SPECIAL REPORT 95-22

Evaluation of Clean Solid Phases for Extraction of Nitroaromatics and Nitramines from Water

Thomas F. Jenkins, Philip G. Thorne, Karen F. Myers,
Erika F. McCormick, Don E. Parker and B. Lynn Escalon

September 1995

Abstract

Salting-out solvent extraction (SOE) was compared with cartridge and membrane solid-phase extraction (SPE) for preconcentration of nitroaromatics, nitramines, and aminonitroaromatics prior to determination by reversed-phase high-performance liquid chromatography. The solid phases used were manufacturer-cleaned materials: Porapak RDX for the cartridge method and Empore SDB-RPS for the membrane method. Thirty-three groundwater samples from the Naval Surface Warfare Center, Crane, Indiana, were analyzed using the direct analysis protocol specified in SW846 Method 8330, and the results were compared with analyses conducted after preconcentration using SOE with acetonitrile, cartridge-based SPE, and membrane-based SPE. For high-concentration samples, analytical results from the three preconcentration techniques were compared with results from the direct analysis protocol; good recovery of all target analytes was achieved by all three preconcentration methods. For low-concentration samples, results from the two SPE methods were correlated with results from the SOE method; very similar data was obtained by the SOE and SPE methods, even at concentrations well below 1 μg/L. The large chromatographic interferences observed for the SPE methods in an earlier study using less clean materials were largely absent here. A small interference was observed for both SPE methods at the retention time of RDX on the primary analysis column that translated to concentrations ranging from 0.2 to 0.6 μg/L RDX. Detection limits for RDX should be raised to 0.6 μg/L if the SPE methods are used for preconcentration due to this potential interference. We recommend that solid-phase extraction be included as an option in SW846 Method 8330 as well as SOE.

For conversion of SI units to non-SI units of measurement consult *Standard Practice for Use of the International System of Units (SI)*, ASTM Standard E380-93, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

Special Report 95-22

US Army Corps of Engineers®
Cold Regions Research & Engineering Laboratory

Evaluation of Clean Solid Phases for Extraction of Nitroaromatics and Nitramines from Water

Thomas F. Jenkins, Philip G. Thorne, Karen F. Myers,
Erika F. McCormick, Don E. Parker and B. Lynn Escalon

September 1995

Prepared for
U.S. ARMY ENVIRONMENTAL CENTER
SFIM-AEC-ET-CR-95037

Approved for public release; distribution is unlimited.

PREFACE

This report was prepared by Dr. Thomas F. Jenkins and Philip G. Thorne, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire; Karen F. Myers, Biologist, and Erika F. McCormick, Chemist, Environmental Chemistry Branch, Environmental Engineering Division, Environmental Laboratory, U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi; and Don E. Parker and B. Lynn Escalon, AScI Corporation, McLean, Virginia.

Funding was provided by the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland, Martin H. Stutz, Project Monitor.

This report was technically reviewed by Dr. C.L. Grant, Professor Emeritus, Chemistry Department, University of New Hampshire, and Thomas E. Myers, Environmental Engineer, WES. In addition, the authors acknowledge Roy Wade (WES) for collection of all groundwater samples and Linda Stevenson for sample management.

This publication reflects the personal views of the authors and does not suggest or reflect the policy, practices, programs, or doctrine of the U.S. Army or the Government of the United States. The contents of this report are not to be used for advertising or promotional purposes. Citation of brand names does not constitute an official endorsement or approval of the use of such commercial products.

CONTENTS

Preface ii
Introduction 1
Objective 2
Experimental 2
Results and discussion 4
Conclusions and recommendations 10
Literature cited 10
Appendix A: Holding-time study results 13

ILLUSTRATIONS

Figure

1. Breakthrough curve for HMX and RDX with SDB-RPS membrane 4
2. Plot of HMX concentrations determined for groundwater samples 7
3. Plot of RDX concentrations determined for groundwater samples 7
4. Plot of TNT concentrations determined for groundwater samples 8
5. LC-18 RP-HPLC chromatograms for sample 30 preconcentrated using SOE, SPE-C, and SPE-M with initial less-clean SPE materials 8
6. LC-18 RP-HPLC chromatograms for sample 30 preconcentrated using SOE, SPE-C, and SPE-M with new manufacturer-cleaned SPE materials showing small RDX interference for SPE-C and SPE-M 9
7. LC-18 RP-HPLC chromatograms for sample 30 preconcentrated using SOE, SPE-C, and SPE-M with new manufacturer-cleaned SPE materials showing small RDX interference for SPE-C and SPE-M 9

TABLES

Table

1. Retention times for various RP-HPLC separations 2
2. Comparison of results from analysis of duplicate samples 5
3. Comparison of recoveries from fortified samples 6
4. Ratio of concentrations obtained for the various preconcentration methods relative to that from the direct method 6
5. Results of regression analyses of SPE-C and SPE-M vs. SOE for low-concentration determinations 8

Evaluation of Clean Solid Phases for Extraction of Nitroaromatics and Nitramines from Water

THOMAS F. JENKINS, PHILIP G. THORNE, KAREN F. MYERS,
ERIKA F. MCCORMICK, DON E. PARKER AND B. LYNN ESCALON

INTRODUCTION

One of the U.S. Army's most serious environmental problems is associated with sites contaminated with residues of secondary explosives. Contamination at these sites was chiefly caused by manufacture of the explosives, loading of explosives into ordnance, and disposal of off-specification or out-of-date material. Residues from these activities contain the explosives, manufacturing impurities, and environmental transformation products (Walsh et al. 1993). Unlike many other organic chemicals, these compounds are quite mobile in the soil and have resulted in serious groundwater contamination (Kayser and Burlinson 1982, Pugh 1982, Rosenblatt 1986, Maskarinec et al. 1986, Spaulding and Fulton 1988). Plumes of contaminated groundwater, often miles in length, have been identified at military sites, with some extending beyond installation boundaries.

A number of laboratory methods have been developed to characterize water samples potentially contaminated with secondary explosives. At present, however, the method most often used by contract laboratories conducting analyses for the Army is SW846 Method 8330 (EPA 1992). This is a reversed-phase, high-performance liquid chromatographic (RP-HPLC) method that specifies 14 target nitroaromatic and nitramine analytes and two protocols for water analysis. When detection limits ranging between 4 and 14 µg/L are adequate for project requirements, a direct injection procedure can be used that does not require sample preconcentration prior to RP-HPLC determination. When lower detection limits are needed, a protocol including a salting-out solvent extraction (SOE) preconcentration step is specified (Miyares and Jenkins 1990, 1991). Winslow et al. (1991, 1992) have proposed the use of solid-phase extraction (SPE) as an alternative to SOE and reported excellent recovery and detection limits that were very similar to those for SOE. Winslow's results were obtained using Porapak R, a divinylbenzene n-vinylpyrrolidone co-polymer, in the cartridge format. LeBrun et al. (1993), using SPE in the membrane format, reported excellent recoveries of the analytes in Method 8330 using a membrane composed of styrene-divinylbenzene. Recently Bouvier and Oehrle (1995) reported on the use of Porapak RDX for cartridge SPE preconcentration of nitroaromatics and nitramines.

