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UNITED STATES ARMY ENVIRONMENTAL HYGIENE AGENCY

ABERDEEN PROVING GROUND, MD 21010-5422

FINAL REPORT

VALIDATION OF A SORBENT TUBE/HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC PROCEDURE FOR THE DETERMINATION OF EIGHT EXPLOSIVES IN WATER

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U.S. Army Toxic and Hazardous Materials Agency

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A new analytical method for the determination of eight explosives in groundwater was independently validated. The following eight explosives were studied: HMX, RDX, Tetryl, TNT, PETN, Nitroglycerin, 2,6-DNT, and 2,4-DNT. The same method had been recently developed and validated by Battelle Laboratories, Columbus Division. USAEHA Certified Reporting Limits ranged from 0.8 to 22 micrograms/Liter, whereas Battelle values had ranged from 0.9 to 15 micrograms/Liter. The method involved collection of explosives in 500 ml of groundwater onto a 600 mg Hayesep R solid sorbent cartridge, followed by elution of the cartridge with acetone. A solvent exchange to 2 ml methanol/water was performed and the solution analyzed by liquid chromatography using tandem ultraviolet/photoconductivity detectors. A study of approximately thirty potential method interferants and explosive precursors was conducted. Some of these were found to be method interferants. Some recommendations for procedural modifications are made to further improve the method.

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I. REFERENCES.

A. Bicking, M. K. L., and S. J. Summer, Evaluation of Solid Sorbent and Detector Technology for Determination of Explosives in Water, 10 February 1988, Contract No. DAAL03-86-D-0001, Battelle Columbus Laboratories.

B. USAEHA Project Scope of Work, Validation of a Sorbent Tube/High Performance Liquid Chromatographic Procedure for the Determination of Eight Explosives In Water, 28 March 1988, prepared for and approved by the U.S. Army Toxic and Hazardous Materials Agency.

C. USATHAMA Installation Restoration Quality Assurance Program, December 1985 (2d Edition, March 1987). U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland.

D. Popovich, D. J., J. B. Dixon, and B. J. Ehrlich, The Photo-Conductivity Detector -- A New Selective Detector for HPLC, Journal of Chromatographic Science, Vol.17, p.643, 1979.

E. Jenkins, T. F., P. H. Miyares, and M. E. Walsh, An Improved RP-HPLC Method for Determining Nitroaromatics and Nitramines in Water, November 1988, CRREL Special Report 88-23.

II. AUTHORITY.

A. Memorandum of Understanding between U.S. Army Health Services Command and the U.S. Army Materiel Command, 11 September 1987, subject: Installation Restoration Program.

B. AEHA Form 250-R, U.S. Army Toxic and Hazardous Materials Agency, 28 March 1988.

III. INTRODUCTION.

A. Battelle Columbus Laboratories recently developed a new procedure for determination of eight explosives in ground water under U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) contract DAAL03-86-D-0001 (reference A). The USATHAMA sought additional, independent laboratory validation of the Battelle method to obtain U.S. Environmental Protection Agency (EPA) approval of the procedure as an official EPA method. The EPA requires that a minimum of three separate laboratories perform a method satisfactorily before approval is given.

Use of trademarked names does not imply endorsement by the U.S. Army but is intended only to assist in identification of a specific product.

B. The U.S. Army Environmental Hygiene Agency (USAEHA) typically provides monitoring of explosives in environmental samples as part of its mission services, and came to an agreement with USATHAMA (reference B) to provide the required validation. The USATHAMA also requested additional work on potential chemical interferences in the method be performed, to include a study of the impact of five explosive precursors/degradation products on method performance.

C. The explosives to be analyzed were the following: 1,3,5,7-tetranitro-1,3,5,7-tetraazacycloactane (HMX), Hexahydro-1,3,5-trinitro-1,3,5-triazine (RMX), Tetryl, TNT, 2,4-Dinitrotoluene (DNT), 2,6-DNT, Pentaerythritoltetranitrate (PETN), and Nitroglycerin (NG). Additional chemical nomenclature information on the above compounds can be found in Appendix A. The materials were collected from simulated ground water onto Hayesep R® solid sorbent cartridges and, after desorption and concentration, analyzed by high performance liquid chromatograpny (HPLC) using ultraviolet (UV) and photoconductivity (PC) detectors in tandem. Chromatographic conditions were set to duplicate those developed by Battelle as closely as possible. Validation procedures as published in the USATHAMA Quality Assurance (QA) Manual (reference C) were to be followed, to include both Precertification and Certification procedures as promulgated in that manual.

D. This report documents successful USAEHA performance of the above tasks. Several recommendations are made which USAEHA feels will further enhance the capabilities of the validated method if implemented in the future.

IV. EXPERIMENTAL PROCEDURES.

A. Equipment.

1. Perkin Elmer Series 4 HPLC, equipped with a column heating jacket assembly.

2. Perkin Elmer Model ISS100 Autosampler.

3. Tracor® Model 790A UV Absorbance Detector.

4. Tracor Model 965 Photoconductivity Detector, with Zinc lamp (Tracor is the only known vendor of this detector).

® Haysesep R is a registered trademark of Hayes Separation Incorporated, Bandera, Texas.
® Tracor is a registered trademark of Tracor Inc., Austin, Texas.

5. Hewlett Packard Model 3357 Laboratory Automation System, with CPLOT software.

6. Hewlett Packard model 3390A Integrator/Recorders (2)

7. Zenith Personal Computer, Model Z248, containing USATHAMA Certification software.

B. Reference Materials.

1. Standard Analytical Reference Materials (SARMs). All explosives were obtained from the USATHAMA repository for SARMs. The SARMs included: HMX (lot 1217), RDX (lot 1130), Tetryl (lot 1149), NG solution (lot 1150), TNT (lot 1129), 2,6-DNT (lot 1148), 2,4-DNT (lot 1147), PETN solution (lot 1151), nitrobenzene (99.91-percent purity), 4,6-dinitro-o-toluidine (99.94-percent purity), 1,3-dinitrobenzene (99.94-percent purity), and 1,3,5-trinitrobenzene (lot 1154).

2. Interim Reference Materials (IRMs).

a. 1-Nitrobutane.

(1) Fluka Chemical Company, catalog no. 73250, label indicating purity of approximately 99 percent by gas chromatography. The material was further assayed by USAEHA. Mass and infrared spectra of the purchased material were consistent with the 1-nitrobutane assignment.

(2) The material was assayed by gas chromatography/ mass spectrometry (GC/MS), and the indicated purity was 98.1 percent. The purchased chemical was also assayed by HPLC/PC detector on the method chromatographic column, and had an indicated purity of 99.2 percent. It was stored at -30 degrees Centigrade.

