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DETERMINATION OF MUNITIONS COMPONENTS IN WATER BY RESIN ADSORPTION AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY–ELECTROCHEMICAL DETECTION*

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SUMMARY

A method has been developed for the determination of several munitions components (nitro-organic compounds) in environmental waters. The method is based on Porapak resin adsorption of the munitions components from aqueous samples. Following desorption with acetone, the nitro compounds are measured by high-performance liquid chromatography with electrochemical detection at a gold–mercury electrode, which is maintained at −1.0 V *vs.* a silver–silver chloride reference electrode. This technique provides a high degree of selectivity and sensitivity for these compounds in actual samples. Detection limits approach 1 μg/l for many components.

INTRODUCTION

Nitrated organic compounds are the most widely used munitions components. These compounds have been and continue to be produced in large quantities, and are therefore subject to regulation by environmental agencies. For the most part, these compounds are non-volatile and sparingly soluble in water. The main concern, from an environmental standpoint, thus becomes contamination of aquifers, both surface water and groundwater. While various toxicology studies have been carried out on these compounds[1–5], there exists no definitive toxicology data base for the establishment of acceptable levels of aquifer contamination. Furthermore, reliable analytical methodology for the determination of these components in aqueous samples is lacking. This paper reports the development of a resin-based isolation scheme for a wide range of munitions components and munitions by-products in surface and groundwater.

The chemical structures of a variety of munitions components are shown in Fig. 1. Three general classes of compounds are normally encountered: nitramines, nitrotoluenes and nitroaliphatics (nitrate esters). The inherent differences in chemical

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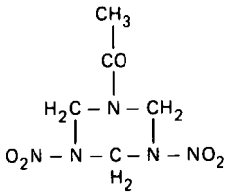
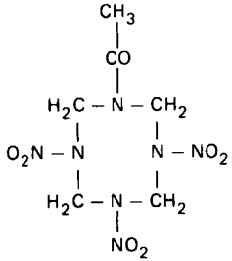
NITRAMINES



TAX



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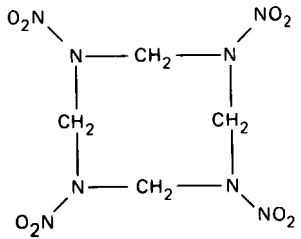
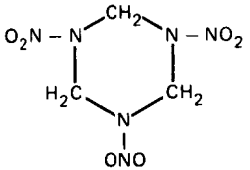
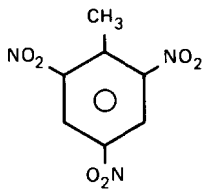


HMX



RDX

NITROTOLUENES



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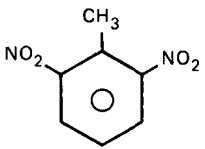
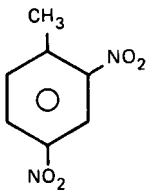
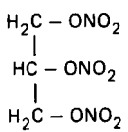


2, 6 DNT

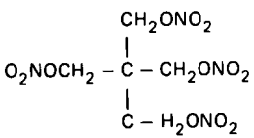


2, 4 DNT

NITROALIPHATICS (NITRATE ESTERS)



NG



PETN

Fig. 1. Structures of munitions.

structure lead, of course, to significant differences in chemical properties. For example, the nitrotoluenes have in general greater water solubility than the nitramines. Conversely, the nitramines have much lower solubility in organic solvents than the nitrotoluenes. The octanol–water partition coefficient is therefore higher for the nitrotoluenes than the nitramines. These anomalies make the choice of an extraction solvent or sorbent less than straightforward. Furthermore, these compounds have a wide variability in chemical stability in aqueous systems. The nitrate esters are reported to decompose rapidly[6] while the nitrotoluenes are quite stable. This complicates matters of sample collection and storage.