Because of a number of potential advantages of SPE over SOE, we conducted a three-way comparison of SOE, cartridge-based SPE using Porapak R (SPE-C), and membrane-based SPE (SPE-M) using styrene-divinylbenzene membranes (Empore SDVB) for preconcentration of waters containing nitroaromatics and nitramines (Jenkins et al. 1992, 1994). This evaluation included estimating detection capability and analyte recovery using fortified reagent-grade water, and analyte recovery for a series of field-contaminated groundwater samples from the U.S. Naval Surface Warfare Center (NSWC), Crane, Indiana. Overall, the results can be summarized as follows:

1) The three methods were comparable with respect to low-concentration detection capability, ranging from 0.05 to 0.30 µg/L.

2) Percent recoveries generally exceeded 80%, except for HMX (octahydro–1,3,5,7-tetranitro–1,3,5,7-tetrazocine) and RDX (hexahydro–1,3,5-trinitro–1,3,5-triazine) by membrane SPE where recoveries were lower.

3) Large interferences were found on about half of the groundwater samples from the NSWC using the two SPE methods but none were found by SOE.

4) The SPE interferences were traced to a matrix interaction of the SPE polymers with low pH

groundwaters that apparently caused the release of unreacted monomers or other contaminants from the interior of the polymeric materials.

At least partly in response to the problems identified above, several manufacturers of SPE materials sought to improve the retention of SPE materials for very polar organics such as HMX and RDX and experimented with new cleaning procedures to better remove interferences from the SPE materials. As a result, Waters Corporation released a new ultra-clean SPE material for use in cartridge SPE under the name Porapak RDX (Bouvier and Oehrle 1995), and 3M Corporation developed a new surface-modified styrene-divinylbenzene membrane that also had been cleaned more extensively (Empore SDB-RPS). Initial tests at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) and elsewhere indicated that these materials were indeed cleaner than the original SPE materials.

OBJECTIVE

The objective of this study was to reassess SPE for preconcentration of nitroaromatic and nitramine explosives from water, using the newly released, manufacturer-cleaned SPE materials. Special attention was given to recovery of HMX and RDX, because of the low recoveries found for these analytes with membrane SPE in the initial study. Assessment of the level of contamination resulting from use of these manufacturer-cleaned materials was conducted using both reagent water samples and some groundwaters from the Naval Surface Warfare Center (NSWC). These groundwaters included some of the low-pH waters that had revealed the contamination problem with the initial SPE materials.

EXPERIMENTAL

Conduct of study

This work was jointly conducted by the U.S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, and CRREL, using fortified reagent-grade water and actual groundwater samples from the NSWC.

Collection of groundwater samples

Groundwater samples were taken with bailers that were rinsed once with isopropyl alcohol and three times with distilled water between samples. Wells were purged with a PVC bailer to a depth midway down the well stream, allowed to recharge a minimum of 2 hours, then sampled with Teflon bailers. Samples were collected in 1-liter precleaned amber glass bottles and were stored and shipped at 4°C.

RP-HPLC analysis

All water samples were analyzed by RP-HPLC at WES. Depending on the specific test conducted, water samples were either analyzed using the direct method specified in SW846 Method 8330 (EPA 1992) or were preconcentrated using either SOE, SPE-C, or SPE-M as described below (Jenkins et al. 1992).

Primary analysis was conducted on a 25-cm × 4.6-mm (5-µm) LC–18 column (Supelco) eluted with 1:1 methanol / water (v / v) at 1.2 mL / min. Injection volume was 50 µL introduced using a 200-µL sample loop. Concentration estimates were obtained from peak heights from a Waters 820 Maxima chromatography workstation. The identity of target analytes and transformation products was confirmed by analysis of the samples on a 25-cm × 4.6-mm (5-µm) LC-CN column from Supelco eluted with 1:1 methanol / water (v / v) at 1.2 mL / min (EPA 1992). Quantitative results for the 2-amino- and 4-aminodinitrotoluenes (2ADNT and 4ADNT) were also taken from the LC-CN determination, since better separation of these two analytes were obtained on this column. Retention times of the analytes of interest for both separations are shown in Table 1.

Table 1. Retention times for various RP-HPLC separations.

Analyte	*Retention time (min)*	
	*LC–18**	*LC-CN**
HMX	2.4	11.4
RDX	3.5	7.3
TNB	4.6	4.3
DNB	5.6	4.4
3,5-DNA	6.1	5.6
tetryl	6.2	9.2
NB	6.6	4.0
TNT	7.4	5.2
4ADNT	8.0	6.0
2ADNT	8.4	6.4
2,6-DNT	8.8	4.9
2,4-DNT	8.9	5.2
2NT	10.6	4.5
4NT	11.8	4.7
3NT	12.4	4.8
tetryl breakdown product	4.6	8.1
2-amino-4-nitrotoluene	5.6	4.2
3-nitroaniline	4.2	3.8
2,4-diamino-6-nitrotoluene	4.0	6.3
2,6-diamino-4-nitrotoluene	2.1	4.8
4-amino-2-nitrotoluene	8.1	4.3

*Separations were conducted at 1.2 mL / min with an eluent of 1:1 methanol / water.

Primary analyses were conducted using a Waters Model 600 system controller, Model 610 fluid unit, Model 717 plus auto injector set for a 50-µL injection, a 486 UV variable wavelength detector set at 245 nm, and a Maxima chromatography work station. Confirmation analysis was conducted on a Waters LC Module 1 with a 486 UV variable wavelength detector (245 nm), a 717 plus auto injector (50 µL), and a Maxima 820 chromatography work station.

Salting-out solvent extraction/nonevaporative preconcentration procedure

A 251.3-g portion of reagent-grade sodium chloride was added to a 1-L volumetric flask. A 770-mL sample of water was measured with a 1-L graduated cylinder and added to the flask. A stir bar was added and the contents stirred at maximum rpm until the salt was completely dissolved. A 164-mL aliquot of acetonitrile (ACN), measured with a 250-mL graduated cylinder, was added while the solution was being stirred, and stirring was continued for at least 15 minutes. If the ACN was slow in dissolving due to poor mixing, a Pasteur pipette was used to withdraw a portion of the undissolved ACN layer and reinject it into the vortex of the stirring aqueous phase. After equilibrium has been established, only about 5 mL of ACN should remain in a separate phase. The stirrer was turned off and the phases allowed to separate for 15 min. If no emulsion was present, the ACN phase was removed and placed in a 100-mL volumetric flask and 10 mL of fresh ACN was added to the 1-L flask. The 1-L flask was again stirred for 15 min, followed by 15 min for phase separation. The ACN was removed and combined with the initial extract in the 100-mL volumetric flask. When emulsions were present, that portion of the sample was removed from the volumetric flask with a Pasteur pipette, placed in a 20-mL scintillation vial and centrifuged for 5 min at 2000 rpm. The supernate was also pipetted into the 100-mL volumetric flask, the scintillation vial was rinsed with 5 mL of acetonitrile, and the acetonitrile was added to the 100-mL volumetric flask. For the first extraction, the pellet that formed after centrifugation was added back to the 100-mL flask, but if it occurred in the second extraction, it was discarded.

To reduce the volume of ACN, an 84-mL aliquot of salt water (325 g NaCl per 1000 mL of water) was then added to the 100-mL volumetric flask. The flask was placed on a vertical turntable and rotated at about 60 rpm for 15 min. After allowing the phases to separate for 15 min, the ACN phase was carefully removed using a Pasteur pipette and placed in a 10-mL graduated cylinder. An additional 1.0-mL aliquot of ACN was then added to the 100-mL volumetric flask, and the flask was rotated on the turntable for 15 min. Again the phases were allowed to separate for 15 min, and the resulting ACN phase was added to the 10-mL graduated cylinder. The volume of the resulting extract was measured and diluted 1:1 with reagent-grade water prior to analysis.