(3) 1-Nitrobutane was used as an internal standard in detection and quantitation of PETN and NG using the PC detector.

b. 3,4-DNT.

(1) Phaltz and Bauer catalog no. D48080, with a vendor indicated purity of 99 percent. The chemical was further assayed by USAEHA. Mass and infrared spectra were consistent with the assignment of the material as 3,4-DNT.

(2) The purchased material was assayed by GC/MS and had an indicated purity of 99 percent. The chemical was also assayed by HPLC/UV detector on the method analytical chromatographic column and had an indicated purity of 98.3 percent. It was stored at -30 degrees Centigrade.

(3) The 3,4-DNT was used as an internal standard in detection and quantitation of HMX, RDX, Tetryl, TNT, 2,4-DNT, and 2,6-DNT using the UV detector.

c. Tetramethylammonium Chloride (TMAC). Fluka Chemical Company catalog no. 87720, with a vendor indicated purity of greater than 98 percent by chloride analysis. The material was further assayed by USAEHA. The infrared spectrum was consistent with the assignment of TMAC. The chemical was stored at room temperature.

3. Additional Reference Materials. Chemicals used for interference testing were obtained from the EPA repository of reference standards, with the exception of four chemicals. Tributyl phosphate, 1,4-dithiane, sulfur, and dimethyl methyl phosphonate were purchased from Aldrich Chemical Company. All materials were stored at 4 degrees Centigrade until used.

4. Miscellaneous Chemicals and Supplies. Other chemicals and solvents employed in the project were reagent grade quality. Hayesep R cartridges (600 mg/tube) were obtained from Supelco, Inc. as a special order item.

5. Deionized Water. The deionized water used for all project work was obtained fresh daily from a Millipore® Milli-Q System finish of the building deionized water. The water from the Milli-Q system [American Society for Testing and Materials (ASTM) Type I] was not collected until the resistivity was measured at 17 megohm/cm or better on the Millipore monitoring meter on the unit. The ASTM Type II water containing sulfate and chloride was prepared using the above ASTM Type I water as described by USATHAMA (reference C).

C. Selected Procedures.

1. HPLC Analysis.

a. These procedures are documented in the final method Standing Operating Procedure (SOP) (Appendix). Additional in-house procedures developed for proper performance of the analysis system are included following the SOP. These included the two procedures below:

(1) Procedure for Obtaining ASTM Type I Water.

(2) Procedure for Filtering Solvents for HPLC.

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b. Only the highest quality, freshly prepared deionized water could be used for satisfactory performance of the PC detector. If the water was of insufficient quality, a negative baseline drift of the PC detector during the HPLC solvent gradient occurred.

c. Proper operation of the PC detector was also affected by inadequately degassed HPLC solvents. If HPLC solvents were inadequately degassed, gas bubbles formed in the PC detector solvent intake lines (which are Teflon® and not "high pressure") causing severe signal spikes as these bubbles traversed the conductivity cells of the PC detector.

2. Standards Preparation. Standards preparation procedures are described in the final method SOP in the Appendix.

3. Daily Quality Control. At the start of each test day, a standard containing all analytes of interest at 10 times the Target Reporting Level (10X TRL) was analyzed and evaluated for proper instrument performance before any additional samples were assayed.

4. Hayesep R Treatment.

a. All analytes of interest, whether explosives or a potential chemical interferant, were added to 500 mL ASTM Type II water containing 100 mg/L each of sulfate and chloride, prepared as described in the USATHAMA QA Manual (reference C). The simulant ground-water samples were then passed through prerinsed Hayesep R cartridges at approximately 10 mL/minute (pretreatment of cartridges included passing 100 mL of acetone, followed by 100 mL of ASTM Type 1 water through the cartridges at approximately 10 mL/minute prior to introduction of sample).

b. After removal of excess water, cartridges were eluted with 10 mL acetone. The acetone solutions were reduced to approximately 0.5 mL volume under nitrogen, using a commercially available heater assembly maintained between 42 and 47 degrees Centigrade. Concentration required about two hours under these conditions, at which point the residual solutions were mostly water. Internal standard solutions were added and the concentrates were quantitatively transferred to 2 mL volumetric flasks and diluted to 2 mL final volume with methanol/water (50/50) for HPLC analysis.

c. A blank Hayesep R cartridge was included with every set of samples treated as a quality control check.

® Teflon is a registered trademark of E. I. DuPont de Nemours, Inc., Wilmington, Delaware.

5. Chemical Interferant Testing.

a. The chromatographic and/or Hayesep R behavior of approximately 40 chemical compounds was examined. The chemicals included potential chemical interferants, explosive precursors or degradation products, and candidate alternate internal standards. Identical evaluation procedures were employed for all of the materials screened, as described below.

b. Individual chemical standards were prepared at a concentration of 100 ug/ml in methanol/water (50/50). These were analyzed directly by HPLC without any further standard addition to establish chromatographic behavior and detector response characteristics. Normal method HPLC run conditions were used, with a daily 10X TRL explosives standard analyzed initially on each test day.

c. If positive response occurred on either the UV or PC detector in any region of the chromatogram, the chemical standards were then applied to 500 mL ASTM Type II water containing 100 mg/L concentrations of both sulfate and chloride. Amounts (200 ug) of chemical standards were added to simulant ground water to achieve a final concentration of 100 ug/ml in the 2 mL final volume for HPLC analysis, as were assayed above (without Hayesep R treatment). Internal standards were applied to these solutions to more accurately measure relative retention behavior and detector response.

V. METHOD VALIDATION. As described in the USATHAMA QA Manual (reference C), validation of a method for USATHAMA involves a standard format. Two distinct phases of validation are identified - precertification and certification.

A. Precertification.

1. Method precertification is an initial calibration of the instrumental analysis system using the target analytes bracketing the anticipated concentration range to be tested. Each standard is prepared and analyzed in duplicate instrumentally (not through the entire method).

2. Concentrations of explosives were chosen to bracket the anticipated testing range and corresponded to blank, 0.5, 1, 2, 5, and 10 times the TRL as defined for Class 1 methods. Also, an additional standard at each end of the testing range extended by 25 percent was measured to compensate for fluctuations from a theoretical 100 percent recovery. These additional standard concentrations at 0.4 and 20 times the TRL were also, therefore, assayed.

3. Data from analysis of the calibration solutions and blank were tabulated, and graphs of response versus concentration

were generated using software provided by USATHAMA. The calibration curves were analyzed for Lack of Fit (LOF) and Zero Intercept (ZI) output with the USATHAMA software.