Resin adsorption techniques would seem to offer certain advantages over classical solvent partition schemes for the determination of these compounds. Since the first description of the use of resin columns in water extraction[7], these systems have received a great deal of attention. For the purposes of the present work, these systems appear to have several advantages over solvent partition systems. First, resins should be available which exhibit specific sorptivity toward nitro groups, allowing the use of one isolation technology for all compounds of interest. Second, the resin sorption can be done in the field immediately after sampling, ensuring that the sample integrity is maintained. Third, the sorption of these compounds on resins would be expected to increase stability, therefore allowing for a greater time span from sample isolation to analysis. Preliminary investigations[8] indicated that three resins, Amberlite XAD-4, Porapak-R and Porapak-S, would meet the above criteria. While XAD-4 represents a semi-standard approach to resin adsorption (macroreticular styrene–divinylbenzene resin), the use of the hydrophilic Porapaks as sorbents for aqueous systems has been minimal, even though the use of these resins in gas phase sampling and gas chromatography is well known. The polar nature of the compounds in this investigation indicated potential utility of these hydrophilic resins.

Both gas chromatographic (GC) and high-performance liquid chromatographic (HPLC) methods have been applied to the quantitation of nitrated munitions components. A variety of GC detectors, including the nitrogen–phosphorous detector[9], electron-capture detector[10], thermionic ionization detector[11] and thermal energy analyzer[12] detect these species with good to excellent sensitivity and selectivity. However, these thermally-labile species are subjected to a significant degree of heating during any GC analysis, thereby introducing the likelihood of partial and irreproducible degradation. GC quantitation of these compounds, consequently, would be suspect at best.

By contrast, thermal degradation is not a consideration in HPLC methods. Nitrated munitions components may be detected by using the following four approaches: (a) UV absorption[13,14]; (b) chemical reduction to the corresponding amine followed by fluorescence detection[15–17]; (c) photolytic cleavage of the C–NO_2 bond to form nitrite ions which are later electrochemically oxidized to nitrate[18]; and (d) electrochemical reduction of the nitro group to the corresponding amine[19,20]. Both spectroscopic approaches would be appropriate for aromatic munitions, but comparatively insensitive for saturated species such as nitroglycerin (NG) and pentaerythritol tetranitrate (PETN). The wide variation in spectral properties makes this less than feasible. Photolysis followed by electrochemical oxidation[18] is a very new and promising approach which deserves careful and extensive testing using a wide variety of "real-world" samples. The liquid chromatography–electrochemical detec-

tion (LC–ED) of munitions components has been investigated extensively by Bratin and co-workers[19,20]. These workers not only elucidated the reduction mechanism for nitrated compounds, but also established a detection limit of approximately 0.1–0.4 ng per explosive tested. Similar calculations for a variety of explosives using the UV detector (254 nm) indicated a sensitivity of 1–160 ng per explosive. Thus, LC–ED possesses the sensitivity required to detect trace concentrations of munitions components in aqueous samples. Furthermore, the detector response will be affected primarily by the number of nitro groups per molecule. This approach could then be applied to the determination of by-products and degradation products of the compounds of interest, and yet still be somewhat selective.

The overall objective of this work was to develop a resin adsorption system suitable for the isolation of nitro compounds from water, and to combine this isolation with reductive LC–ED to achieve detection limits of 1 μg/l.

EXPERIMENTAL

Sample collection and handling

Standard compounds were obtained from the Department of Defense, Dover, NJ, U.S.A. All water samples were collected in 3.8-l amber bottles. Sufficient sample was collected (6 l) to allow for triplicate analysis by solvent partition and each of three resin adsorption systems. Well water samples were collected using a PTFE bailer (Cole-Parmer, Chicago, IL, U.S.A.); surface water samples were collected using a grab sampler (Bel-Art, Pequawnok, NJ, U.S.A.). After collection, the samples to be analyzed using solvent partition were divided into three 500-ml aliquots and stored in the dark at 4°C until extraction. Samples for resin adsorption were extracted immediately.