Cartridge solid-phase extraction

Prepacked cartridges of Porapak RDX (Sep-Pak, 6 cc, 500 mg) were obtained from Waters Corporation. The cartridges were cleaned by placing them on a Visiprep solid-phase extraction manifold (Supelco) and passing 15 mL of acetonitrile through each using gravity flow. The acetonitrile was then flushed from the cartridges using 30 mL of reagent-grade water. Care was taken to ensure that the cartridges were never allowed to dry after the initial cleaning.

A connector was placed on the top of each cartridge and fitted with a length of $^{1}/_{8}$-in.-diameter Teflon tubing. The other end of the tubing was placed in a 1-L fleaker containing 500 mL of sample. The vacuum was turned on and the flow rate through each cartridge was set at about 10 mL/min. If the flow rate declined significantly due to partial plugging from suspended material, it was readjusted. After the sample had been extracted, the top plug containing the fitted tubing was removed from each cartridge, and 10 mL of reagent-grade water was passed through the cartridge, using gravity flow unless the cartridges were sufficiently plugged to require vacuum. A 5-mL aliquot of acetonitrile was used to elute retained analytes from the cartridges under gravity flow. The volume of the recovered ACN was measured and diluted 1:1 with reagent-grade water.

Membrane solid-phase extraction

Empore styrene-divinylbenzene membranes (47 mm) were obtained from 3M Corporation. The membranes were designated SDB-RPS and were not commercially available at the time the study was conducted. The styrene-divinylbenzene used in these membranes had been modified to provide extra retention for polar organics such as HMX.* The membranes were precleaned by cen-

* Craig Markell, 1995, 3M Corporation, personal communication.

tering them on a 47-mm vacuum filter apparatus and adding several mL of acetonitrile to swell the membrane before clamping the reservoir in place. A 15-mL aliquot of ACN was then added and allowed to soak into the membrane for 3 min. The vacuum was then turned on and most (but not all) of the solvent was pulled through the membrane. A 30-mL aliquot of reagent-grade water was then added and the vacuum resumed. Just before the last of this water was pulled through the membrane, the vacuum was removed, the reservoir filled with a 500-mL sample, and the vacuum resumed. This sample extraction took from 5 minutes to an hour, depending on the amount of suspended matter present. Once the water was eluted, air was drawn through the membrane for 1 min to remove excess water. These extractions were conducted six at a time using an Empore extraction manifold (3M Corporation). Vials (40 mL) were placed below the outlets of the six membranes, a 5-mL aliquot of ACN was added to each reservoir, the acetonitrile was allowed to soak into the membrane for 3 min, and then the vacuum was applied to pull the acetonitrile through the membranes into the vials. Each resulting extract was removed with a Pasteur pipette, the volume was measured in a 10-mL graduated cylinder, and it was diluted 1:1 with reagent-grade water before analysis.

Preparation of analytical standards

All standards were prepared from standard analytical reference materials (SARMs) obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland. Individual stock standards were prepared in HPLC-grade acetonitrile (Baker). Combined working standards were in acetonitrile and were diluted 1:1 with Milli-Q Type I water (Millipore Corp.).

RESULTS AND DISCUSSION

Determination of retention capacity of the SDB-RPS membrane for HMX and RDX

The retention of HMX and RDX by the SDB-RPS membranes was tested by extracting a 2-L aliquot of reagent-grade water that had been spiked with 100 µg/L of HMX and RDX using aqueous stock standards. Samples of the water passing through the membrane were collected every 250 mL and analyzed by RP-HPLC using the direct analysis protocol. Results are plotted in Figure 1. No detectable breakthrough occured for either analyte until more than 1 L of water had been extracted. Thus, it appears that the SDB-RPS membranes have an increased retention capacity for the very polar nitramines relative to that observed with the initial SDB membranes used in an earlier study (Jenkins et al. 1992, 1994).

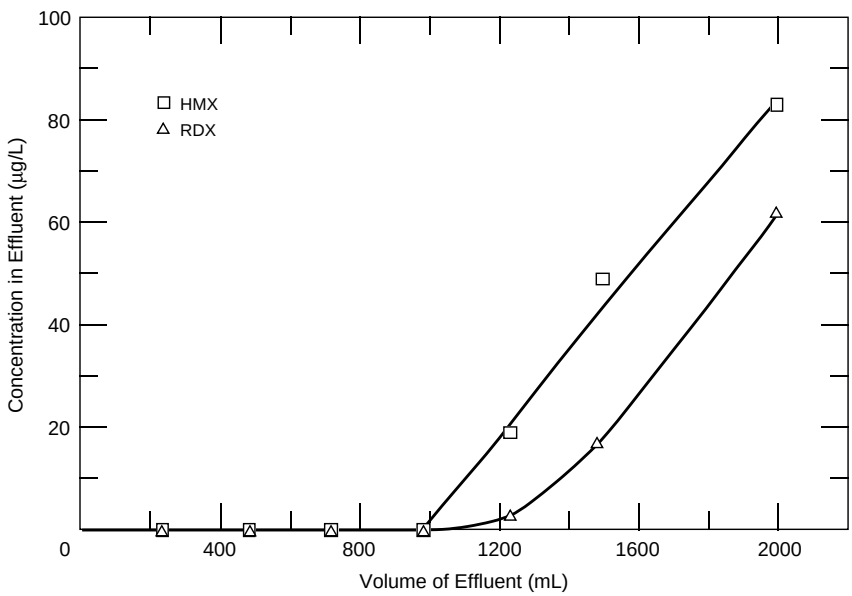

Figure 1. Breakthrough curve for HMX and RDX with SDB-RPS membrane.

Cleanliness of Porapak RDX cartridges and SDB-RPS membranes

Aqueous solutions of individual analytes were prepared by placing several hundred milligrams of each SARM into brown glass bottles and stirring for 2 days at room temperature. Each solu-

Table 2. Comparison of results from analysis of duplicate samples.

		*Relative percent difference**								
Sample		*HMX*	*RDX*	*TNB*	*DNB*	*DNA*	*TNT*	*24D*	*4A*	*2A*
4	Dir	0	24							
	SOE	0	15		6	100	8		18	11
	SPE-C	1	12			0	45		8	5
	SPE-M	3	8			0	17		2	1
29	Dir									
	SOE									
	SPE-C		26							
	SPE-M		7							
B (spike)	Dir	1	0	0			1	1		
	SOE	4	4	4			3	3		
	SPE-C	6	1	7			6	6		
	SPE-M	5	7	7			13	6		

* Relative percent difference calculated by subtracting the two values obtained from duplicates, dividing by the mean value, and multiplying by 100.

tion was then filtered through a 0.45-µm nylon–66 membrane (Supelco) into clean brown glass bottles and stored at room temperature. Test solutions were made by diluting these stocks with reagent-grade water.

The retention of HMX and RDX by the modified SDB membranes was tested by extracting a 2-L aliquot of reagent-grade water that had been spiked with 100 µg/L of HMX and RDX using aqueous stocks. Samples of the membrane run-through were taken every 250 mL and analyzed by RR-HPLC. The results are plotted in Figure 1. No breakthrough occured for either analyte until more than 1 L had been extracted. This is a substantial improvement in retention of these two polar analytes compared with that experienced with the original SDB membranes.