4. The documentation package specified in the USATHAMA QA Manual was submitted to the USATHAMA for evaluation and, after some modifications, was approved. The Precertification Data Package is not provided in this report.

B. Certification.

1. Method certification began after approval of the precertification package. Solutions spiked at each of the levels used in precertification (blank, 0.5, 1, 2, 5, and 10 times the TRL) were processed through the entire procedure. This involved extraction of the explosive analytes from simulated ground water with Hayesep R cartridges, elution off the Hayesep R, followed by concentration, and HPLC analysis.

2. Certification tests were conducted on four separate days. The above standards were applied to ASTM Type II water. This is ASTM Type I water modified by the addition of sulfate and chloride.

3. Data were tabulated in graphs of found concentration versus target concentration, using USATHAMA software. The Certified Reporting Limit (CRL), method precision, and method accuracy were also automatically determined with the software.

4. The USAEHA assembled the data package specified in the USATHAMA QA Manual for method certification and submitted the package to the USATHAMA. After some modifications, USATHAMA approved the Certification Data Package, which is not included in this report.

C. Comparison of USAEHA and Battelle Method Validation Data.

1. Comparison of USAEHA and Battelle Relative Detector Responses.

a. The detector responses of both the UV and PC detectors, relative to the respective internal standard peak area at the TRL, were calculated by Battelle and by USAEHA. The USAEHA used data generated in the precertification testing (4 total data points - 2 test days in duplicate).

b. These relative detector responses (RDRs) compare performance of the different detectors at the two separate laboratories. Table 1 lists the RDRs of the USAEHA and Battelle instrument systems used in the method validation work.

TABLE 1. COMPARISON OF USAEHA AND BATTELLE RELATIVE DETECTOR RESPONSES

Explosive	USAEHA RDR*	Battelle RDR	Detector
HMX	0.065	0.096	Absorbance
RDX	0.092	0.097	Absorbance
Tetryl	0.18	0.17	Absorbance
TNT	0.028	0.039	Absorbance
2,6-DNT	0.012	0.011	Absorbance
2,4-DNT	0.031	0.023	Absorbance
NG	0.11	0.12	Photoconductivity
PETN	0.068	0.065	Photoconductivity

* RDR is the relative detector response for each analyte, relative to the internal standard peak area at the TRL.

c. Battelle used a Kratos Model 757 UV absorbance detector, while USAEHA employed a Tracor Model 790A UV absorbance detector for measurement of HMX, RDX, Tetryl, TNT, 2,4-DNT, and 2,6-DNT. Responses were very similar for the two detectors; since UV detectors are common HPLC devices of known signal stability, the comparison was not unexpected.

d. Both USAEHA and Battelle used a Tracor Model 965 PC detector in project work. The PC detector is a less commonly employed detector, and less data on its operating characteristics have been published.

e. Nitroglycerin and PETN were measured with the PC detector. The RDRs were almost identical between USAEHA and Battelle for these two explosives, indicating nearly the same PC detector performance in this respect.

2. Comparison of USAEHA and Battelle Certified Reporting Limits.

a. The USATHAMA certification software automatically generated CRLs from experimental values measured on four separate days. The USAEHA and Battelle CRLs are compared in Table 2.

TABLE 2. COMPARISON OF USAEHA AND BATTELLE CERTIFIED REPORTING LEVELS

Explosive	USAEHA CRL (ug/L)	Battelle CRL (ug/L)*
HMX	5.1	6.9
RDX	7.5	7.7
Tetryl	14	4.1
NG	22	15
TNT	1.3	1.0
2,6-DNT	2.7	1.3
2,4-DNT	0.79	0.92
PETN	6.3	5.1

* Reference A

b. Again, USAEHA and Battelle values compare closely. The Tetryl CRL generated by USAEHA was somewhat higher (14 ug/L) than the analogous value obtained by Battelle (4.1 ug/L). The USAEHA noted some evidence of Tetryl decomposition (solution discoloration) during the Hayesep R treatment for this compound, which would have increased the calculated CRL value.

c. It was concluded that the method CRLs, as reported by Battelle, were comparable to those found by USAEHA for the explosive analytes measured. Method validation by USAEHA was achieved.

3. Comparison of USAEHA and Battelle Chromatographic Retention Times.

a. Retention time (RT) comparisons between USAEHA and Battelle data for the explosives are shown in Table 3. Reported USAEHA data are averaged from four values measured during precertification testing (2 test days with duplicate analyses on each day). Table 3 also lists the experimental retention time window for each explosive, defined as three times the standard deviation of the retention time for the four USAEHA values. It is a measure of variability in the values.

TABLE 3. COMPARISON OF USAEHA AND BATTELLE CHROMATOGRAPHIC RETENTION TIMES

Explosive	USAEHA RT	USAEHA Window*	Battelle RT	Battelle Window
	(min)		(min)	
HMX	5.7	0.3	6.5	0.2
RDX	10.9	0.7	12.5	0.2
Tetryl	20.5	1.5	21.3	0.2
NG	23.8	1.9	22.6	0.2
TNT	23.5	1.9	23.0	0.2
2,6-DNT	27.5	1.3	25.1	0.2
2,4-DNT	28.4	1.1	25.8	0.2
PETN	35.7	0.2	28.3	0.2
3,4-DNT (I.S.)	24.2	1.9	23.6	0.3
Nitrobutane (I.S.)	18.7	1.0	18.3	0.3

* Window is defined as three times the standard deviation of the retention time for the individual explosive analyte.

b. The USAEHA data are more variable than that of Battelle, as measured by the larger retention time windows calculated by USAEHA. Larger than expected variability in analyte retention times continued through certification and method interference testing, even though the Zorbax HPLC column temperature was maintained at 35 degrees Centigrade by the HPLC system column jacket assembly. Nevertheless, proper quantitation of project explosives on individual test days was achieved by USAEHA. Initial daily analysis of a 10 times TRL standard containing all analytes provided updating of analyte retention times and responses before actual daily sample testing; this successfully minimized the effect of retention variations.

VI. EVALUATION OF POTENTIAL METHOD INTERFERENCES. To better evaluate the potential method interferences which may be present in complex ground-water samples, some common classes of chemical compounds were selected by USAEHA and USATHAMA for examination. These included:

phthalates (3)
phenols (6)
chlorinated compounds (5)
nitrogen-containing compounds (4)
phosphorus-containing compounds (6)
sulfur-containing compounds (3)

Direct injection of chemicals from these classes were made onto the liquid chromatographic system. If a UV/PC detector signal was observed in any chromatographic region for any of the above compounds, the chemical was reevaluated for recovery through the Hayesep R collection procedure to determine if Hayesep R might remove the interferant. Results of the preliminary study involving direct injection of the interferants onto the HPLC system are summarized in Table 4. Compounds producing a positive response on either detector were then added individually to 500 mL ASTM Type II water and passed through Hayesep R cartridges for collection, followed by acetone desorption, concentration and analysis of the extracts. Results of the Hayesep R treatment of interferants are summarized in Table 5. Comments on the results of this study are discussed below by chemical class.

