Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Water Using Solid-Phase Extraction and Gas Chromatography–Electron Capture Detection: Comparison With High-Performance Liquid Chromatography

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Abstract

An analytical method for nitroaromatic, nitramine, and nitrate-ester explosives and co-contaminants in water based on solid-phase extraction (SPE) and gas chromatograph-electron capture detector (GC–ECD) is described. Samples are preconcentrated using cartridge or membrane SPE followed by elution with acetonitrile. The extract is compatible with GC and liquid chromatography, allowing direct comparison of concentration estimates obtained by different methods of determination and confirmation based on different physical properties. Quantitative GC analyses are obtained with deactivated direct-injection port liners, short wide-bore capillary columns, and high linear carrier gas velocities. Recoveries are 90% or greater for each of the nitroaromatics and nitrate esters and greater than 70% for nitramines and amino-nitrotoluenes. Concentration estimates for well water extracts from military sites analyzed by GC–ECD and high-performance liquid chromatography (HPLC) methods show good agreement for the analytes most frequently detected (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, hexahydro-1,3,5-trinitro-1,3,5-triazine, 2,4,6-trinitrotoluene, and 1,3,5-trinitrobenzene). The GC provides lower method detection limits than HPLC for most analytes, but accurate calibration is more difficult. The ultraviolet detector used for HPLC has a much greater linear range than the ECD. The GC requires more care than the HPLC. Specifically, the injection port liner must be changed frequently for accurate determinations.

Introduction

Nitroaromatic and nitramine explosives are present in the groundwater at many military installations in the United States (1) and Europe (2). Potential contamination of drinking water has led to extensive networks of groundwater-monitoring wells. Water samples from wells in the U.S. are generally analyzed by U.S. Environmental Protection Agency SW-846 Method 8330 (3). This method involves the extraction of water samples using either salting-out or solid-phase extraction and analysis of the acetonitrile (AcN) extract using a high performance liquid chromatograph equipped with an ultraviolet detector (HPLC–UV) (4). Certified reporting limits (5) range from 0.03 to 0.3 µg/L (4,6) and are sufficiently low enough for determining if water quality criteria are met for most of the analytes for which criteria have been determined.

Because of the prevalence of gas chromatographs (GC) in environmental labs, an alternative method for explosives based on GC would provide another option for analysis. Some of the Method 8330 analytes are already included as analytes in current GC SW-846 methods (3). These include the nitroaromatics nitrobenzene (NB), 2,4-dinitrotoluene (DNT), 2,6-DNT, 1,3-dinitrobenzene (DNB), 1,3,5-trinitrobenzene (TNB), and the isomers of nitrotoluene (NT). The physical properties of some of the other Method 8330 analytes, principally the nitramines, would lead one to believe that GC analysis would be impractical. High melting points, low vapor pressures, and thermal lability are characteristic of the nitramines. For example, the melting point of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is 275°C (7), and HMX is reported to decompose prior to boiling. In addition, the vapor pressure of HMX (10^{-14} torr at 20°C) (8) is well below what is typical for GC analytes. Nonetheless, explosives (including the nitramines) have been determined by GC for many years, primarily for forensic applications such as determination of post-blast residues (9). While GC methods for the determination of some explosives in water are reported (2,10–18), environmental analyses of explosives have been dom-

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inated by HPLC protocols for the most part because quantitative GC results have been limited to the nitroaromatics (2).

Hable et al. (17) were the first to report the quantitative GC determination of HMX in water. The nitroaromatics (2,4-DNT, 2,6-DNT and trinitrotoluene {TNT}) were extracted using toluene, and the more polar nitramines (HMX and hexahydro-l,3,5-trinitro-l,3,5-triazine {RDX}) were extracted from a separate subsample with glass-distilled iso-amyl acetate. Successful GC analysis was obtained using deactivated injection port liners, high injection port temperatures, and short, wide-bore capillary columns. Another factor was the elimination of contact between the analytes and metal parts of the injector. Elution of intact HMX (which is not a thermal degradation product) from the GC column was confirmed by GC-MS. The certified reporting limits were similar to those obtained using Method 8330 (19) for RDX, TNT, and 2,4-DNT; significantly higher for HMX; and lower for 2,6-DNT.

The goal of our work was to develop a GC method that included all the Method 8330 analytes in a single extraction step and uses commercially available and routinely used instrumentation. We included other analytes that might be present in explosives-contaminated water as well. We added 3,5-dinitroaniline (DNA), the biotransformation product of TNB, and the nitrate esters nitroglycerine (NG) and pentaerythritoltetranitrate (PETN). To complement Method 8330, we sought to use a compatible sample preparation method so that a single extract could be subjected to both GC and HPLC analysis, thereby allowing direct comparisons of concentration estimates obtained by the two methods and providing another method for analyte confirmation.

Experimental

Calibration Standards

Analytical standards were prepared from standard analytical reference material obtained from the U.S. Army Environmental Center (Aberdeen Proving Ground, MD). Stock solutions (1 g/L) were prepared in acetonitrile. Calibration standards were prepared in acetonitrile by dilution of the stock solutions.

Matrices

Blank matrices used for spike recovery and method detection limit studies were reagent-grade water (type 1, MilliQ, Millipore, Bedford, MA) and groundwater from a domestic well in Weathersfield, VT. Field-contaminated samples were obtained from Louisiana AAP (Doyline, LA), Kansas AAP (Parsons, KS), Umatilla Army Depot (Hermiston, OR), and CFB-Valcartier (Quebec, Canada).

Sample Preparation

For each sample, up to 1000 mL of water was preconcentrated using solid-phase extraction (SPE). Both Waters Sep-Pak Vac Porapak RDX Cartridges (Milford, MA) and Empore SDB-RPS 47-mm membranes (St. Paul, MN) were used. The Sep-Pak Vac Porapak RDX cartridges were conditioned according to the manufacturer's directions, which specify passage of acetonitrile followed by reagent-grade water through the solid phase prior to the water sample. For the SDB-RPS membranes, Empore recommends rinsing the membranes with acetone, isopropanol, methanol, and then water. We followed this solvent sequence, except that after methanol and before water, we also rinsed with acetonitrile, which thereby became the last organic conditioning solvent. After passage of each water sample through the solid phase, air was drawn through the solid phase for 15–20 min to remove as much residual water as possible. The solid phases were eluted with 4–5 mL of acetonitrile, and each extract was directly injected into the GC–ECD. When necessary, field sample extracts were diluted with acetonitrile so that peak heights would be bracketed by calibration standards.