Quality control

QC spiking stock solutions were prepared in acetonitrile. Spikes for the direct injection method were made to produce an added concentration about 5 times the average method detection limit (MDL) at 100 µg/L. Spikes for the samples to be preconcentrated using SOE and SPE were made to produce an added concentration of 2.00 µg/L, approximately 100 times the average MDL reported for the SOE method. Blanks and matrix spikes were prepared in 1-L volumetric flasks, then subsampled for the appropriate method. Two groundwater samples from NSWC were collected in sufficient quantity to allow analysis of matrix duplicates and spikes. In addition, two sets of reagent-grade water blanks (one on each day samples were preconcentrated), blank spikes, and blank spike duplicates were analyzed.

Analytical precision was assessed by computing the relative percent difference (RPD) between duplicate samples based on a single analysis of each (Table 2). In only four cases were the RPD values greater than 20%: sample 4, RDX–direct analysis; sample 4, DNA–SOE; sample 4, TNT–SPE-C; and sample 29, RDX–SPE-C. In all of these cases, the concentration values were near MDL values where errors calculated on a percentage basis are magnified. Otherwise, analytical precision was excellent for both the direct and preconcentration methods, even at low concentration.

Accuracy was assessed from spike recovery data. For spiked reagent-grade water (blank spikes), recoveries of all analytes, for both the direct and preconcentration methods, ranged from 78 to 102%, with the majority of the recoveries above 90% (Table 3). Recoveries of matrix spikes for the direct analysis protocol were also excellent for all analytes in both sample 4 and 29 with recoveries ranging from 92.8 to 105.5% (Table 3). Recoveries for matrix-spiked sample 29 ranged from 65 to 107% for the three preconcentration methods, again indicating excellent recovery. Recoveries for matrix-spiked sample 4 are quite variable, with values ranging from 23 to 191% for the SOE method, 49 to 308% for the SPE-M method, and 91 to 351% for SPE-C (Table 3). However, to interpret these results, one must remember that spike recovery is calculated by subtracting the concentration obtained for the original sample from the concentration obtained from the spiked sample and expressing the result as a ratio of the spike recovered relative to the spike added. This procedure is useful when the concentration of the

Table 3. Comparison of recoveries from fortified samples.

Sample		Percent recovery*								
		HMX	*RDX*	*TNB*	*DNB*	*DNA*	*TNT*	*24D*	*4A*	*2A*
B (spike)	Dir	99.5	98.5	95.6			96.5	98.1		
	SOE	94.2	91.2	92.9			83.2	92.1		
	SPE-C	99.0	101.0	96.6			94.1	95.1		
	SPE-M	92.5	95.6	89.3			88.6	86.9		
B (spike)	Dir	98.8	98.2	95.9			97.2	99.2		
	SOE	91.0	95.0	89.0			81.0	89.0		
	SPE-C	93.5	100.0	89.8			89.1	89.3		
	SPE-M	88.0	102.0	83.0			78.0	82.0		
29	Dir	95	95.5	95.2			92.8	93		
	SOE	107	89	85			89	65		
	SPE-C	103	107	104			105	102		
	SPE-M	80	78	76			78	77		
4	Dir	105.5	105	103			104	105		
	SOE	23†	191†	76.0			83	76		
	SPE-C	351†	95†	92.2			91.1	93.7		
	SPE-M	308†	49.5†	87.4			85.6	90.8		

* % recovery calculated by subtracting the value obtained from the analysis of the unspiked sample from the value obtained for analysis of the fortified sample, dividing by the concentration spiked and multiplying by 100.

† For an explanation of these unreliable estimates, see text.

spike added is greater than that already present in the matrix. If, on the other hand, the spike concentration is small relative to the matrix concentration, a situation encountered here, the result is obtained by subtraction of two similar concentrations to obtain a much smaller value. This can result in widely ranging percent recoveries. This problem has been discussed in detail by Provost and Elder (1983) who stated "Regardless of how percent recovery is defined, it can be shown that percent recovery data tend to be unreliable when the spike/background ratio is small." In sample 4, for example, the concentrations determined in the unspiked sample for HMX were 45.7, 48.0, and 40.8 µg/L for the SOE, SPE-C, and SPE-M methods, respectively. Sample fortification added only another 2 µg/L and hence it is not surprising that percent recoveries, calculated as described above, were 23, 351, and 308% for SOE, SPE-C, and SPE-M, respectively. As shown by Provost and Elder (1983) this is not a surprising result and does not indicate that the methods were out of control. The excellent results for the other QC samples provide convincing evidence that both the direct and preconcentration procedures were in-control and providing very reliable concentration estimates.

Comparison of results using groundwater samples from Naval Surface Warfare Center

Analytical results for 33 groundwater samples from NSWC are presented in Appendix A. These samples were all analyzed by the direct RP-HPLC method (without preconcentration) and by RP-HPLC after preconcentration using salting-out solvent extraction (SOE), cartridge solid-phase extraction (SPE-C), and membrane solid-phase extraction (SPE-M). The following target analytes were detected in these samples (the number of samples where the analytes were detected in at least one of the four analyses is given in parentheses): HMX (19), RDX (22), TNB (4), DNB (5), 3,5-DNA (6), TNT (11), 2,4-DNT (2), 4ADNT (15), and 2ADNT (15). Concentrations measured for HMX and RDX in these groundwater samples were generally much higher than for the nitroaromatics and aminonitroaromatics.

Although results from the direct method are certainly not error free, they are subject to many fewer sources of error than methods employing a

Table 4. Ratio of concentrations obtained for the various preconcentration methods relative to that from the direct method.

Analyte	*n*	Concentration-preconc./Concentration-direct		
		SOE	*SPE-C*	*SPE-M*
HMX	11	0.870±0.188	0.957±0.147	0.833±0.129
RDX	13	0.800±0.184	0.975±0.192	0.882±0.158
TNT	4	1.010±0.252	1.143±0.331	1.015±0.244
4ADNT	5	0.909±0.128	0.996±0.106	0.925±0.095
2ADNT	5	0.865±0.106	1.021±0.066*	0.871±0.057

n = number of ratios in each mean.

* Value significantly different at the 95% confidence level.

preconcentration step. For that reason, we treated the results from the direct analysis as "true values" for purposes of comparison with results from the three preconcentration techniques. Table 4 summarizes results for samples where analytes were detected by the direct RP-HPLC method. Of the 33 groundwater samples analyzed, 11 had detectable HMX using direct analysis, with concentrations ranging from 25 to 325 µg/L. Likewise, RDX was detected in 13 groundwaters using the direct method with concentrations ranging from 13 to 608 µg/L; TNT in four samples with concentrations ranging from 14 to 180 µg/L; 4ADNT and 2ADNT in five samples with concentrations ranging from 9 to 59 µg/L and 7 to 65 µg/L, respectively; and TNB was detected in two samples at 5 and 8 µg/L. For a given analyte, the ratio of the concentration obtained for each preconcentration technique relative to that for the direct method was computed, and the mean and standard deviation was obtained (Table 4). Mean ratios ranged from 0.800 for RDX using the SOE method to 1.143 for TNT using the SPE-C method. Only for 2ADNT was a significant difference among methods detected (by ANOVA) at the 95% confidence level (SPE-C was different from SOE and SPE-M, which were not significantly different from each other). The results of this analysis indicate that, for relatively high concentrations, all three preconcentration techniques produced concentrations similar to that from the direct analysis method, with analyte recoveries in all cases at or above 80%. These results demonstrate a marked improvement in the recovery of HMX and RDX using the SDB-RPS membrane relative to that observed in our original study where the SDB membrane was used (Jenkins et al. 1992, 1994). This improvement is particularly striking for HMX, where recoveries improved from about 49% to 83%, and appears to be due to an improvement in retention for polar compounds resulting from sulfonation of the styrene-divinylbenzene. Recovery of HMX and RDX using the Porapak RDX cartridge remains excellent at 96 and 98%, respectively.