For solvent extraction, 500 ml sample was extracted three times with 50 ml methylene chloride. The methylene chloride was taken to near dryness with nitrogen. Eight ml of acetone and 0.5 ml water were added, then taken to near dryness with nitrogen, and diluted with mobile phase to a final volume of 2 ml. The sample was filtered through a 0.45-μm filter into a 4-ml vial.

For resin adsorption, the resin cartridges were prepared as follows. The resin was prewashed with acetone by Soxhlet extraction for two or more hours. After drying in a vacuum oven at 30°C for one or more hours, it was used as follows: 5 ml graduated disposable pipets were packed with approximately 1.1 g (3 ml) of the sorbent, retained by plugs of glass wool. After packing, the sorbent was further cleaned by pumping several hundred millilitres of acetone through each pipet. The columns were then conditioned by pumping *ca.* 100 ml of distilled water through them. One ml of water was left on the columns and the columns were sealed with plastic column caps until ready for use.

On-site sampling for sorbent was done as follows: Sampling was accomplished by pumping (Lab Pump, FMI, Oyster Bay, NY, U.S.A.) 500 ml of sample through a conditioned sorbent column. The loaded sorbent column was rinsed with 5 ml of distilled water and was kept wet with 1 ml of distilled water. It was then sealed for transport back to the lab. The loaded columns were dried for several minutes with a stream of nitrogen to drive off water. The sample was stripped from the loaded sorbent column with 10 ml of acetone by gravity flow. Acetone was exchanged with

ethanol under a stream of dry, flowing nitrogen, making sure that the sample was never taken to dryness. The final volume was adjusted to 2 ml with mobile phase and filtered through a 0.45-μm filter (Nylon 66, Rainin, Woburn, MA, U.S.A.) into a 4-ml vial.

Liquid chromatography–UV detection

A Beckman Model 334 gradient liquid chromatograph equipped with a Model 500 autosampler and an analytical-scale UV detector (254 nm) (Beckman, Instruments, Berkeley, CA, U.S.A.) was used for all of the HPLC–UV measurements performed on the ethanol extracts. The samples were eluted from a 25 cm × 4.6 mm I.D. Zorbax (7-μm) ODS reversed-phase column. The eluent (flow-rate 1.5 ml/min) changed linearly from 40 to 55% methanol in water over 10 min and remained at 55% methanol in water for an additional 17 min before returning to the starting concentration. Turnaround time was 55 min per sample. The species HMX, RDX, TNT, 2,4-DNT and 2,6-DNT were recorded, and quantitated in each sample using a Hewlett-Packard 3390 recording integrator. The sensitivity of the measurement at a signal-to-noise ratio of 2 was estimated to be 1 μg munition/ml of ethanol extract.

Liquid chromatography–electrochemical detection

The HPLC system consisted of a Perkin-Elmer Series 2 liquid chromatograph fitted with the essential oxygen removal apparatus as recommended by Bratin and co-workers[19,20]. All PTFE lines in the system were replaced with Type 316 stainless-steel to prevent oxygen permeation of the mobile phase. A Bioanalytical Systems (BAS) Model MF 4000 flow-through pulse damper was installed between the pump outlet and the injection valve. The mobile phase [1-propanol–0.025 *M* sodium acetate, 0.025 *M* monochloroacetic acid (30:70, v/v)] was heated to *ca.* 60°C and purged with helium or nitrogen at 3 to 4 ml/min overnight to expel dissolved oxygen. The temperature was decreased to 30°C and the inert gas-flow was adjusted to about 2 ml/min for the chromatographic experiments. All solvents and sample solutions were filtered through 0.45-μm Nylon-66 filters. The top of the reflux condenser was fitted with a small trap so that the inert gas-flow bubbled out through about 2 in. of water in a test tube so as to maintain a slight overpressure in the system. This precaution minimized any back-diffusion of air into the mobile phase flask.

The electrochemical detector was a BAS Model LC-3 amperometric detector. This detector was modified for reductive-mode applications per recommendations from BAS[21].