Solvents used for conditioning the solid phases were HPLC grade from Sigma-Aldrich (Milwaukee, WI) or Baker (Phillipsburg, NJ).

Instrumentation

We configured the GC based on the work of Hable et al. (17). The GC was a Hewlett-Packard HP5890 (Wilmington, DE) with an electron capture detector (Ni^{63}). The column was a J&W Scientific (Folsom, CA) DB-1 (6 m × 0.53-mm i.d., 1.5-µm fused-silica 100% polydimethylsiloxane). The injection port liners were Restek (Bellefonte, PA) direct injection Uniliners (deactivated). The injection port temperature was 250°C (varied from 200 to 300°C). The injection volume was 1 µL. The carrier gas was hydrogen (linear velocity varied from 30 to 185 cm/s) and the makeup gas was nitrogen (38 mL/min). The oven program was as follows: 100°C for 2 min, to 200°C at 10°C/min, to 250°C at 20°C/min, held for 5 min. The detector temperature was 300°C. Temperature programs for confirmation columns are given in figure captions later in this paper.

Results and Discussion

GC Setup

Injection Port

The GC injection port is frequently the site of loss of thermally labile analytes (20). Deactivation of the liners reduces loss (2) but is a laborious process involving acid soaking, water rinsing, silanization in an inert atmosphere, and solvent rinsing. In the last few years, deactivated injection port liners have become commercially available, which has greatly facilitated the analysis of labile analytes.

Trace analysis by GC may be performed by splitless or direct injection. Splitless injection is not generally appropriate for reactive or compounds with high boiling points, such as explosives, due to adsorption, condensation, and discrimination against high-boiling compounds in the injection port. However, splitless injection is required for narrow-bore capillary columns. Wide-bore capillary columns (0.32- and 0.53-mm i.d.) permit direct injection in which all sample and solvent is transferred to the column. The column press-fits into the hourglass-shaped end of the glass inlet liner, eliminating contact with metal parts in the injector. Direct injection liners are commercially available that fit split/splitless ports or packed-column injection ports modified

to accept wide-bore capillary columns. We chose to use deactivated direct injection Uniliners available from Restek. Uniliners are available for both split/splitless and packed ports.

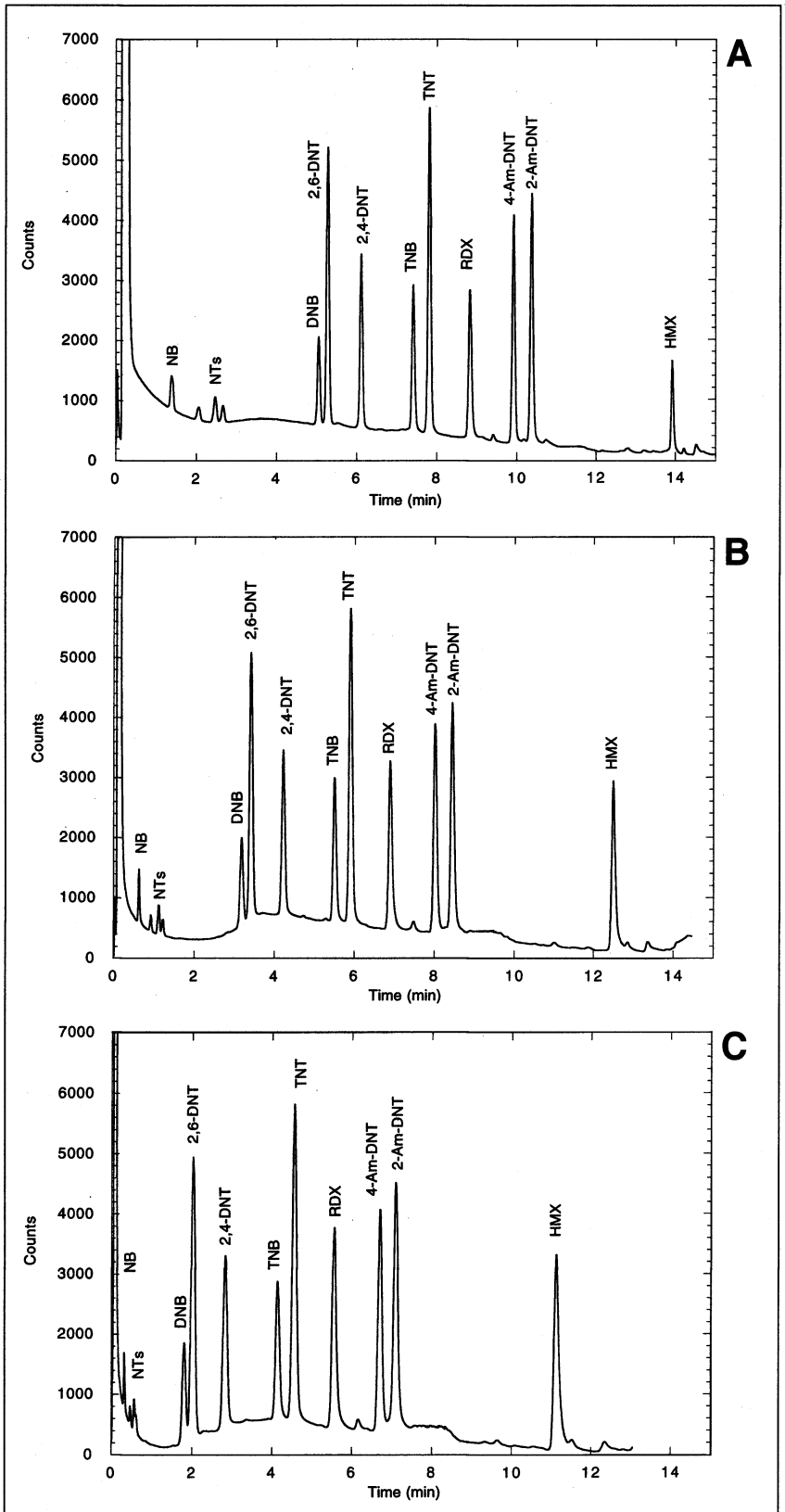

Figure 1. Calibration standard (50 µg/L) analyzed using DB-1 at three carrier gas velocities. Higher linear velocities resulted in higher HMX peak heights. Linear velocities: A, 44 cm/s; B, 76 cm/s; C, 126 cm/s.