Since the value of a preconcentration technique is to enable determination at concentrations below those that can be determined directly, it is important to evaluate its performance when concentrations are below the detection limits of the direct method. Since the SOE method is the procedure currently recommended in SW846 Method 8330, results for SPE-C and SPE-M were compared with those obtained for SOE for samples with analyte concentrations below the detection limits of the direct method. In Figures 2, 3, and 4 the concentrations of HMX, RDX, and TNT, determined using SPE-C and SPE-M, are plotted against the concentrations obtained using SOE. In the absence of bias, the plots should have a slope of 1.00 and an intercept of 0. Regression analyses were conducted for the SPE-C vs. SOE and SPE-M vs. SOE individually for each analyte, and the resulting

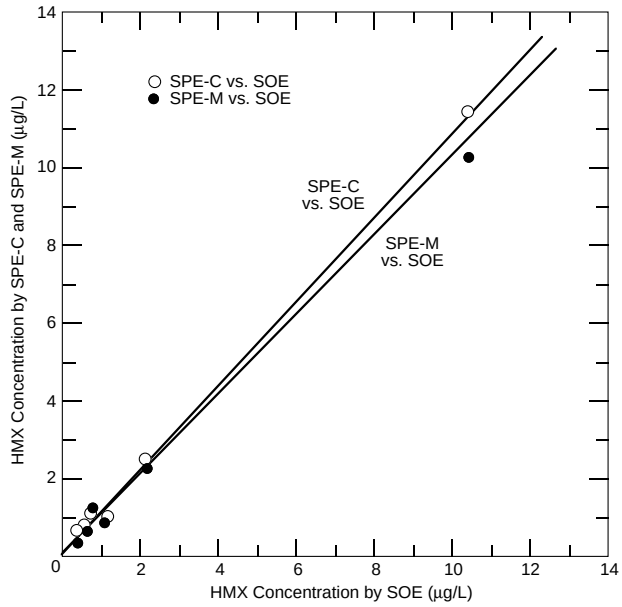

Figure 2. Plot of HMX concentrations determined for groundwater samples using SOE with those using SPE-C and SPE-M.

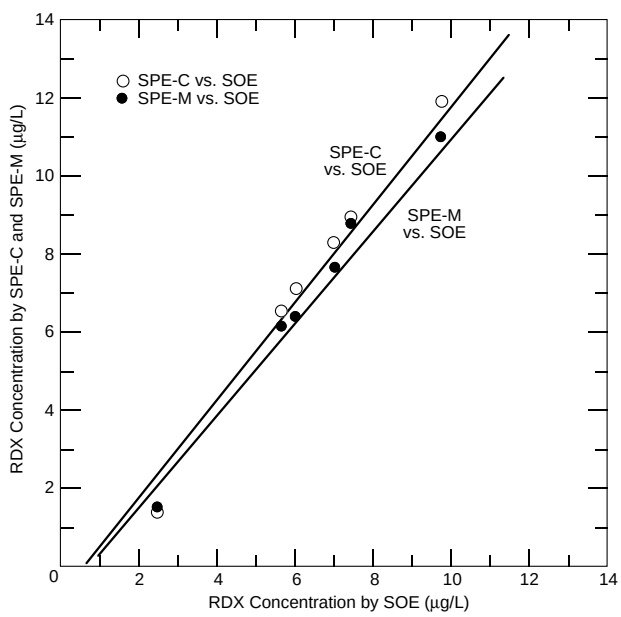

Figure 3. Plot of RDX concentrations determined for groundwater samples using SOE with those using SPE-C and SPE-M.

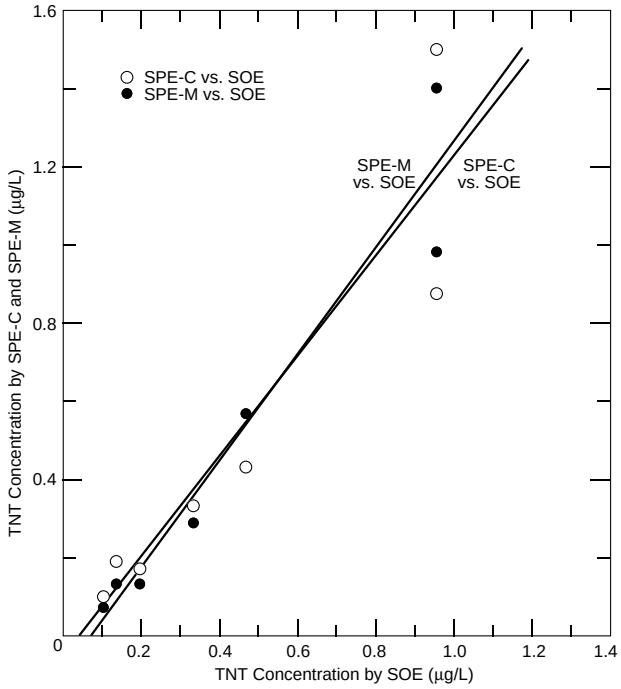

Figure 4. Plot of TNT concentrations determined for groundwater samples using SOE with those using SPE-C and SPE-M.

slopes, intercepts, and correlation coefficients squared are presented in Table 5. Similarly, regression analyses were conducted for 4ADNT, 2ADNT, and 3,5-DNA (Table 5). Slopes for these 12 regression analyses range from 0.930 to 1.400, with intercepts ranging from –1.044 to +0.875. Values for the square of the correlation coefficients range between 0.933 and 0.999. The results from these regression analyses indicate that the two SPE methods are producing data that are very similar to those obtained from SOE, even at concentrations below 1 µg / L. The TNT data for concentrations below 0.5 µg / L is particularly striking in this respect (Fig. 4).

Table 5. Results of regression analyses of SPE-C and SPE-M vs. SOE for low-concentration* determinations.

	SPE-C vs. SOE			*SPE-M vs. SOE*		
Analyte	*m*	*b*	r^2	*m*	*b*	r^2
HMX	1.083	0.125	0.999	0.972	0.113	0.999
RDX	1.255	–1.044	0.987	1.160	–0.850	0.980
TNT	1.264	–0.052	0.933	1.325	–0.085	0.972
4ADNT	1.400	–0.448	0.994	1.208	–0.360	0.992
2ADNT	1.270	0.110	0.981	1.484	0.875	0.974
3,5–DNA	0.972	0.007	0.996	0.930	0.014	0.996

* Concentrations below that detectable using the direct method.
m — Slope.
b — Intercept.
r^2 — Correlation coefficient squared.