A. Phthalates.

1. Phthalates are important interferants. The three phthalates examined are widely used industrial plasticizers and are common laboratory contaminants. Sample collection, handling, and analysis equipment might be expected to occasionally contain small, variable amounts of each or all of these particular materials unless precautions are made to eliminate them.

2. Dibutyl phthalate and bis 2-ethylhexyl phthalate produced no chromatographic signal in the analytical region of interest when injected directly. They were therefore considered as noninterferants in the procedure and were not further considered.

3. Diethyl phthalate responded on both the UV and PC detectors, but the UV detector response was much greater than that of the PC detector. Hayesep R treatment had only a minimal, if any, effect on removing diethyl phthalate. This compound elutes well after the eight target explosives and should not interfere unless very high concentrations are present.

4. The major phthalates expected to be present as routine contaminants in sample handling are not interferants.

B. Phenols.

1. Phenol, 2-methyl phenol, 3-methyl phenol, and 4-methyl phenol responded on the UV detector, but no signal was obtained on the PC detector. These phenols were retained through the Hayesep R procedure and are therefore not removed as interferants by Hayesep R.

TABLE 4. HPLC BEHAVIOR OF SELECTED CHEMICAL INTERFERANTS

Compound	UV Det.* R.R.T.	UV Det.* R.A	PC Det.+ R.R.T.	PC Det.+ R.A.
HMX	0.24		0.35	
RDX	0.47		0.63	
Tetryl	0.86		ND**	
TNT	1.00		ND	
3,4-DNT (UVD STD)	1.00		ND	
2,6-DNT	1.10		ND	
2,4-DNT	1.14		ND	
1-Nitrobutane (PCD STD)	ND		1.00	
NG	ND		1.27	
PETN	ND		1.77	
Diethyl phthalate	1.46	3.02	1.95	0.17
Dibutyl phthalate	ND		ND	
Bis-2-ethylhexyl phthalate	ND		ND	
Phenol	0.44	1.51	ND	
2-Methyl phenol	0.70	1.26	ND	
4-Methyl phenol	0.69	0.71	ND	
3-Methyl phenol	0.69	0.86	ND	
2-Chlorophenol	0.71	0.85	0.96	4.5
Pentachlorophenol	ND		ND	
Chlorobenzene	ND		ND	
1,4-Dichlorobenzene	ND		ND	
1,2,4-Trichlorobenzene	ND		ND	
Hexachlorobenzene	ND		ND	
PCB 1254	ND		ND	
Aniline	0.38	3.05	0.50	?
2-Nitrophenol	0.87	7.21	1.17	0.57
Atrazine	1.30	4.44	1.60	4.23
Bromacil	0.83	4.78	1.12	0.66
Malathion	ND		ND	
Methyl parathion	ND		ND	
Parathion	ND		ND	
Chlorpyrifos	ND		ND	
Dimethyl methyl phosphonate	ND		ND	
Tributyl phosphate	ND		ND	
Sulfur	ND		ND	
Diazinon	0.34		ND	
1,4-Dithiane	ND		ND	

Retention time (in minutes) of the explosives is an average of all runs of the 10 times TRL standard.
* Relative to 3,4-DNT for both relative retention time (R.R.T.) and UVD absorbance (R.A.).
+ Relative to 1-nitrobutane for both relative retention time (R.R.T.) and PCD absorbance (R.A.).
** Not detected

TABLE 5. RECOVERY OF INTERFERANTS THROUGH HAYESEP R TREATMENT

Compound	UV Det.* R.R.T.	UV Det.* R.A.	PC Det.+ R.R.T.	PC Det.+ R.A.
1. EXPLOSIVES				
HMX	0.23	0.57	0.36	1.30
RDX	0.46	0.46	0.61	1.87
Tetryl	0.84	1.54	ND	--
TNT	0.97	0.28	ND	--
2,6-DNT	1.17	1.29	ND	--
2,4-DNT	1.22	0.26	ND	--
NG	ND	--	1.27	2.18
PETN	ND	--	2.01	0.39
2. INTERFERANTS				
Diethyl phthalate	1.57	1.82	ND	--
Phenol	0.47	1.02	ND	--
2-Methyl phenol	0.76	0.91	ND	--
4-Methyl phenol	0.72	0.61	ND	--
3-Methyl phenol	0.72	0.81	ND	--
2-Chlorophenol	0.78	0.16	1.06	0.49
Aniline	0.40	1.72	0.56	0.13
2-Nitrophenol	0.91	3.91	1.22	0.30
Atrazine	1.37	4.02	1.83	3.88
Bromacil	0.86	4.29	1.15	0.81
Diazinon	0.34	0.07	ND	--

* Relative to 3,4-DNT for both relative retention time (R.R.T.)and UV absorbance (R.A.). Average retention time for 3,4-DNT was 24.33 minutes and UV absorbance was 249580.
+ Relative to 1-Nitrobutane for both relative retention time (R.R.T.) and PCD absorbance (R.A.). Average retention time for 1-Nitrobutane was 18.79 minutes and PCD absorbance was 1761355.

2. Phenol has almost the same retention behavior as RDX and would elute with RDX if present in the ground-water sample. Actual presence of phenol in water samples could be distinguished from RDX by a close evaluation of both UV and PC detector chromatographic traces, since phenol responds only on the UV detector while RDX responds on both detectors.

3. The three methyl phenols elute in a clean region of the chromatogram between RDX and Tetryl and are not interferants in the procedure. In fact, each of these compounds might be excellent alternatives to 3,4-DNT for use as the UV detector internal standard, because of problems experienced by USAEHA with the current UV standard. This is discussed more fully in Section X.

4. 2-Chlorophenol responds on both UV and PC detectors, is recovered by Hayesep R, and might interfere with the measurement of 1-nitrobutane, which is the PC detector internal standard. However, the presence of 2-chlorophenol would be indicated by a positive UV response, whereas 1-nitrobutane does not produce a UV response. Therefore, 2-chlorophenol should be detected as a method interferant by the analyst on inspection of the sample chromatogram.