The electrochemical cell was a BAS TL-GA thin-layer cell assembly which consisted of a gold–mercury thin-film working electrode, glassy carbon counter electrode and RE-1 silver–silver chloride reference electrode. The reference electrode is housed down-stream in an RC-2A reference electrode compartment. The preparation of the gold–mercury thin-film electrodes and electrode maintenance was according to the recommendations of Bratin *et al.*[19,20] and the manufacturer (BAS). The LC columns were 25 × 0.46 cm I.D. DuPont Zorbax ODS (5 μm) and Alltech Spherisorb ODS (5 μm) columns. The injection valve was a Rheodyne 7120 fitted with a 20-μl loop and mounted vertically for syringe degassing of the sample similar to the method of Lloyd[22] (see below). A Hewlett-Packard Model 7045A *X-Y* recorder and a Hewlett-Packard Model 3390A reporting integrator were used for data read-out.

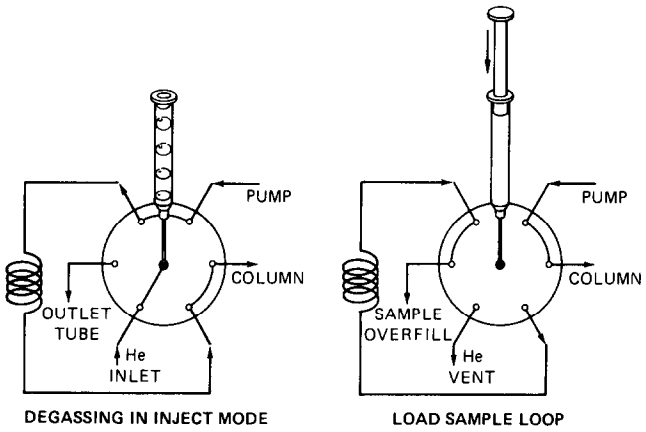


Fig. 2. Syringe sample deoxygenation.

Deoxygenation of sample. With the vertically mounted injection valve, which is illustrated in Fig. 2, in the Injection position, the 1 ml syringe (without plunger) is inserted into the needle port and the valve turned to the Load position. Inert gas-flow is started, as indicated by bubbling through the gas saturation vials, and at this point mobile phase from the loop and excess sample solution from the previous injection are backed up into the syringe. This solution is removed with a disposable pipet. Approximately 200 μl of ethanol is added and allowed to bubble through for about 10 sec to rinse the syringe, and the residual is removed with a disposable pipet. Approximately 200 μl of sample is placed in the syringe and degassed at *ca.* 1 bubble/sec for about 3 min. The plunger is inserted just at the top of the syringe, and the gas is turned off. The plunger is pushed in to fill the loop with sample, and the valve is turned to Inject.

RESULTS AND DISCUSSION

The first attempts in this work utilized UV detection for measurement of the munitions following LC separation. Nitroglycerin and PETN were detected at 210 nm while HMX, RDX, TNT, 2,4-DNT and 2,6-DNT were measured at 254 nm. No insurmountable difficulties were encountered in the separation and detection of authentic standard solutions. However, when the munitions were subjected to sorption and desorption from the resins (Porapak-R, Porapak-S), troublesome background and extraneous peaks appeared and severely hampered reliable measurements by the UV method.

In view of these difficulties and because of the low sensitivity of the UV detector for NG and PETN, we considered the use of ED for the determination of these munitions. The amperometric detector is operated in the reductive mode utilizing a gold–mercury thin-film electrode which is operated at -1.0 V *versus* a silver–silver chloride working electrode.

ED is more sensitive and selective than UV detection. Thus, troublesome and non-reproducible background peaks should be of less consequence. Nevertheless, a

sample should be reasonably clean because non-electroactive species which are specifically adsorbed on the electrode surface may cause irreproducible responses.

Chromatograms of a standard mixture of munitions, illustrating ED and UV (210 nm) detection following adsorption and desorption using Porapak-R are shown in Fig. 3. The unacceptable background observed by the UV detector was not encountered with the electrochemical detector. The sensitivity and chromatographic resolution of the peaks, in general, were much improved. While the UV background from the resins was less severe at 254 nm, the HMX and RDX peaks were often completely obscured by interferences, particularly at low concentrations. This problem was expected to be much more severe in the analysis of environmental samples.