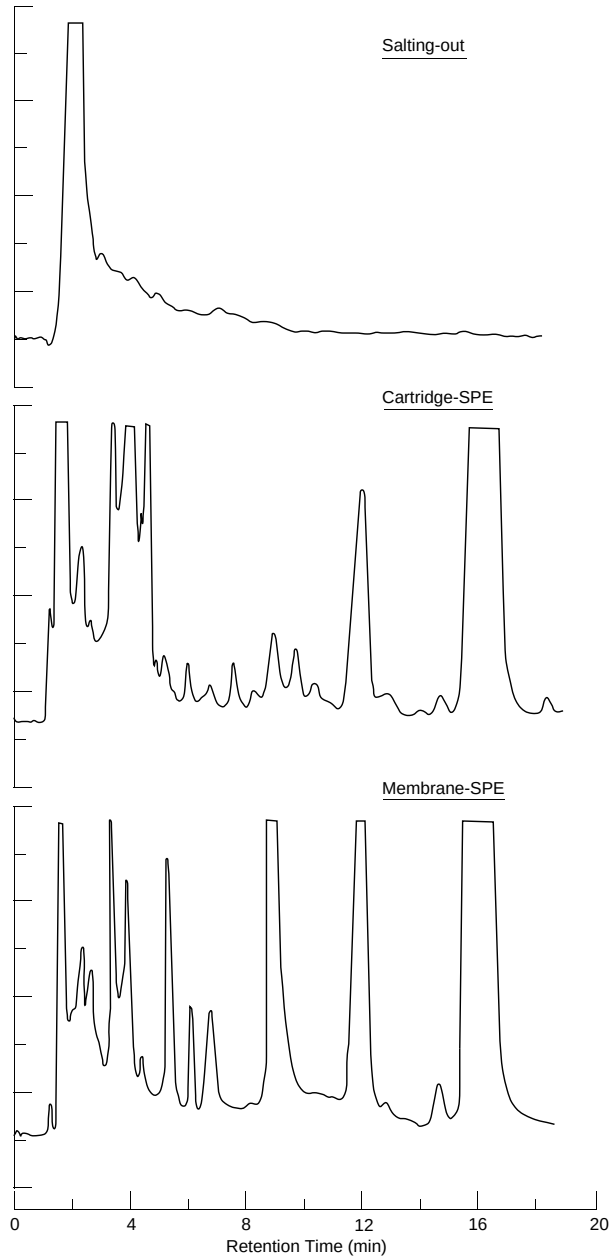

Figure 5. LC–18 RP-HPLC chromatograms for sample 30 preconcentrated using SOE, SPE-C, and SPE-M with initial less-clean SPE materials.

Examination of chromatograms for groundwater samples

In our initial comparison of SOE, SPE-C, and SPE-M, we found a series of groundwater samples that caused the solid-phase materials to release high concentrations of interferences. This is illustrated for the chromatograms obtained for sample 20641 (Well 10C40P2) in 1992 using SOE, Porapak R (SPE-C), and Empore SDB (SPE-M) (Fig. 5). Chromatograms for this same sample obtained using the new, manufacturer-cleaned Porapak RDX and SDB-RPS are shown

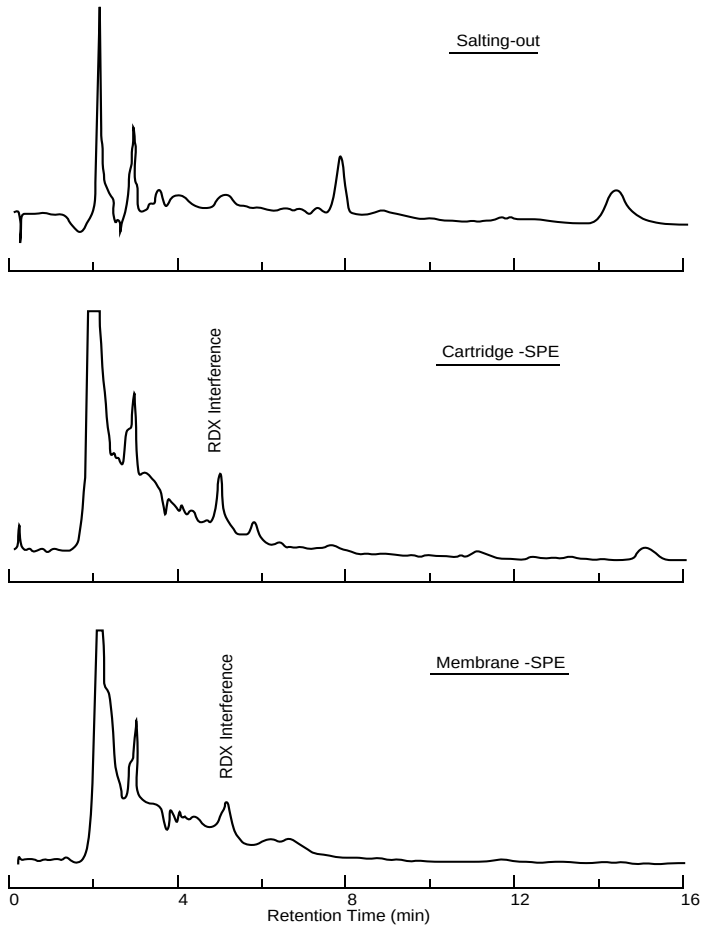

Figure 6. LC–18 RP-HPLC chromatograms for sample 30 preconcentrated using SOE, SPE-C, and SPE-M with new manufacturer-cleaned SPE materials showing small RDX interference for SPE-C and SPE-M.

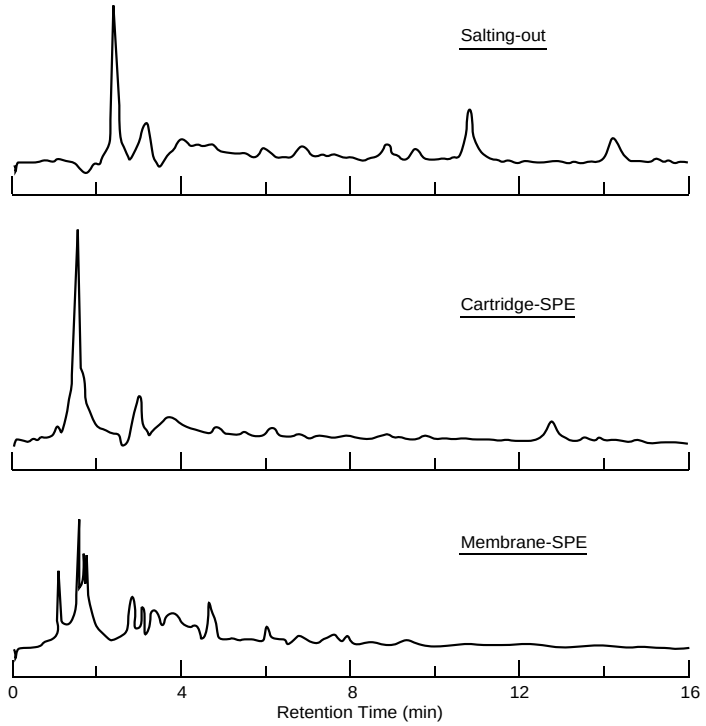

Figure 7. LC-CN RP-HPLC chromatograms for sample 30 preconcentrated using SOE, SPE-C, and SPE-M with new manufacturer-cleaned SPE materials showing small RDX interference for SPE-C and SPE-M.

in Figure 6. Clearly there is a vast decrease in interferences released from the two solid phases. There remains, however, a small interference peak at the retention time for RDX in the two chromatograms for the SPE methods that is not observed for the SOE (Fig. 6) and does not confirm as RDX using the LC-CN confirmation column (Fig. 7). This peak was observed in the LC-18 chromatograms for both SPE-C and SPE-M for the same six well waters that resulted in release of interferences in the original study. Observation of these peaks would require that a confirmation analysis be conducted and would result in quantitative RDX estimates ranging from 0.2 to 0.6 µg/L if careful scrutiny of an LC-CN confirmation analysis had not been done. Thus, when SPE preconcentration is used, the detection limit for RDX should be raised to about 0.6 µg/L to eliminate the chance for misidentification due to this small interference peak.