5. Pentachlorophenol was not detected in the direct injection and is not a method interference.

C. Chlorinated Compounds. None of the five chlorinated compounds evaluated in this classification - chlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene, and polychlorinated biphenyl 1254 -responded on either detector in the region of interest and are not method interferants.

D. Nitrogen-Containing Compounds.

1. The four compounds in this classification produced positive signals on both detectors and, as was typically the case, were not removed by the Hayesep R procedure.

2. Aniline eluted between HMX and RDX and does not mask detection of any of the explosives of interest.

3. 2-Nitrophenol and bromacil both exhibited strong UV absorbance, coeluted with Tetryl, and would be problem compounds if present in the ground-water specimen. Evidence of 2-nitrophenol and/or bromacil may be indicated by the presence of PC detector response in the Tetryl region, since Tetryl itself gives no PC detector response. Again, the analyst would have to inspect the chromatogram (carefully) to determine if some interference from these compounds is present.

4. Atrazine, a triazine herbicide with a similar chemical structure to explosives, generates strong response on both detectors but elutes in a region of the chromatogram (between 2,4-DNT and PETN) where it will not interfere with measurement of the eight explosive analytes of interest. Because of its strong signal and innocuous retention behavior, atrazine

may have future potential for improved method performance monitoring. The possible use of atrazine in implementation of this method is discussed in the Recommendations section.

E. Phosphorus-Containing Compounds. The phosphorus containing species investigated (malathion, methyl parathion, parathion, chlorpyrifos, dimethyl methyl phosphonate, and tributyl phosphate) were not detected in the direct chromatographic analysis and are not method interferences.

F. Sulfur-Containing Compounds. Sulfur and 1,4-dithiane did not respond on either detector and are not a problem as interferants. Diazinon exhibited a small UV absorbance signal in the chromatographic area between HMX and RDX, and would not affect the signal of either of these explosives if present. Diazinon was retained through the Hayesep R treatment.

VII. EVALUATION OF SELECTED EXPLOSIVE PRECURSORS/DEGRADATION PRODUCTS.

A. Retention Time/UV Detector Response Data.

1. Potential method interferences produced by five explosive precursors/degradation products were evaluated:

a. Nitrobenzene.

b. 1,3-Dinitrobenzene.

c. 1,3,5-Trinitrobenzene.

d. 4,6-Dinitro-o-toluidine.

e. Isophorone.

2. Standards [100 micrograms (ug)/milliliter (mL)] of each of the above materials were assayed. The usual internal standards 3,4-DNT and 1-nitrobutane were not added to ensure that no interferences were added through use of these compounds. Results of single injections of the materials are shown below.

Compound	Retention Time	UV Absorbance Area
Nitrobenzene	24.2 Min	3,778,018
1,3-Dinitrobenzene	20.1 Min	5,819,699
1,3,5-Trinitrobenzene	16.1 Min	4,049,295
4,6-Dinitro-o-toluidine	23.9 Min	4,041,882
Isophorone	25.3 Min	3,359,885

Each of the potential interferants produces substantial UV detector response in the approximate chromatographic region in which the eight method explosive compounds elute. Retention times indicate potential interference primarily in the Tetryl/TNT/3,4-DNT region of the chromatogram.

B. Effect of Hayesep R Treatment. The five compounds were reevaluated individually at a lower concentration level (5 ug/mL). Standards were added to ASTM Type I water and passed through Hayesep R cartridges, then desorbed with acetone. HMX was added to each extract as an internal standard since no interference in the HMX chromatographic region was encountered in the initial work. 3,4-DNT, the usual internal standard, could not be used. Duplicate tests were conducted; results are tabulated in Table 6, summarized in Table 7, and discussed compound by compound below.

TABLE 6. HPLC BEHAVIOR OF SELECTED EXPLOSIVE PRECURSORS/ DEGRADATION PRODUCTS THROUGH HAYESEP R PROCEDURE

Compound	UV Detector R.T.	UV Detector Abs.	Relative to HMX* R.T.	Relative to HMX* Abs.
1. Explosives (10X TRL)				
HMX	5.94	184195	1.00	1.00
RDX	11.31	108110	1.90	0.59
Tetryl	20.72	406122	3.49	2.20
TNT	23.90	69710	4.02	0.38
3,4-DNT (UV Std)	24.62	242891	4.14	1.32
2,6-DNT	28.69	33137	4.83	0.18
2,4-DNT	29.91	66857	5.03	0.36
2. Precursors/Degradation Products (5 microgram/mL)				
Nitrobenzene	24.03	9074	3.86	0.06
1,3-Dinitrobenzene	19.99	274679	3.35	1.62
1,3,5-Trinitrobenzene	15.84	207285	3.35	1.62
4,6-Dinitro-o-toluidine	23.49	209318	3.94	1.13
Isophorone	25.91	111900	4.36	0.64

* HMX was used as the internal standard in the recovery studies because preliminary work (Table 6) found coelution with 3,4-DNT.

TABLE 7. SUMMARY OF EXPLOSIVE PRECURSOR/DEGRADATION PRODUCT BEHAVIOR

Compound	Comment
Nitrobenzene	Interferant in TNT monitoring Low recovery through Hayesep R procedure
1,3-Dinitrobenzene	Possible interferant in Tetryl monitoring High recovery through Hayesep R procedure
1,3,5-Trinitrobenzene	No interference in method monitoring High recovery through Hayesep R procedure Potential method target compound
4,6-Dinitro-o-toluidine	Interferant in TNT monitoring High recovery through Hayesep R procedure
Isophorone	No interference in method monitoring Partial recovery through Hayesep R

C. Nitrobenzene. Nitrobenzene, if present in a ground-water sample, is an interferant in the procedure. The retention behavior of nitrobenzene (24.0 minutes) is almost the same as TNT (23.9 minutes) and 3,4-DNT (24.6 minutes). However, nitrobenzene recovery through the Hayesep R procedure was low in both extractions - about 5 percent - probably because of its evaporation during solvent blowdown, reducing the effect of its presence on proper method performance.

D. 1,3-Dinitrobenzene. 1,3-Dinitrobenzene elutes (retention time of 20.0 minutes) less than a minute before Tetryl (retention time of 20.7 minutes). Recovery through Hayesep R appears to be nearly quantitative. Actual sample chromatograms will need to be examined carefully to prevent false positive detection of Tetryl if 1,3-dinitrobenzene is present in the ground-water sample.

E. 1,3,5-Trinitrobenzene. 1,3,5-Trinitrobenzene, which elutes from the method column at 15.8 minutes, is not an interferant to the eight validated explosives. Recovery through Hayesep R appears quantitative from the two extractions performed. In fact, the chromatographic behavior of 1,3,5-trinitrobenzene shows that this procedure can also be used for monitoring of this compound if appropriate USATHAMA certification procedures are first conducted.