Selection of analytical column

Initially, we tested a 0.53-mm i.d. polydimethylsiloxane (DB-1) column at a length (15 m) typically provided by the manufacturer to see if the Method 8330 analytes were resolved. With the exception of HMX, which did not produce a peak, the 8330 analytes eluted as individual peaks in order of decreasing vapor pressure, indicating that this column provides adequate resolution for these analytes. However, the additional analyte PETN, which has a vapor pressure almost identical to that of RDX, coeluted with RDX. At explosives-contaminated sites, RDX is by far the more commonly found of these two analytes. Further work with mid-range polarity columns resolved PETN from RDX but led to co-elutions with other analytes.

We experimented with different column temperature programs and injected a high-concentration solution of HMX onto the 15-m column. With a high temperature (250°C) isothermal run, HMX eluted as a broad, jagged peak on the 15-m column. We then shortened the GC column to 6 m, as suggested by Hable et al. (17) and found that HMX now eluted as a sharp peak (Figure 1). This dramatic improvement was not caused by the total time in the GC but rather the decreased column length and therefore less surface area to which the analyte was exposed. Tamari and Zitrin (21) reported similar results when they observed that PETN and RDX failed to elute intact from a 30-m column but did elute from a 15-m column. Thus, the length of a typical GC capillary column is an important consideration for successful chromatographic analysis of the most thermally labile explosives.

We also tested an Alltech (Deerfield, IL) MultiCapillary SE-54 (5% phenyl methylpolysiloxane) column. These columns are only 1 m in length and are composed of a bundle of over 900 liquid-phase-coated 40-µm capillaries. They provide rapid analysis of pesticides and accommodate high carrier gas velocities, so we reasoned that they might be suitable for the analysis of explosives. We tested numerous chromatographic conditions and found that the column was suitable for the analysis of NB, the nitrotoluenes, DNB, and the DNTs. Resolution of the other analytes was poor; the peaks for TNB, TNT, and RDX were uncharacteristically small, and HMX did not elute at all. Here again, large internal column surface area, not total time in the GC, may contribute to HMX loss.

Confirmation columns

We tested four 0.53-mm i.d. columns for suitability as confirmation columns. In order of increasing polarity, these columns were J&W Scientific DB1301 (6% cyanopropylphenyl

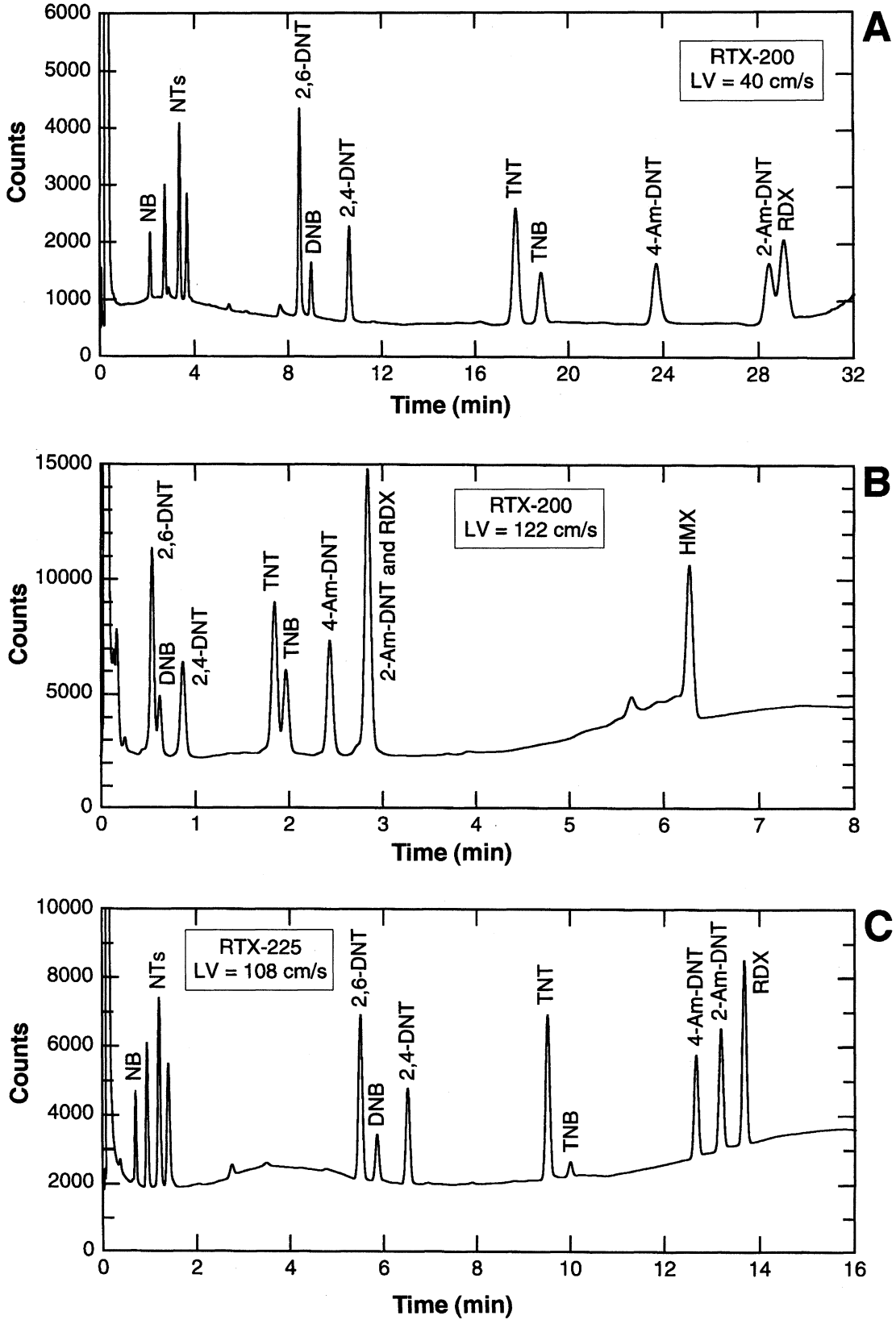

Figure 2. Chromatograms obtained on confirmation columns. DNB, 2,6-DNT, 2,4-DNT, TNB, TNT, 4-Am-DNT, 2-Am-DNT at 50 µg/L; RDX at 100 µg/L; and NB, *o*-NT, *p*-NT, *m*-NT, and HMX at 500 µg/L. A: oven program, 100°C for 1.2 min, to 140°C at 5°C/min, to 160°C at 1°C/min, to 250°C at 20°C/min and held; injector, 250°C; detector, 290°C. B: oven program, 150°C for 1 min, to 250°C at 20°C/min and held; injector, 270°C; detector, 290°C. C: oven program, 100°C for 2 min, to 220°C at 10°C/min and held for 8 min; injector, 220°C (column maximum); detector, 250°C.