CONCLUSIONS AND RECOMMENDATIONS

Solid-phase extraction, in both the cartridge (SPE-C) and membrane (SPE-M) formats, was evaluated for the ability to preconcentrate nitroaromatics, nitramines, and aminodinitroaromatics from water samples prior to analysis by RP-HPLC (SW846 Method 8330). A series of 33 groundwater samples from the Naval Surface Warfare Center was used for comparison. New, manufacturer-cleaned solid-phase materials (Porapak RDX for SPE-C and SDB-RPS for SPE-M) were compared to salting-out solvent extraction with respect to their recovery of target analytes and their production of chromatographic interferences.

Based on these results, we recommend that solid-phase extraction, in either the cartridge or membrane format, be included as an option along with salting-out solvent extraction for the preconcentration step in SW846 Method 8330. Comparison of the results of this study and earlier work (Jenkins et al. 1992, 1994) demonstrates the necessity of using carefully cleaned solid phases for this purpose, or interferences will be released for certain water matrices.

LITERATURE CITED

Bouvier, E.S.P. and S.A. Oehrle (1995) Analysis and identification of nitroaromatic and nitramine explosives in waters using HPLC and photodiode-array detection. *LC-GC*, **13**(2): 120–130.

EPA (1989) *Trinitrotoluene Health Advisory*. Office of Drinking Water. Washington, D.C.: U.S. Environmental Protection Agency.

EPA (1988a) *Health Advisory for RDX*. Criteria and Standards Division, Office of Drinking Water. Washington, D.C.: U.S. Environmental Protection Agency.

EPA (1988b) *Health Advisory for HMX*. Criteria and Standards Division, Office of Drinking Water. Washington, D.C.: U.S. Environmental Protection Agency.

EPA (1988c) *Health Advisory for 1,3-Dinitrobenzene*. Criteria and Standards Division, Office of Drinking Water. Washington, D.C.: U.S. Environmental Protection Agency.

EPA (1992a) *Nitroaromatics and Nitramines by HPLC*. Second Update SW846 Method 8330. Washington, D.C.: U.S. Environmental Protection Agency.

EPA (1992b) *Dinitrotoluene Health Advisory*. Criteria and Standards Division, Office of Drinking Water. Washington, D.C.: U.S. Environmental Protection Agency.

Etnier, E.L. (1987) Water quality criteria for 2,4-dinitrotoluene and 2,6-dinitrotoluene. AD-ORNL–6312. Oak Ridge National Laboratory Report, Oak Ridge, Tennessee.

Jenkins, T.F., P.H. Miyares, K.F. Myers, E.F. McCormick and A.B. Strong (1994a) Comparison of solid-phase extraction with salting-out solvent extraction for preconcentration of nitroaromatic and nitramine explosives from water. *Analytica Chimica Acta*, **289**: 69–78.

Jenkins, T.F., P.G. Thorne and M.E. Walsh (1994b) Fieldscreening method for TNT and RDX in groundwater. USA Cold Regions Research and Engineering Laboratory, Special Report 94-18.

Jenkins, T.F., P.H. Miyares, K.F. Myers, E.F. McCormick and A.B. Strong (1992) Comparison of cartridge and membrane solid-phase extraction with salting-out solvent extraction for preconcentration of nitroaromatic and nitramine explosives from water. USA Cold Regions Research and Engineering Laboratory, Special Report 92-25.

Kayser, E.G. and N.E. Burlinson (1982) Migration of explosives in soil. Naval Surface Weapons Center Report TR 82–566.

LeBrun, G., P. Rethwill and J. Matteson (1993) Determination of explosives in surface and groundwater. *Environmental Laboratory*, p. 12–15.

Miyares, P.H. and T.F. Jenkins (1990) Salting-out solvent extraction method for determining low levels of nitroaromatics and nitramines in water. USA Cold Regions Research and Engineering Laboratory, Special Report 90–30.

Miyares, P.H. and T.F. Jenkins (1991) Improved salt-

ing-out extraction–preconcentration method for the determination of nitroaromatics and nitramines in water. USA Cold Regions Research and Engineering Laboratory, Special Report 91-18.

Provost, L.P. and R.S. Elder (1983) Interpretation of percent recovery data. *American Laboratory*, December, p. 57–63.

Pugh, D.L. (1982) Report DRXTH-FR–8213, Milan Army Ammunition Plant contamination survey. USA Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland.

Rosenblatt, D.H. (1986) Contaminated soil clean-up objectives for Cornhusker Army Ammunition Plant. Technical Report 8603, USA Medical Bioengineering Research and Development Laboratory, Fort Detrick, Maryland.

Spaulding, R.F. and J.W. Fulton (1988) Groundwater munition residues and nitrate near Grand Island, Nebraska, U.S.A. *Journal of Contaminant Hydrology*, **2**: 139–153.

Walsh, M.E., T.F. Jenkins, P.H. Miyares, P.S. Schnitker, J.W. Elwell and M.H. Stutz (1993) Evaluation of SW846 Method 8330 for characterization of sites contaminated with residues of high explosives. USA Cold Regions Research and Engineering Laboratory, CRREL Report 93-5.

Winslow, M.G., B.A. Weichert and R.D. Baker (1991) Determination of low-level explosives residues in water by HPLC: Solid phase extraction vs. salting-out extraction. In *Proceedings of the 7th Annual Waste Testing and Quality Assurance Symposium, 8–12 July*, Environmental Protection Agency, Washington D.C.

Winslow, M.G., B.A. Weichert, R.D. Baker and P.F. Dumas (1992) A reliable and cost-effective method for the determination of explosives compounds in environmental water samples. In *Proceedings of the 8th Annual Waste Testing and Quality Assurance Symposium, 13–17 July*, Environmental Protection Agency, Washington D.C.

APPENDIX A: HOLDING-TIME STUDY RESULTS

Table A1. Comparison of results for direct analysis (Dir) with those using salting-out (SOE), cartridge SPE (SPE-C) and membrane SPE (SPE-M) for groundwater samples from NSWC.