An HPLC chromatogram for the separation of HMX, RDX, TNT, NG, 2,6-DNT, 2,4-DNT and PETN is shown in Fig. 4. This chromatogram was recorded

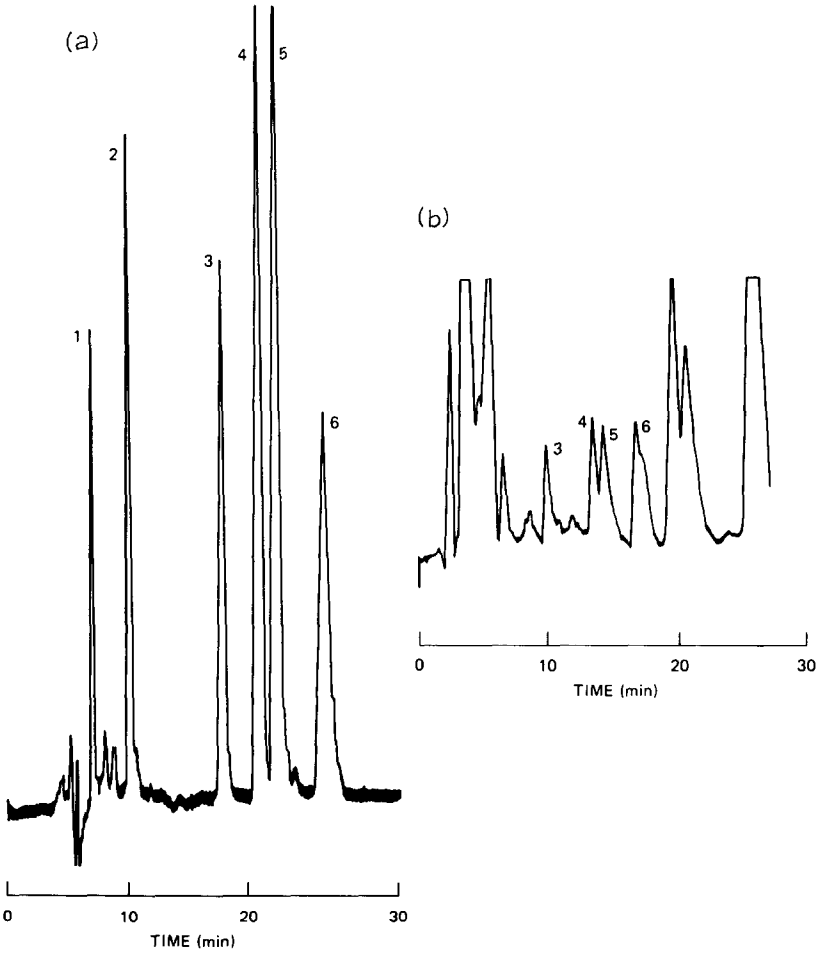


Fig. 3. Detection of munitions following adsorption and desorption using Porapak-R. (a) ED, 100 nA f.s.; injection volume, 20 μl; (b) UV, 210 nm, 0.02 a.u.f.s.; injection volume, 50 μl. Peaks: 1 = HMX (8 μg/ml), 2 = RDX (2 μg/ml), 3 = NG (4 μg/ml), 4 = 2,6-DNT (2 μg/ml), 5 = 2,4-DNT (2 μg/ml) and 6 = PETN (6 μg/ml).