F. 4,6-Dinitro-o-toluidine. Some interference with TNT detection and measurement (retention time of 23.9 minutes) can be anticipated if 4,6-dinitro-o-toluidine (retention time of 23.5 minutes) is present in the ground water. Recovery through the Hayesep R treatment appears to be quantitative (two tests). Therefore, TNT may be misidentified or misquantitated if this degradation product is present.

G. Isophorone. Isophorone elutes from the method column at 25.9 minutes, in the chromatographic region between 3,4-DNT (retention time of 24.6 minutes) and 2,6-DNT (retention time of 28.7 minutes). Recovery through Hayesep R is somewhat less than quantitative, estimated at 70 percent in the two extractions tested, and may reflect the known instability of the compound as found in EPA priority pollutant monitoring. Isophorone is not considered to be a method interference, particularly if another internal standard material is substituted for 3,4-DNT (as is recommended by USAEHA).

VIII. INVESTIGATION OF ALTERNATIVE INTERNAL STANDARD MATERIALS.

A. The problems encountered with 3,4-DNT as an internal standard (elution behavior very similar to TNT) suggest that an alternative material eluting in a less critical chromatographic region would be a better choice. Actually, HMX or RDX would be ideal choices as internal standards if they were not analytes to be measured, since they exhibit detector response on both the UV and the PC detectors.

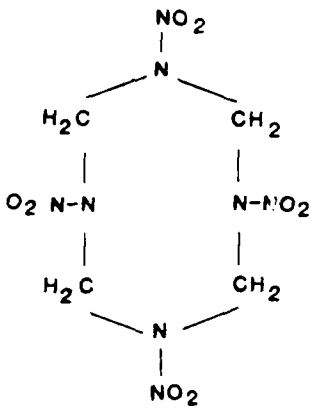
B. If the chemical structures of these two compounds relative to the six other target explosive compounds are examined (Figure 1), some explanation of why HMX and RDX respond on both detectors can be made. Nitroglycerin and PETN respond selectively on the PC detector and not on the UV detector, because they contain only aliphatic nitro groups (which give response) but do not have aromatic ring structures (which normally impart UV response). On the other hand, TNT, Tetryl, 2,4-DNT, and 2,6-DNT contain nitro groups attached directly to aromatic ring structures and therefore respond only to UV detection and not to PC detection. HMX and RDX contain both aliphatic nitro group functionality and ring structures containing nitrogen and thus respond on both detectors.

C. In the method interference testing, atrazine gave strong response on both detectors much like HMX and RDX. Inspection of the chemical structure of atrazine (Figure 2) demonstrates the similarity between the chemical structures of atrazine, HMX, and RDX. Atrazine appeared to potentially be an excellent internal standard. It produces strong response on both detectors; this would mean that only one material would have to be handled in performance of the method. Atrazine, however, does elute later in the chromatogram than the desirable internal standard region

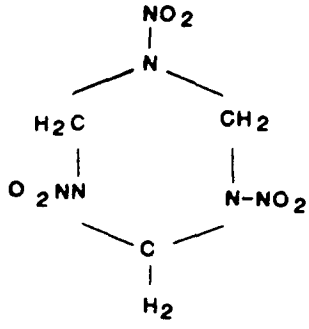
FIGURE 1

CHEMICAL STRUCTURES OF THE EIGHT EXPLOSIVE ANALYTES STUDIED

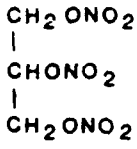
1. HMX



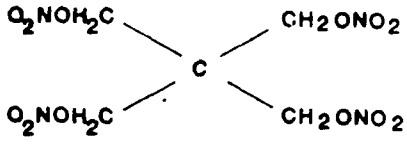
2. RDX



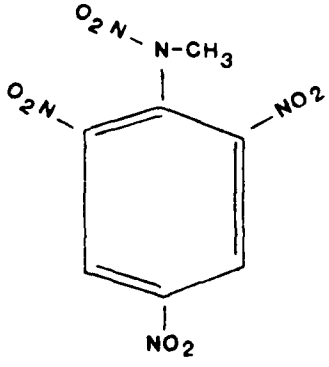
3. NITROGLYCERIN



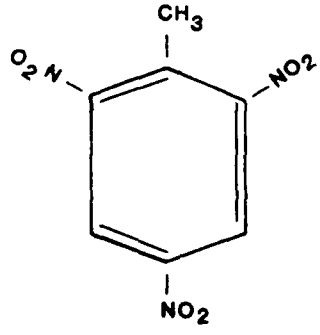
4. PETN



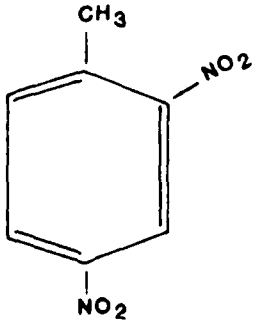
5. TETRYL



6. TNT



2,4-DNT



8. 2,6-DNT

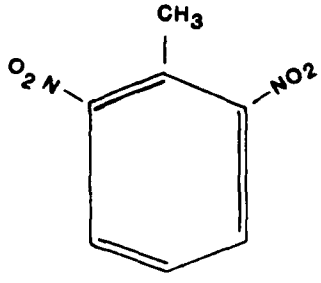
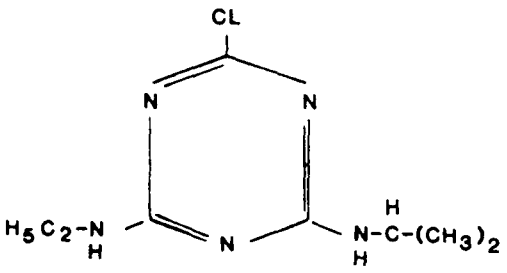