		Concentration (µg/L)								
Sample	*Type*	*HMX*	*RDX*	*TNB*	*DNB*	*DNA*	*TNT*	*24D*	*4A*	*2A*
1	Dir									
	SOE	1.04	2.45				0.47		0.36	0.32
	SPE-C	1.00	1.33				0.44		0.29	0.3
	SPE-M	0.93	1.35				0.57		0.28	0.56
2	Dir	94	79							
	SOE	54.2	63.8			0.3	0.33		3.08	1.36
	SPE-C	64.0	83.1			0.3	0.34		3.34	2.27
	SPE-M	57.1	71.8			0.3	0.29		2.89	2.05
3	Dir	93	91							
	SOE	85.7	75.3			0.2	0.19	0.08	2.43	1.31
	SPE-C	93.1	88.8			0.2	0.17	0.11	2.49	1.65
	SPE-M	78.9	74.7			0.2	0.13	0.07	1.99	1.89
4	Dir	45	14							
	SOE	45.7	16.4		0.17	0.3	0.13		2.18	1.21
	SPE-C	48.0	21.6			0.2	0.19		2.31	1.42
	SPE-M	40.8	18.9			0.2	0.13		2.07	1.64
5	Dir									
	SOE	0.76	5.77						0.13	0.05
	SPE-C	1.16	6.48						0.16	0.05
	SPE-M	1.19	6.11						0.16	0.14
6	Dir									
	SOE	10.5	6.17				0.10		0.71	0.33
	SPE-C	11.5	7.03				0.10		0.79	0.40
	SPE-M	10.3	6.34				0.07		0.82	0.70
7	Dir	134	365							
	SOE	75.4	202				0.98		8.12	1.80
	SPE-C	115	308				1.51		11.3	3.44
	SPE-M	109	291				1.41		9.81	3.30
8	Dir									
	SOE	0.61	10.9							
	SPE-C	0.64	11.9							
	SPE-M	0.64	11.0							
9	Dir	25	13							
	SOE	30.2	12.1						1.14	0.56
	SPE-C	31.2	12.7						1.50	0.79
	SPE-M	27.5	11.0						1.34	0.79
10	Dir									
	SOE	0.33	7.12							
	SPE-C	0.62	8.23							
	SPE-M	0.26	7.60							
11	Dir									
	SOE									
	SPE-C									
	SPE-M									
12	Dir									
	SOE									
	SPE-C									
	SPE-M									

Table A1 (cont'd). Comparison of results for direct analysis (Dir) with those using salting-out (SOE), cartridge SPE (SPE-C) and membrane SPE (SPE-M) for groundwater samples from NSWC.

		Concentration (µg/L)								
Sample	*Type*	*HMX*	*RDX*	*TNB*	*DNB*	*DNA*	*TNT*	*24D*	*4A*	*2A*
13	Dir									
	SOE									
	SPE-C									
	SPE-M									
14	Dir	13								
	SOE	5.98								
	SPE-C	12.0								
	SPE-M	11.6								
15	Dir									
	SOE									
	SPE-C									
	SPE-M									
16	Dir	40								
	SOE	0.58	28.7			0.04			0.39	0.13
	SPE-C	0.77	33.8			0.03			0.43	0.17
	SPE-M	0.66	32.7			0.03			0.44	0.22
17	Dir									
	SOE									
	SPE-C									
	SPE-M									
18	Dir	165	58						9	7
	SOE	141	39.1			0.80	0.96		8.5	5.62
	SPE-C	152	44.4			0.93	0.88		9.5	7.01
	SPE-M	138	40.9			0.90	0.9		99.3	6.03
19	Dir	173	76				17		59	54
	SOE	172	69.5			2.6	23.1	1.20	65.2	56.4
	SPE-C	142	75.6		0.11	2.5	20.9	1.08	57.7	50.5
	SPE-M	136	72.7		0.11	2.4	20.3	1.23	55.0	48.0
20	Dir									
	SOE									
	SPE-C									
	SPE-M									
21	Dir	252	157	5			110		47	65
	SOE	227	132	6.62	0.30		102		42.6	56.5
	SPE-C	238	146	6.90	0.33		104		48.0	63.5
	SPE-M	226	141	6.45	0.31		102		47.0	61.8
22	Dir	218	40							
	SOE	201	35.9						2.20	1.90
	SPE-C	203	36.5						2.74	2.24
	SPE-M	199	35.8						2.78	2.08
23	Dir									
	SOE									
	SPE-C									
	SPE-M									
24	Dir									
	SOE	2.15	7.54							
	SPE-C	2.47	8.91							
	SPE-M	2.34	8.84							
25	Dir									
	SOE									
	SPE-C		0.59							
	SPE-M		0.63							

Table A1 (cont'd).

		Concentration (µg/L)								
Sample	*Type*	*HMX*	*RDX*	*TNB*	*DNB*	*DNA*	*TNT*	*24D*	*4A*	*2A*
26	Dir									
	SOE									
	SPE-C									
	SPE-M									
27	Dir	112	608	8			180		10	8
	SOE	82.8	429	4.45	0.79		137		7.71	6.20
	SPE-C	91.0	510	9.53	0.90		149		8.25	7.67
	SPE-M	77.3	445	7.37	0.79		128		8.16	6.33
28	Dir	325	102				14		51	40
	SOE	290	87.5	0.37	0.10	5.6	13.9		42.3	33.5
	SPE-C	319	109	0.87	0.17	7.5	22.0		56.2	45.0
	SPE-M	249	85.7	0.65	0.13	6.1	17.2		43.0	34.5
29	Dir									
	SOE									
	SPE-C		0.43							
	SPE-M		0.28							
30	Dir									
	SOE									
	SPE-C									
	SPE-M									
31	Dir									
	SOE		0.21							
	SPE-M		0.23							
32	Dir									
	SOE									
	SPE-C									
	SPE-M	0.38								
33	Dir									
	SOE									
	SPE-C									
	SPE-M									

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestion for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
September 1995

3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE
Evaluation of Clean Solid Phases for Extraction of Nitroaromatics and Nitramines from Water

5. FUNDING NUMBERS

6. AUTHORS
Thomas F. Jenkins, Philip G. Thorne, Karen F. Myers, Erika F. McCormick, Don E. Parker and B. Lynn Escalon

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, New Hampshire 03755-1290

8. PERFORMING ORGANIZATION REPORT NUMBER
Special Report 95-22

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Environmental Center
Aberdeen, Maryland

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
SFIM-AEC-ET-CR-95037

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

Available from NTIS, Springfield, Virginia 22161.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)
Salting-out solvent extraction (SOE) was compared with cartridge and membrane solid-phase extraction (SPE) for preconcentration of nitroaromatics, nitramines, and aminonitroaromatics prior to determination by reversed-phase high-performance liquid chromatography. The solid phases used were manufacturer-cleaned materials: Porapak RDX for the cartridge method and Empore SDB-RPS for the membrane method. Thirty-three groundwater samples from the Naval Surface Warfare Center, Crane, Indiana, were analyzed using the direct analysis protocol specified in SW846 Method 8330, and the results were compared with analyses conducted after preconcentration using SOE with acetonitrile, cartridge-based SPE, and membrane-based SPE. For high-concentration samples, analytical results from the three preconcentration techniques were compared with results from the direct analysis protocol; good recovery of all target analytes was achieved by all three preconcentration methods. For low-concentration samples, results from the two SPE methods were correlated with results from the SOE method; very similar data was obtained by the SOE and SPE methods, even at concentrations well below 1 µg/L. The large chromatographic interferences observed for the SPE methods in an earlier study using less clean materials were largely absent here. A small interference was observed for both SPE methods at the retention time of RDX on the primary analysis column that translated to concentrations ranging from 0.2 to 0.6 µg/L RDX. Detection limits for RDX should be raised to 0.6 µg/L if the SPE methods are used for preconcentration due to this potential interference. We recommend that solid-phase extraction be included as an option in SW846 Method 8330 as well as SOE.

14. SUBJECT TERMS
Analysis, Explosives, Preconcentration, RDX, Salting out, Solid-phase extraction, TNT, Water

15. NUMBER OF PAGES
14

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT
UNCLASSIFIED

20. LIMITATION OF ABSTRACT
UL