methylpolysiloxane) and DB-17 (50% phenyl methylpolysiloxane) and Restek RTX-200 (crossbond trifluoropropyl methylpolysiloxane) and RTX-225 (50% cyanopropylmethyl–50% phenyl methylpolysiloxane). The DB-1301 was not acceptable because TNB coeluted with TNT and DNB coeluted with 2,6-DNT. The DB-17 was not suitable because TNB coeluted with TNT. The Restek RTX-200 resolved the 8330 analytes at low linear velocity, but HMX was not detected (Figure 2). At high linear velocity, HMX was detected (Figure 2, Table I), but PETN coeluted with RDX and 2-Am-DNT, and DNA was not resolved from 4-AmDNT (Table I). Finally, on the RTX-225, tetryl coeluted with RDX, and HMX was not detected (Figure 2). However, in subsequent analyses of well water samples from Louisiana AAP, we found this column to be excellent for confirmation of the amino-DNTs. Thus, extracts must be analyzed under the appropriate conditions for confirmation. Both the RTX-200 and RTX-225 look promising for confirmation because the elution order of several analytes is the reverse of that on the DB-1. For example, 2,6-DNT and DNB are reversed in order, as are TNT and TNB. In addition, RDX elutes after the amino-DNTs, whereas it elutes before the amino-DNTs on the DB-1 (Table I).

Effect of carrier gas linear velocity

While testing various temperature programs and carrier gas linear velocities, we noticed that the HMX peak height changed significantly with changes in linear velocity (Figure 1). We systematically changed the linear velocity to document this effect.

Van Deemter curves indicate that optimum linear velocity for peak resolution is 26 cm/s when using hydrogen carrier gas and a 0.53-mm i.d. column. When using direct injections, the manufacturer of the inlet liners recommends using twice the optimum linear velocity to prevent tailing of the solvent front and to sharpen early eluting peaks. We tested the effect of increasing carrier gas linear velocity over the range of 30 to 185 cm/s and found a significant increase in response from HMX, RDX, NG, and PETN (Figure 3). For example, no peak was observed for HMX at the lowest linear velocity tested. The linear velocity was increased to 55 cm/s and HMX eluted as a sharp peak. Thereafter, the HMX peak height approximately doubled with each doubling of the linear velocity (Figure 3). Some degradation in peak resolution did occur. Widths of the later-eluting peaks increased with increasing carrier gas linear velocity, and the peak for DNA merged with the peak for 4-amino-DNT. Thus, a mid-range carrier gas velocity would be appropriate for most analyses.

The calibration factors for 50 µg/L solutions of all the analytes were determined at three carrier gas velocities (Table II). The calibration factors for HMX, NG, and PETN were two to three times greater at the highest linear velocity compared with the lowest linear velocity. Also, the response of the ECD varied considerably from analyte to analyte. For the nitrotoluenes, the calibration factor for TNT was more than ten times greater than those for the mono-NTs. This variability in relative response needs to be considered when preparing calibration standards and in setting expectations for detection limits.

Table I. Retention Times (min) Obtained for Analytical and Confirmation Columns using Carrier Gas Linear Velocities and Temperature Programs*

	DB-1‡			RTX-200		RTX-225
Analyte†	LV§ = 126 (cm/s)	LV= 76 (cm/s)	LV= 44 (cm/s)	LV = 40 (cm/s)	LV = 122 (cm/s)	LV= 108 (cm/s)
NB	0.32	0.63	1.38	2.15		
o-NT	0.47	0.92	2.06	2.78		0.95
m-NT	0.57	1.12	2.47	3.40		1.20
p-NT	0.62	1.22	2.69	3.72		1.40
NG	1.18	2.00	3.84	8.57	0.52	6.25
DNB	1.84	3.18	5.05	9.01	0.63	5.86
2,6-DNT	2.07	3.42	5.28	8.51	0.55	5.50
2,4-DNT	2.88	4.22	6.12	10.64	0.88	6.51
TNB	4.19	5.50	7.42	18.90	1.98	9.99
TNT	4.61	5.91	7.82	17.81	1.86	9.51
PETN	5.62	6.83	8.79	28.52	2.74	11.57
RDX	5.62	6.89	8.83	29.19	2.86	13.66
4-Am-2,6-DNT	6.77	8.02	9.92	23.80	2.45	12.65
3,5-DNA	6.83	8.11	10.07	26.08	2.65	13.32
2-Am-4,6-DNT	7.17	8.45	10.38	28.57	2.85	13.17
Tetryl	8.05	9.34	11.26	32.11	3.54	13.65
HMX	11.21	12.50	13.92	not eluted	6.29	not eluted

* Retention times reflect those in Figure 2.
† Abbreviations: NB, nitrobenzene; DNB, dinitrobenzene, TNB, trinitrobenzene; NT, nitrotoluene; DNT, dinitrotoluene; TNT, trinitrotoluene; RDX, hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; DNA, dinitroaniline; NG, nitroglycerine; PETN, pentaerythritoltetranitrate.
‡ Temperature program for DB-1: 100°C for 2 min, to 200°C at 10°C/min, to 250°C at 20°C/min and held.
§ Linear velocity.

Effect of injection port temperature

Hable et al. (17) found increased HMX response with increasing injection port temperature and recommended an injection port temperature of 270°C for the determination of TNT, DNTs, RDX, and HMX. High injection port temperatures are needed to volatilize the nitramines. We reexamined the effect of injection port temperature at high linear carrier gas velocity (133 cm/s) for the 8330 analytes and NG, PETN, and DNA. We found that maximum GC response was obtained at different temperatures for the different analytes. In general, the lowest temperatures tested (200–220°C) resulted in the highest response for the nitrotoluenes and nitrate esters. Higher temperatures (250–270°C) were best for HMX, RDX, the amino-DNTs, and DNA. However, the effect of injection port temperature was minor for most of the analytes. Only HMX, NG, and PETN showed somewhat consistent trends. An injection port temperature of 250°C would be suitable for most analyses.

Calibration

Traditional ECDs typically have a narrow linear range (approximately 40-fold), with a dynamic range of about 1000-fold (22). This narrow linear range is inconvenient for quantitative analysis of samples that can vary over three orders of magnitude in analyte concentrations.