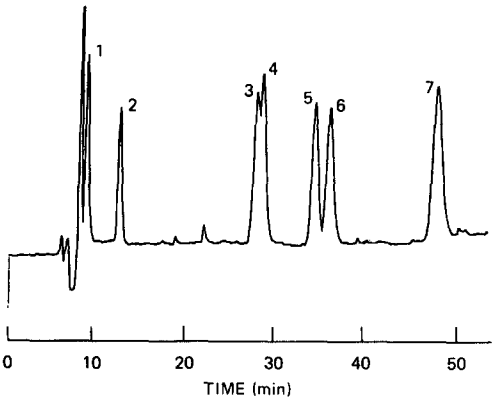


Fig. 4. Separation of munitions by LC–ED. Peaks: 1 = HMX, 2 = RDX, 3 = TNT, 4 = NG, 5 = 2,6-DNT, 6 = 2,4-DNT and 7 = PETN.

using a new DuPont Zorbax-ODS column and was the best separation we obtained of TNT and NG. After further use of the column (about 30 injections), the NG and TNT peaks could no longer be resolved. With the present chromatographic system, we have not yet been able to achieve a satisfactory separation of these two munitions. However, with the exception of the HMX (which is eluted close to the solvent front), good resolution and reproducibility of the other munitions peaks were consistently achieved.

DuPont Zorbax ODS (5 μm) and Alltech Spherisorb ODS (5 μm) columns were used interchangeably. While both columns performed approximately equally well, the resolution of the 2,6-DNT and 2,4-DNT peaks was consistently better using the Zorbax column.

The gold–mercury thin-film electrodes were prepared carefully. The mercury film was made as thin as possible consistent with complete coverage of the electrodes. In our system, the background current at -1.0 V was usually 70–100 nA for an oxygen free mobile phase and a "good" electrode. The background current slowly increases with use, and the electrode was generally renewed when the background current exceeded about 200 nA. Considerable variation was observed for the useful lifetime for the electrodes. Sometimes as much as three weeks' use could be obtained; on other occasions, the baseline drift and noise level became intolerable after a few days. In general, our practice was to renew the electrode weekly (more often if necessary) when working with the resin-processed samples. For overnight conditions, the voltage was maintained on the electrode, and the mobile phase flow-rate was reduced to 0.1 ml/min. The next morning, about 30–45 min were required for stabilized operative conditions. If the measurement of HMX and RDX is not required, the operative voltage can be reduced to -0.8 V, which drastically reduces the background current and extends the useful life of the electrode. While long term performance of the gold–mercury electrode leaves something to be desired, it does provide a system which responds more or less uniformly and selectively to the nitro organics. Since most environmental samples associated with munitions production and use would be analyzed for these compounds, the detector provides a useful tool for quantitative

TABLE I

ANALYSIS OF MUNITIONS IN TEST SAMPLES

Solv. ext. = solvent extraction.

Sample	*Method*	*Concentration μg/l (average ± S.D. for n = 3)*				
		HMX	*RDX*	*TNT*	*2,4-DNT*	*2,6-DNT*
1	Porapak-R	3690 ± 390	15,000 ± 1450	10,200 ± 1610	93.2 ± 12.4	
	Porapak-S	3650 ± 334	15,400 ± 1510	10,400 ± 852	101.1 ± 13.6	
	XAD-4	3390 ± 700	19,500 ± 832	12,200 ± 4060	95.2 ± 13.6	
	Solv. ext.	1630 ± 185	12,500 ± 1612	11,300 ± 1840	105.3 ± 11.6	
	Direct	2110	26,300	11,500	82.6	
2	Porapak-R	39.3 ± 4.0	193 ± 24	223 ± 4	4.8 ± 0.5	
	Porapak-S	23.5 ± 1.6	198 ± 19	218 ± 22	3.2 ± 0.3	
	XAD-4	19.0 ± 2.3	156 ± 19	178 ± 28	2.8 ± 0.1	
	Solv. ext.	15.5 ± 0.8	185 ± 15	213 ± 8	3.5 ± 0.6	
	Direct	< 50	313	213	3.1	
3	Porapak-R	8.6 ± 1.6	33.4 ± 3.6	61.7 ± 9.3	1.2 ± 0.2	1.3 ± 0.5
	Porapak-S	11.8 ± 1.3	34.1 ± 7.2	79.0 ± 8.8	1.5 ± 0.4	1.9 ± 0.6
	XAD-4	10.2 ± 1.5	32.1 ± 6.2	63.7 ± 6.3	0.7 ± 0.2	0.8 ± 0.2
	Solv. ext.	6.1 ± 0.1	29.7 ± 6.0	60.2 ± 12.3	1.2 ± 0.6	1.6 ± 0.6
	Direct	< 50	46.4	60.8	< 50	< 50
4	Porapak-R		3.0 ± 0.4			
	Porapak-S		3.3 ± 0.6			
	XAD-4		2.6 ± 0.6			
	Solv. ext.		2.9 ± 0.5			
	Direct		< 50			