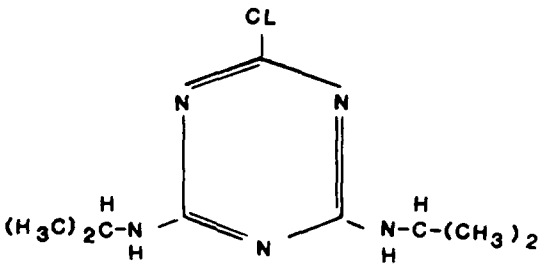
FIGURE 2

CHEMICAL STRUCTURES OF ALTERNATIVE INTERNAL STANDARDS STUDIED

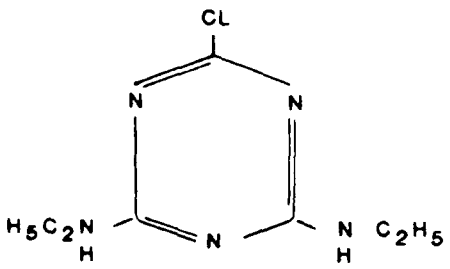
1. ATRAZINE



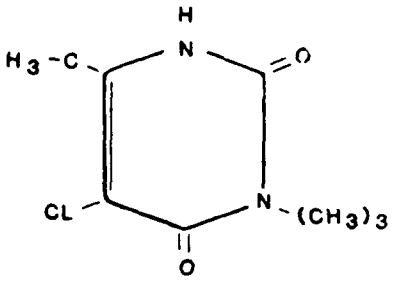
2. PROPAZINE



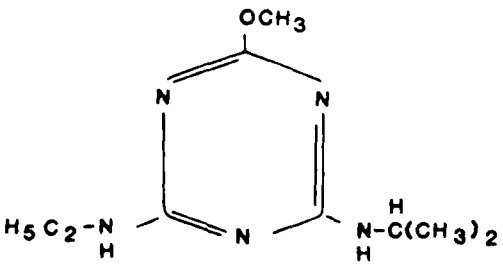
3. SIMAZINE



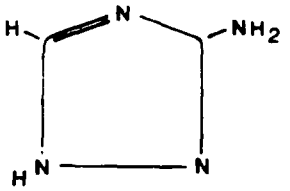
4. TERBACIL



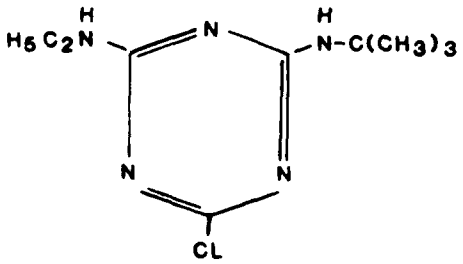
5. ATRATON



6. AMITROLE



7. TERBUTYLAZINE



(elution between RDX and Tetryl). This is a drawback for use of atrazine as an internal standard, but does not negate it as a useful compound for surrogate use.

D. Several other alternative potential internal standard compounds to 1-nitrobutane and 3,4-DNT were investigated. A series of triazine herbicides very similar structurally to HMX, RDX, and atrazine were selected (Figure 2). Standards of each of the following were prepared:

propazine	atraton
simazine	amitrole
terbacil	terbuthylazine

These were analyzed under the normal method HPLC conditions, and results are summarized in Table 8.

E. Of the six triazines studied, none were satisfactory substitute internal standards. Propazine, amitrole, and terbuthylazine gave no response, probably because of elution after the normal run time. Simazine gave substantial response on both detectors but eluted in the TNT chromatographic region and would be an interferant in measurement of this explosive. Terbacil and atraton gave some response with both detectors but were not in desired regions of the chromatogram.

F. The study was concluded at this point. Future work with a more substantial number of target triazines should produce a good candidate standard.

IX. DISCUSSION OF RESULTS.

A. HPLC Analysis Procedure.

1. The HPLC procedure as developed by Battelle uses a Zorbax ODS column (250 X 4.6 mm, 5 um) for separating the eight explosives and two internal standard compounds using the two detector system. Typical chromatograms obtained in the USAEHA work are shown in Figure 3 and Figure 4 for the UV and PC detectors, respectively.

TABLE 8. HPLC BEHAVIOR OF POTENTIAL ALTERNATIVE METHOD INTERNAL STANDARDS

Compound	CAS Number	Comment
Propazine	139-40-2	No peak detected ; probable elution after chromatographic run time completed
Simazine	122-34-9	Large peak in both UVD and PCD traces; however, elution occurs at TNT retention time
Terbacil	5902-51-2	Some absorbance in both UVD and PCD traces; however, elution occurs at approximate 3,4-DNT retention time
Atraton	1610-17-9	Some absorbance in both UVD and PCD traces; however, too late in the chromatogram to be of analytical value
Amitrole	61-82-5	No peak detected; probable elution after chromatographic run time completed
Terbuthylazine	5915-41-3	No peak detected; probable elution after chromatographic run time completed