From the shapes of the curves of peak height data for TNT, 2-Am-DNT, and RDX over the range of 0.5 to 100 µg/L (Figure 4), which are representative of calibration curves for the other analytes, we see that fitting the data to straight lines, whether through the origin or not, is not at all appropriate. This very limited linear range of the ECD is a disadvantage in comparison with HPLC–UV, which has a broad linear range. For GC–ECD, sample

extracts would need to be diluted within the proper calibration range. For samples with multiple analytes at varying concentrations, a single extract may require several determinations at different dilution factors. Alternatively, non-linear models in the form of second order polynomials fit the data over broader concentration ranges (Figure 4). Using non-linear calibration models complicates computations, but reduces the number of reanalyses of multianalyte samples.

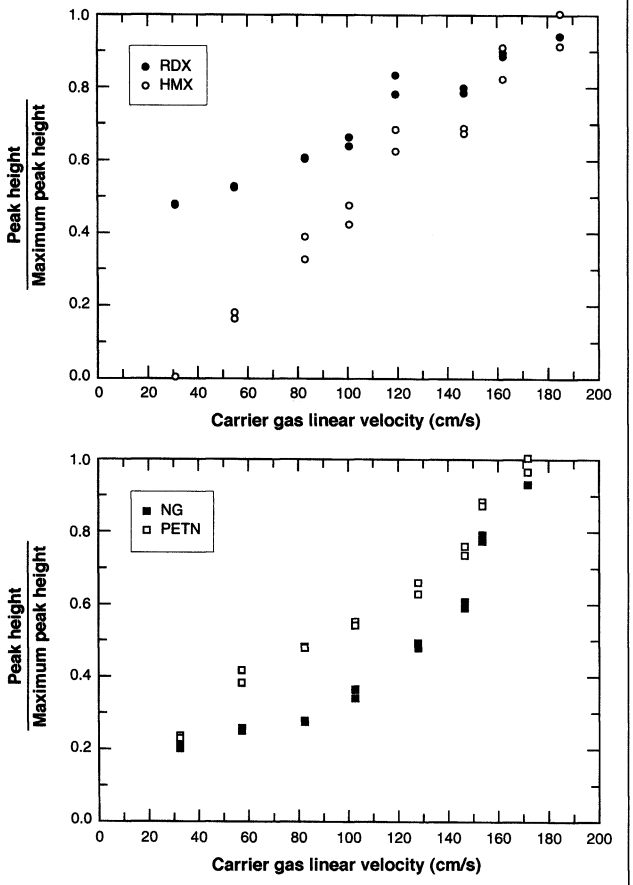

Figure 3. Effect of carrier gas linear velocity on peak height.

Table II. Calibration Factors (Peak Height/[µg/L]) Obtained for 1-µL Injections of 50-µg/L Solutions onto a DB-1 Column at Different Carrier Gas Linear Velocities

Analyte	Calibration factors (peak height/[µg/L]) 126 cm/s	76 cm/s	44 cm/s
TNT	104	106	109
2,6-DNT	91	90	92
2-Am-DNT	80	77	83
RDX	79	57	52
HMX	75	59	32
4-Am-DNT	71	71	76
DNA	69	65	69
2,4-DNT	58	55	58
Tetryl	46	48	59
TNB	45	48	50
DNB	30	29	28
NB	18	21	9.9
PETN	17	13	8.1
NG	12	4.9	4.5
m-NT	7.5	7.0	7.4
o-NT	5.9	6.6	3.6
p-NT	2.5	5.8	4.5

Instability of low concentration tri-nitroaromatic standards

The low concentration calibration standards for TNB, TNT, and tetryl were unstable when left at room temperature in amber autosampler vials. Previous stability studies had shown that these analytes were stable for several days in acetonitrile (23). However, the standards in this previous study were much higher in concentration (3 mg/L). We found that analyte loss was most noticeable at the lower concentrations (50 µg/L versus 500 µg/L), differed with different brands of acetonitrile, and was slowed by refrigeration of the solution. The decreases in concentrations of TNB and TNT were confirmed by HPLC to ascertain that the loss was not associated with GC analysis. Only the tri-nitroaromatics exhibited this instability. We were particularly concerned about this instability because samples and standards could potentially sit in an autosampler for several hours in close proximity to a heated injection port and GC oven vent. The autosampler we used (HP 6890) was designed so that a coolant could be circulated through the tray containing the sample vials. With this modification, the standards were stable over a typical 12-h analytical shift. The solid-phase extracts of water samples did not exhibit instability, which led us to suspect that residual water from the SPE might stabilize the extracts. However, experiments to establish a link between analyte stability and moisture in the acetonitrile were inconclusive.

Residual water in AcN

Solid-phase extracts will inevitably contain some water. For mid- to non-polar elution solvents, this water is removed from the solvent with anhydrous sodium sulfate. As stated previously, we wanted to develop a method in which the sample extract could be analyzed by both GC and RP-HPLC using Method 8330. Acetonitrile is the most efficient solvent for extraction of the Method 8330 analytes, especially the nitramines. Polar solvents such as acetonitrile are not readily dried.

We prepared acetonitrile solutions with water concentrations of 0–20% and analyte concentrations of 25 µg/L DNB, 2,6-DNT, 2,4-DNT, TNB, TNT, 4-Am-DNT, and 2-Am-DNT; 50 µg/L RDX; and 250 µg/L HMX. Using blocked analysis of variance (ANOVA) to compare mean peak heights, we found no significant difference among 0, 10, 15, and 20% water. A small difference was observed for 5% water.

We also made a series of standards (2.5–30 µg/L) in acetonitrile containing water at a concentration of 10%. We compared the GC response of standards with and without water by linear regression. Slopes ranged from 0.977 to 1.145, bracketing the expected value of 1.00. However, repeated injections of standards containing 10% water resulted in tailing peaks and decreased peak heights of the nitramines and the amino compounds. We suspect that the water degrades the deactivation layer of the injection port liner. Therefore, air-drying of the solid phase prior to elution with acetonitrile is important if the extract is to be analyzed by GC.

Feasibility of SPE and GC–ECD for explosives

Initial spike recovery

SPE has been used to concentrate explosives from water for many years (19). Problems such as low recovery of the nitramines and interfering peaks in HPLC chromatograms have been solved (24). We performed an initial spike recovery study using the two SPE protocols that are expected to be included in SW-846 update IV for Method 8330A. These protocols specify preconcentration with Empore SDB-RPS (47-mm diameter) disks or the Water Sep-Pak Vac Porapak RDX cartridges and analyte elution with acetonitrile. The purpose of this initial spike recovery was to determine if a solid-phase extract prepared for analysis by Method 8330 could also be analyzed by GC–ECD.