analysis. In addition, nitrated by-products or degradation products of the munitions would likely be detected as well.

The analysis of RDX in Sample 4 is illustrated by the chromatograms in Fig. 5. The data are shown in Table I. The peaks represent *ca.* 3 μg/l RDX after processing 500 ml of water using the Porapak-R and Porapak-S adsorbents as well as solvent extraction. The final volume of 2 ml represents *ca.* 0.75 μg/ml RDX injected onto the column. As indicated by the similarity of the peak heights and the data in Table I, the recovery of RDX by the three methods was comparable.

The combination of resin adsorption with HPLC–ED analysis was compared with on-site direct aqueous injection (HPLC–UV at 235 nm) of a series of water samples. The results are shown in Table I. The results from the three resins for all samples were comparable. The agreement between the resin adsorbed samples and the solvent partition is reasonable for all compounds at all levels. There does appear to be a low bias in the measurement of RDX at the higher levels when the resins are used. This bias could have been due to the fact that different lots of standards were used. The concentrations obtained with HPLC–ED for the samples given in Table I were compared with HPLC–UV measurements at 254 nm as a quality assurance measure. The agreement between the mean values for each detector was typically

TABLE II

RESIN BREAKTHROUGH STUDIES USING WATER FROM SAMPLE 1

Component	*Concentration in water (μg/l)*	*Breakthrough for resin*					
		*XAD-4**		*Porapak-R*§		*Porapak-S*§§	
		*Conc. (μg/l)***	*Percentage****	*Conc. (μg/l)***	*Percentage****	*Conc. (μg/l)***	*Percentage****
HMX	2110	816 ± 353	39	< 10	< 0.5	34.5	1.6
RDX	26,300	6940 ± 3170	26	7.4	0.03	391	1.5
TNT	11,500	1490 ± 1360	13	6.6	0.06	< 10	< 0.09
DNT	82.6	< 10	< 12	< 10	< 12	< 10	< 12

* Average ± S.D. for $n = 3$.

** Concentration in water passed through cartridge. < 10 = Not detected, but limit of detection used to calculate upper bound on breakthrough.

*** Percentage breakthrough = concentration in water passed through cartridge/concentration in original water sample × 100%.

§ Average for $n = 2$.

§§ Result for $n = 1$.

