages of added water would have to be carefully determined to avoid the reductions in recovery seen by Snyder et al. (1993). In that report, recoveries of polar pesticides were greatest at 5–10% moisture, while dropping considerably at 0% and 25%. Turning the cells around so that the wet soil is ahead of the packing sand might alleviate the cell plugging.

A different approach to the extraction of polar analytes uses gases that become more polar solvents as supercritical fluids compared to CO_2. Nitrous oxide becomes a more polar supercritical fluid and has been used to increase the recovery of polar analytes compared to CO_2 (Ashraf-Khorassani and Zimmerman 1990, Oostdyk et al. 1993a,b). However, it is a highly reactive gas requiring stringent safety precautions. A recent explosion in one lab during the exaction of coffee (Raynie 1993) makes one wonder about the safety of exposing soils that can have percent levels of explosives to this fluid. Freon-22 has been used successfully (Hawthorne et al. 1992, Paschke et al. 1992) but is environmentally undesirable.

The results here are valid for one sandy soil (of relatively low organic content) from a burning ground. It is to be expected that soils with higher organic or clay content or those contaminated by aqueous solutions would have different binding characteristics. As Burford et al. (1993) pointed out, those analytes that remain in the soil after years of weathering are apt to be the ones most tightly bound and resistant to desorption by polar fluids. The sorption data of Leggett (1985) and the environmental transport evidence from Walsh et al. (1993) suggest that the low recovery of nitramines, particularly HMX, may be attributed more to poor solubility and mass transport than to desorption limitations. It could be speculated that the high affinity of nitroaromatics for soil binding

sites causes their deposition close to the surface of particles, where they are easily recovered by the polar supercritical fluid. In contrast, the less tightly bound nitramines may be carried deep within the mineral core, causing the path length of diffusion to be much greater than that for the nitroaromatics. Furthermore, the solvent modifier may partition into the organic component of soils (Deye et al. 1990, Englehardt and Haas 1993). This removal of modifier from the bulk extraction fluid would have a detrimental effect on both solvation and mass transport of analytes. Without prior knowledge of the organic content of each soil sample, it might be necessary to rely on excess modifier to maintain solvent strength in the supercritical fluid. Thus, methods that are optimized for one matrix type and condition may not work for other samples. The existence of local optima in the most rigorous of experimental work indicates the general sensitivity of SFE, not only to predictable parameters such as temperature, time and pressure but also to matrix effects (Bicking et al. 1993).

Instrumentation and analyte trapping

An important aspect of this comparison was the time requirements for SFE compared to sonic extraction. Although the extraction took only one hour, loading the cells, preparing the collection vials and waiting for the oven to reach temperature took another hour. Time is also required for the oven to cool somewhat between runs before new cells can be installed. If the runs could be done at 31°C, as the water-modifier tests indicate, the time could be cut in half.

Most frustrating is that regardless of the precautions taken to ensure clean sealing surfaces and clean restrictors, leaks and plugs were routine. In the two years that this unit was operated in this lab, it was rare that all eight cells could be completely extracted without incident.

If a leak occurs and the pumps are stopped, all the cells must be reloaded. This unfortunate circumstance was discovered as a result of the time-course experiments. On the Dionex 703 there is no provision for a static extraction where supercritical fluid is held in the cell by valves at either end. Thus, to change trapping vials one must either let extraction fluid escape during the change or stop the pump and allow the fluid to decompress out the inlet vent. The latter technique was chosen for our tests since the manufacturer claimed no loss of analytes during decompression (Dionex Corp. 1991). However, these tests were done with pure CO_2 and low-volatility analytes. The total recover-

ies of TNB and TNT in our "interrupted" experiments were often very low. When the pressure is released during a pump-stop-vent operation, conditions fall through the critical point of the modified fluid. Under these conditions the analytes could exist as solvent–solute clusters entrained in the bulk flow (Deye et al. 1990). These clusters might well blow out of the inlet along with the decompressed CO_2. Restrictor plugging seems to be an insurmountable and unpredictable occurrence. Replicate samples run through all new restrictors would not guarantee 100% success. Adapting cheaper, disposable restrictors might at least reduce the expense and time involved in discarding or cleaning the Dionex capillaries.

The recoveries of TNT and TNB from certain samples was often very low. These are the analytes most often recovered from vent filters, indicating their susceptibility to loss from the trapping vials under normal conditions. It was observed that occasionally the septa seem to tear around the outlet and vent needles. This would certainly result in leaks of these analytes. Reasonable recoveries of RDX and HMX from these same samples support this hypothesis.

Alternatively, solid sorbents cooled to cryogenic temperatures and washed with a few milliliters of solvent could be used (Ashraf-Khorassani et al. 1992, Lopez-Avila et al. 1992, Furton and Lin 1993). These kinds of traps might reduce initial trapping losses, while introducing potential sorbent losses. Such modifications would require the "in-house" construction of some hardware.

Although the modified CO_2 costs twice as much as pure CO_2, the expensive restrictors lasted longer with the modified gas than when pure CO_2 and ACN was added to cells. It was determined that 5% ACN-modified CO_2 was the most cost-effective solution. However, Schweighardt and Mathias (1993) reported that modifier delivery from premixed cylinders is not consistent. A cosolvent addition module is available for the Dionex 703.

CONCLUSIONS

The results from this program have shown that SFE is not a practical method for the routine extraction of explosives from soils. Neither the time nor solvent usage is reduced from the standard method. In fact, they are both increased with a concomitant reduction in analyte extraction efficiency. The trapping vials require 15 mL of solvent compared with 10 mL for the Method 8330 sonic extraction. The best estimate of sample throughput is eight samples per day, run as duplicates. Twenty samples a day with duplicates is routine for the Method 8330 extraction.* The price of the equipment, expendable supplies and high-purity gas with custom-mixed modifiers or co-solvent option is many times higher than the vortex mixers, reagent-grade solvents, small vials and temperature-controlled sonic bath required for Method 8330. SFE may be an excellent alternative to Soxhlet extraction when that is the only available alternative. When the alternative is sonic extraction in small solvent volumes with generally complete recovery of all analytes, there appears little benefit for SFE.

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The use of supercritical fluids to extract explosives and degradation products from soil was compared to SW846 Method 8330, which uses a sonic bath with acetonitrile as a solvent. Pure CO_2 and CO_2 with additional organic solvents were tried under various conditions of time, temperature and pressure. No conditions were found that extracted all of the analytes tested—TNT, TNB, RDX and HMX—with efficiency equal to the standard method. Since the time and solvent usage was greater using supercritical fluids than with solvent extraction, these fluids cannot be recommended as an alternative to acetonitrile.

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Degradation products	Nitramines	Supercritical fluid extraction
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