Using both membranes and cartridges, we preconcentrated duplicate 50-mL samples spiked at 5 µg/L aqueous concentration for most of the analytes (Table III). We divided each 5.0-mL acetonitrile extract and analyzed each by GC–ECD and HPLC–UV (the portion of acetonitrile extract used for HPLC was mixed 1:1 [v/v] with water prior to analysis). We found good recovery for all the analytes by both methods. In general, repeatability was better using HPLC–UV. Overall, the results indicated that SPE with acetonitrile elution was a feasible sample preparation procedure prior to GC–ECD.

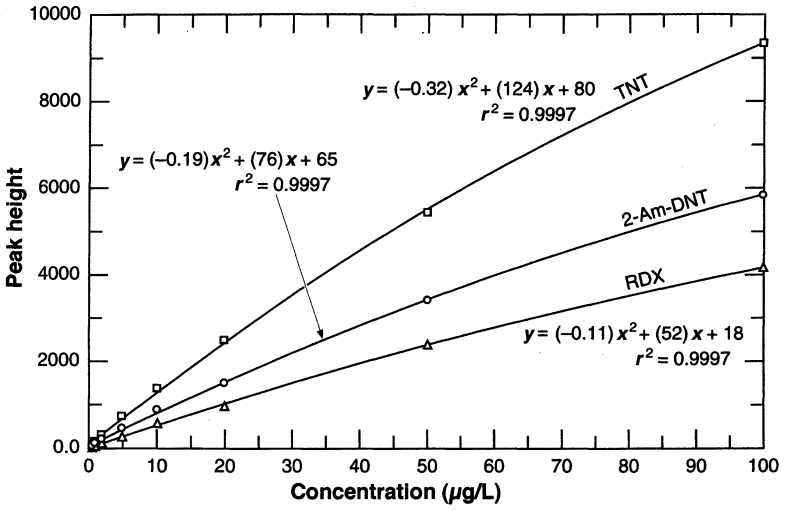

Figure 4. Calibration curves obtained for TNT, 2-Am-DNT, and RDX.

Field Samples

We analyzed several solid-phase extracts of water samples collected from various explosives-contaminated sites. These included extracts from Louisiana AAP in which 500-mL samples were preconcentrated using Porapak RDX cartridges and eluted with 5 mL AcN. These extracts were prepared and analyzed by HPLC at the U.S. Army Engineer Waterways Experiment Station (Vicksburg, MS). Water samples from Umatilla Army Depot and CFB-Valcartier were preconcentrated at U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) using either cartridges or Empore membranes, with the HPLC analysis performed at CRREL. All GC–ECD analysis was done at CRREL. Chromato-

Table III. Recovery and Repeatability of GC and HPLC Determinations of Analyte Concentrations in Spiked Water Samples

		Empore SDB-RPS (47-mm diameter)				Waters Sep-Pak Vac Porapak RDX Cartridges			
	Spiked Concentration (µg/L)	Found Concentration (µg/L) Membrane 1	Membrane 2	Average Recovery	RPD* (%)	Found Concentration (µg/L) Cartridge 1	Cartridge 2	Average Recovery	RPD† (%)
GC–ECD									
DNB	5.06	4.77	4.35	90%	9.4%	5.20	4.66	98%	11.1%
2,6-DNT	5.08	4.88	4.48	92%	8.7%	5.29	4.87	100%	8.3%
2,4-DNT	5.12	4.78	4.50	91%	6.1%	5.03	4.80	96%	4.6%
TNB	5.04	4.33	4.25	85%	1.7%	4.92	4.73	96%	3.8%
TNT	5.01	4.72	4.63	93%	1.9%	5.26	5.07	103%	3.7%
RDX	10.0	9.55	9.32	94%	2.4%	10.8	10.6	106%	1.8%
4-Am-2,6-DNT	5.06	4.51	4.28	87%	5.1%	5.05	4.58	95%	9.6%
2-Am-4,6-DNT	5.02	5.74	5.22	109%	9.5%	5.26	4.85	101%	8.1%
HMX	50.1	49.7	47.0	96%	5.6%	68.8	67.7	136%	1.6%
HPLC–UV									
DNB	5.06	5.45	5.26	106%	3.7%	5.76	5.70	113%	1.1%
2,6-DNT and 2,4-DNT†	10.2	10.6	10.2	102%	3.9%	11.0	11.0	108%	0.3%
TNB	5.04	5.62	5.18	107%	8.1%	5.71	5.67	113%	0.7%
TNT	5.01	6.04	5.48	115%	9.8%	5.97	5.99	119%	0.4%
RDX	10.0	10.3	10.3	103%	0.2%	12.5	12.1	123%	3.3%
4-Am-2,6-DNT and 2-Am-4,6-DNT†	10.1	10.8	10.3	105%	5.2%	10.6	10.6	105%	0.4%
HMX	50.1	45.9	46.9	93%	2.2%	55.5	56.2	111%	1.3%

* Relative Percent Difference.
† Peaks not resolved.