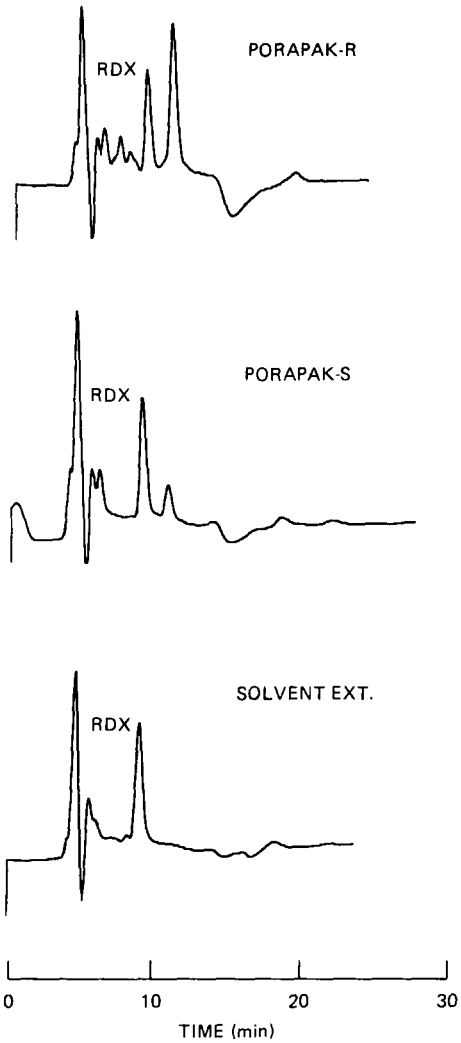


Fig. 5. Analysis of RDX in Sample 4.

within 10%. This comparison could be achieved only with RDX, TNT and the two DNT isomers because the UV detector would not respond to HMX, NG and PETN under the stated conditions.

Flow-rate of the water through the resins was greatest for XAD-4, followed by Porapak-S and Porapak-R. Because of the high levels found in Sample 1, the eluate from the resins was analyzed directly in order to determine the degree of breakthrough. The results are shown in Table II. It is clear that the Porapak resins outperform the XAD-4 in terms of capacity for the components in this sample. However, more important is the relative behavior of each resin toward the components. The XAD-4 behaves in a nonspecific manner. Adsorption on the XAD-4 is related primarily to hydrophobicity. Thus, breakthrough of HMX is greatest, followed by

RDX and TNT respectively. This is precisely in decreasing order of polarity. On the other hand, the Porapaks appear to behave in a manner consistent with specific adsorption of nitro compounds, the breakthrough being more or less equivalent for the four components. The implications for field sampling are that the XAD-4 capacity will be more closely related to the total organic load than to the total munitions load, while the capacity of the Porapaks will be more closely related to the total munitions load. Subsequent work has suggested that other nitro compounds are adsorbed strongly on the Porapaks. Even the very polar SEX or TAX were retained quantitatively, as shown in Table III. Thus, the Porapaks appear to have significant advantages over XAD-4 for this application. This is interesting in view of the historical preference for XAD resins in sorbent sampling systems.

TABLE III

BREAKTHROUGH STUDIES ON WASTEWATER EFFLUENT

Component	*Concentration in water (μg/l)*	*Breakthrough for resin*					
		XAD-4		*Porapak-R*		*Porapak-S*	
		*Conc.**	*%***	*Conc.**	*%***	*Conc.**	*%***
SEX	5030	3000	60	160	3.1	890	18
TAX	960	680	71	< 50	5.2	160	17
HMX	440	220	50	< 50	8.8	< 50	8.8
RDX	230	100	43	< 50	22	< 50	22

* Concentration in water passed through cartridge (μg/l). < 50 = Not detected, but used to calculate upper bounds on breakthrough.

** % = concentration × 100 in water passed through cartridge/concentration in original water.

Several peaks other than the RDX peak were observed, particularly from the Porapak resins, as noted from the chromatograms in Fig. 5. These extraneous peaks appeared to result from resin impurities. Considerable variability in interferences was observed throughout this work (resin batch to batch, treatment, etc.); however, it must be noted that the quantitation of the RDX peak at three times the detection limit was not impaired.

The performance of the three resins *vs.* solvent partition was compared in another way: stability. A set of triplicate samples was analyzed at 3-, 6- and 9-week intervals. The HMX and RDX were stable for the entire period on the resin, while the aqueous samples were stable for *ca.* three weeks. TNT appeared to be less stable, being degraded after *ca.* three weeks on all resins and in the water. No particular resin offered any advantage in this regard.

In summary, a method has been developed which allows the determination of a wide range of nitro organic compounds in environment waters. The method is based on HPLC–ED and resin adsorption using Porapak resins. The sensitivity of the technique is such that detection limits approach 1 μg/l for many components. Analysis time is approximately two hours per sample for isolation and quantitation although many samples can be prepared simultaneously. The major drawback appears to be the inherent problem of oxygen in the system. Current work is addressing this problem.

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