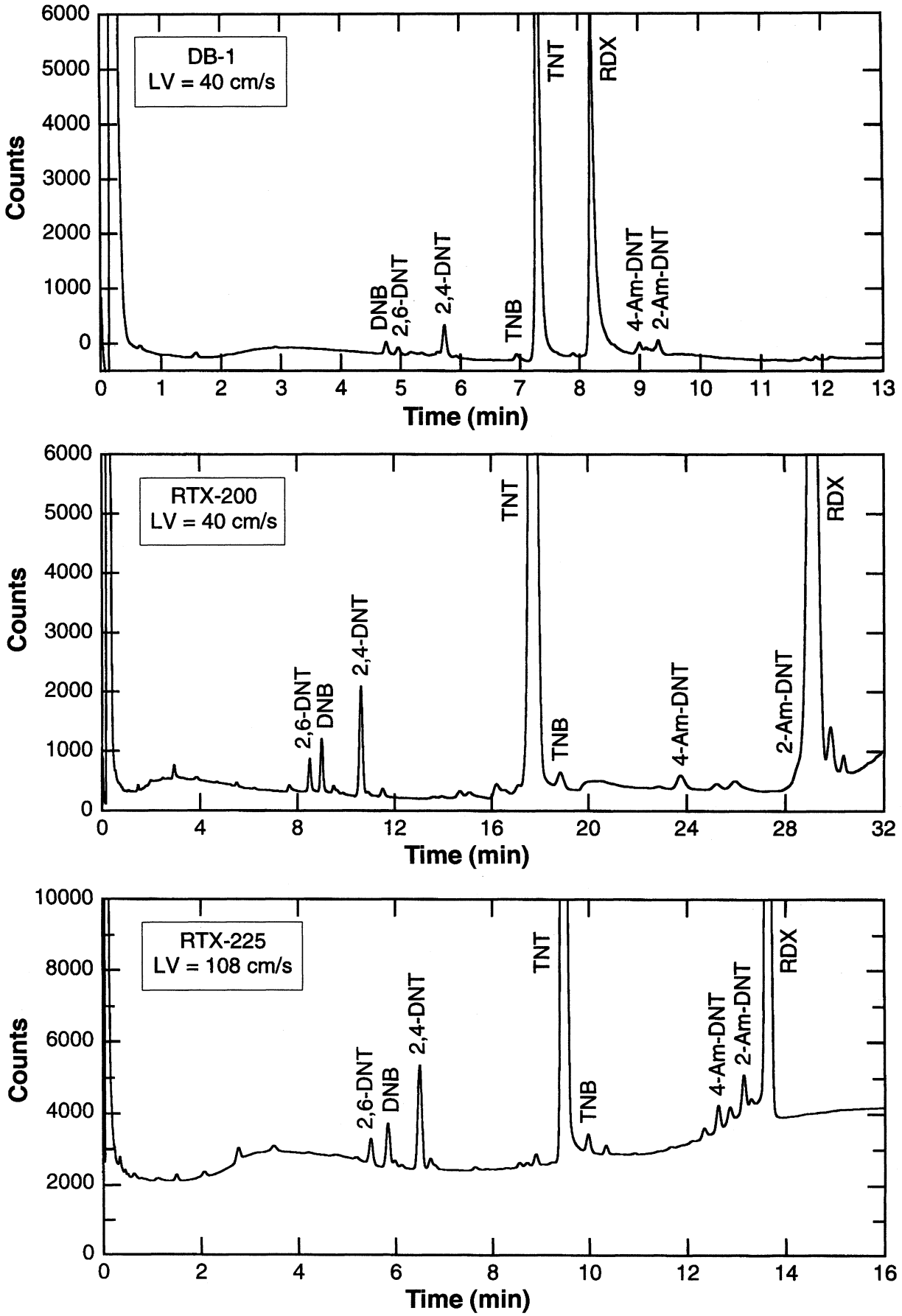

Figure 5. Chromatograms obtained on a DB-1 analytical column and RTX-200 and RTX-225 confirmation columns for one water sample obtained from Louisiana AAP.

Table IV. Concentration Estimates Obtained for the Most Commonly Found Analytes by HPLC and GC–ECD for Water Samples Collected at Explosives-Contaminated Sites

Analyte	Source	SPE method	HPLC	GC–ECD	Analyte	Source	SPE method	HPLC	GC–ECD
HMX	KSS AAP	Cartridge	0.20	0.10		LAAP	Cartridge	11800	8175
	Umatilla	Membrane	0.29	0.60		LAAP	Cartridge	23400	20833
	Umatilla	Membrane	0.22	0.59					
	Umatilla	Cartridge	0.31	0.21	TNT	LAAP	Cartridge	0.3	0.5
	LAAP	Cartridge	19	13		LAAP	Cartridge	0.4	0.1
	CFB-VALCARTIER	Cartridge	26	26		LAAP	Cartridge	0.5	0.3
	CFB-VALCARTIER	Cartridge	97	110		LAAP	Cartridge	2.4	1.2
	LAAP	Cartridge	116	109		LAAP	Cartridge	152	142
	Umatilla	Cartridge	141	179		Umatilla	Cartridge	241	233
	LAAP	Cartridge	182	147		LAAP	Cartridge	390	405
	LAAP	Cartridge	216	217		LAAP	Cartridge	2430	2876
	CFB-VALCARTIER	Cartridge	219	280		LAAP	Cartridge	2890	3721
	CFB-VALCARTIER	Cartridge	250	308		LAAP	Cartridge	7500	7781
	CFB-VALCARTIER	Cartridge	251	285		LAAP	Cartridge	10500	12168
	LAAP	Cartridge	1300	1378					
	LAAP	Cartridge	1860	1842	TNB	LAAP	Cartridge	0.1	0.02
						LAAP	Cartridge	1.0	0.4
RDX	KSS AAP	Cartridge	0.2	0.2		LAAP	Cartridge	1.9	1.0
	Umatilla	Membrane	0.27	0.20		LAAP	Cartridge	15.6	33.8
	KSS AAP	Cartridge	1.6	0.95		LAAP	Cartridge	22.3	34.2
	CFB-VALCARTIER	Cartridge	1.7	1.0		LAAP	Cartridge	649	1128
	CFB-VALCARTIER	Cartridge	2.0	0.56		LAAP	Cartridge	742	782
	LAAP	Cartridge	2.4	0.28		LAAP	Cartridge	9110	11991
	LAAP	Cartridge	3.6	0.6		LAAP	Cartridge	9150	10640
	Umatilla	Membrane	4.9	4.9					
	Umatilla	Membrane	5.2	5.1	2,4-DNT	LAAP	Cartridge	<d*	0.07
	Umatilla	Cartridge	6.5	5.2		LAAP	Cartridge	<d	0.06
	Umatilla	Cartridge	6.7	7.0		LAAP	Cartridge	<d	0.05
	LAAP	Cartridge	8.9	1.2		LAAP	Cartridge	<d	0.15
	CFB-VALCARTIER	Cartridge	29.8	37.7		LAAP	Cartridge	0.69	0.36
	CFB-VALCARTIER	Cartridge	30.9	34.7		LAAP	Cartridge	10.7	11.8
	CFB-VALCARTIER	Cartridge	33.8	44.1		LAAP	Cartridge	24.5	18.7
	LAAP	Cartridge	845	590		LAAP	Cartridge	46.8	33.6
	LAAP	Cartridge	1430	1973		LAAP	Cartridge	127	126
	LAAP	Cartridge	2060	2241		LAAP	Cartridge	142	84.8
	LAAP	Cartridge	3710	3640		LAAP	Cartridge	442	341

* In several extracts, 2,6-DNT was detected by GC–ECD but not by HPLC.

Table V. Recovery Data and MDLs for Various Analytes for 500 mL Water Samples Preconcentrated to 5.0 mL Acetonitrile using SDB-RPS Empore Disks

Analyte	Mean found concentration* (µg/L)	Target concentration (µg/L)	Mean recovery (%)	RSD (%)	MDL (µg/L)
DNB	0.197	0.20	99	9.7	0.06
2,6-DNT	0.187	0.20	93	7.1	0.04
2,4-DNT	0.208	0.20	104	7.6	0.05
TNB	0.189	0.20	94	7.7	0.05
TNT	0.233	0.20	116	8.0	0.06
RDX	0.176	0.20	88	7.2	0.04
4-Am-2,6-DNT	0.150	0.20	75	11.2	0.05
2-Am-4,6-DNT	0.174	0.20	87	11.6	0.06
Tetryl	0.190	0.20	95	8.3	0.05
DNA	0.148	0.20	74	9.2	0.04
NB	0.969	1.0	97	7.1	0.2
o-NT	0.927	1.0	93	5.1	0.2
m-NT	0.918	1.0	92	4.6	0.1
p-NT	0.897	1.0	90	5.3	0.2
NG	0.918	1.0	92	5.5	0.2
PETN	0.992	1.0	99	4.8	0.2
HMX	1.58	2.0	79	8.1	0.4

* Mean of seven replicate 500-mL water samples preconcentrated using Empore SDB-RPS membranes to 5 mL AcN.

Table VI. Method Detection Limits (µg/L) for Some Target Analytes when 1-L Water Samples (Spiked Concentration of 0.01 µg/L) Were Preconcentrated to 4.0 mL Acetonitrile using Cartridge and Membrane Solid-Phase Extraction

	MDLs by GC–ECD	
Analyte	Cartridge	Membrane
DNB	0.004	0.003
2,6-DNT	0.003	0.003
2,4-DNT	0.009	0.01
TNB	0.007	0.003
TNT	0.01	0.02*
RDX	0.004	0.02*
4-Am-2,6-DNT	0.003	0.003
2-Am-4,6-DNT	0.003	0.004
Tetryl	0.009	0.01
HMX	0.004	0.008

* MDLs greater than spiked concentration and therefore not valid.

grams were obtained on the DB-1 analytical column and RTX-200 and RTX-225 confirmation column (Figure 5).

All comparisons of HPLC and GC–ECD determinations were done on extract splits. Concentration estimates obtained by the two methods of determination for the most commonly found analytes (HMX, RDX, TNT, TNB, and 2,4-DNT) (Table IV) compared favorably for most samples over a wide range of concentrations. Discrepancies between the two methods of analysis, however, do exist. The GC appeared to underestimate the concentration of RDX in some of the low-concentration samples. However, the ECD is a more selective detector, so this apparent underestimation may not be real because of an interference with HPLC. Second, tetryl was detected by GC in some Louisiana AAP extracts, but was not detected by HPLC. We suspect that when we analyzed a tetryl standard by GC, the peak we observed actually corresponds to a thermal degradation product of tetryl, possibly *n*-methyl-picramide (21). Several Louisiana AAP water samples are also contaminated with picric acid, and an unidentified co-contaminant of picric acid is potentially the source of the peak we observed on the GC. Finally, 2,6-DNT was detected by GC–ECD in almost every sample that contained 2,4-DNT. These isomers often co-elute on the LC-18 separation specified in Method 8330. However, these isomers can be resolved on other HPLC columns (25), specifically those with 3-µm phase particles, which are less rugged for routine analysis of large numbers of samples.

Almost all the extracts from field samples required dilution prior to GC–ECD analysis so that peak heights would fall within the linear calibration range. Dilution actually appeared to improve the accuracy of the GC determination of HMX when several samples were run sequentially. We suspect that dilution served to "clean-up" the extracts, diluting residual water, slowing the degradation of the deactivation layer in the injection port liner, and reducing the buildup of non-volatile co-extracted contaminants that deposit in the injection port liner. Accurate determination of HMX required that the injection port liner be changed frequently. We changed the liner each time we replaced the injection port septum (at least every 50 injections).

Spike recovery and method detection limits

To obtain an estimate of the accuracy of the GC method, we spiked seven replicate 500-mL reagent-grade water samples at the concentrations shown in Table V. The explosives were extracted from the water using Empore SDB-RPS membranes, which were eluted with 5.0 mL of acetonitrile, resulting in a preconcentration factor of 100. Found concentrations and recoveries were computed using three methods of calibration: average calibration factor, a non-linear calibration curve, and linear interpolation from the calibration curve.

Using estimates based on quadratic calibration models, recovery was 90% or greater for each of the nitroaromatics and nitrate esters. Recoveries were lower for the nitramines and amino-nitrotoluenes, but well within the acceptable range of SW-846 methods. Based on the standard deviations of the means for seven replicates, method detection limits (MDLs) were computed (Table V). These MDLs were all below water quality criteria except for the 10^{-6} increase in cancer risk for 2,6-DNT (which is 0.007 µg/L).

We obtained a lower method detection limit for 2,6-DNT (0.0025 µg/L) by extracting a greater volume of water (1 L), eluting with less acetonitrile (4.0 mL), spiking at lower concentrations (26), and using 10 replicates. We used both cartridge and membrane SPE (Table VI), and the MDLs were generally quite similar for each analyte. If the analyte of most interest is 2,6-DNT, the MDL could be lowered even more by preconcentrating a greater volume of water. We limited the volume we preconcentrated to prevent breakthrough of HMX and RDX. 2,6-DNT is well-retained on both solid phases, and the volume of water preconcentrated is more likely limited by practical considerations such as time or possible plugging of the solid phase.

Conclusion

A GC method for the determination of explosives in water was developed to serve as an alternative to and/or complement the current HPLC SW-846 Method 8330. Water samples were preconcentrated using SPE, and the acetonitrile extracts were directly injected onto a short (6 m) DB-1 analytical column. High linear carrier gas velocities resulted in higher peak heights for the nitramines and nitrate-esters, the most thermally labile analytes. Method detection limits ranged from 0.04 to 0.4 µg/L when 0.5-L water samples were preconcentrated to 5.0 mL acetonitrile. Lower method detection limits for some analytes, such as 2,6-DNT, were obtained by preconcentrating a larger volume of water.

Analysis of extracts from field samples showed good agreement between the GC–ECD and the standard HPLC method.

Potential advantages over the current HPLC method include lower detection limits, improved chromatographic resolution, and the utilization of instrumentation most commonly found in environmental labs. Disadvantages of the GC method include non-linear calibration, limited dynamic range of the detector, and increased attention to instrument maintenance (i.e., frequent changes of the injection port liner). Also, the low concentration calibration standards used for GC require refrigeration to

maintain analyte stability.

Combined use of GC–ECD and HPLC will provide an improved method for analyte confirmation, because chromatographic separations are based on different physical properties (vapor pressure and polarity) and the detectors are based on different principles (electronegativity and UV absorption).

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