FIGURE 3

CHROMATOGRAM OF A 10XTRL STANDARD - ULTRAVIOLET DETECTOR

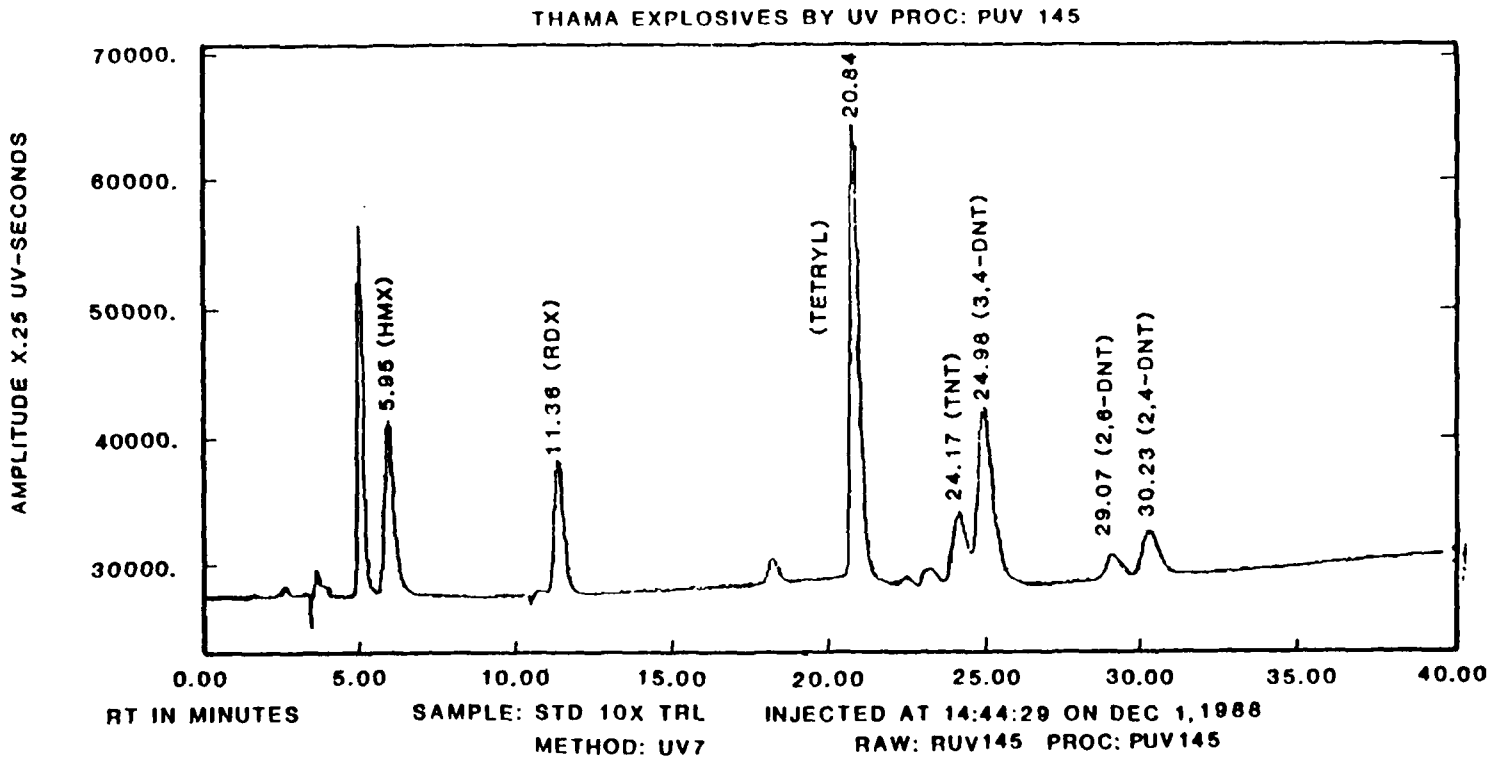
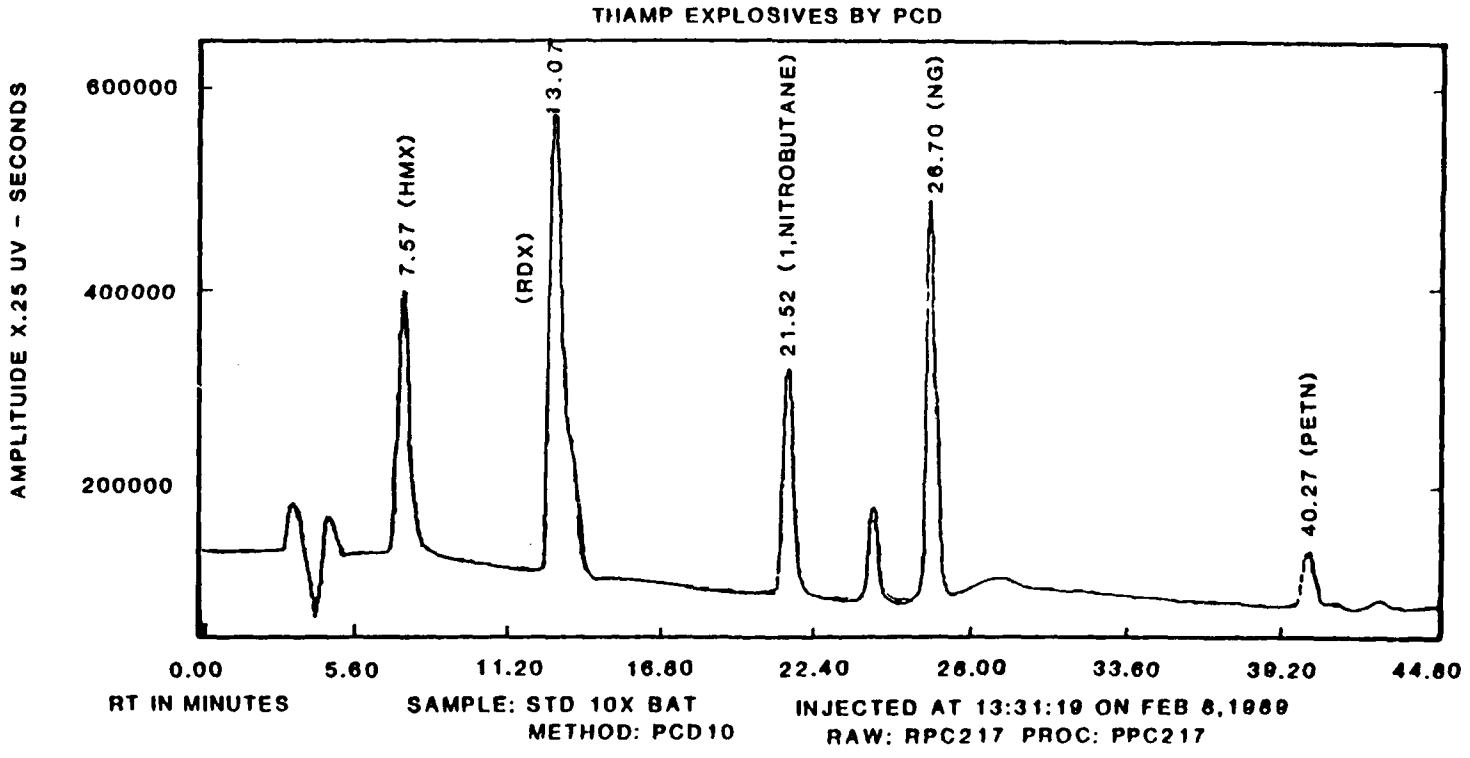


FIGURE 4

CHROMATOGRAM OF A 10XTRL STANDARD - PHOTOCONDUCTIVITY DETECTOR



2. Figure 3 shows that baseline resolution between all of the explosive compounds (HMX, RDX, Tetryl, TNT, 2,4-DNT, and 2,6-DNT) was achieved, but that the UV internal standard (3,4-DNT) was incompletely separated from TNT. On several occasions during project work, the separation between these two species was found to be insufficient and project work was delayed until the separation was again optimized. The TNT/3,4-DNT separation is the critical method performance test.

3. The USAEHA adjusted the mobile phase gradient somewhat from 40/60 methanol/water programmed to 80/20 methanol/water in 30 minutes (Battelle) to 35/65 methanol/water programmed to 70/30 methanol/water in 35 minutes to attain equivalent chromatography to that shown by Battelle.

4. Figure 4 shows baseline resolution for the three analytes being measured (NG, PETN, and 1-nitrobutane) on the PCD. Method performance was satisfactory for these materials.

B. UV Detector Performance.

1. The UV detector is the most common detector used in HPLC and has been successfully applied for some years to HPLC analysis of explosives. The sensitivity and linearity of the detector for these compounds is well documented. One weakness of the UV detector, however, is that it is not particularly selective for explosives.

2. Many organic compounds, particularly aromatics, respond on the UV and are potential or real interferants in HPLC procedures employing this detector. A significant number of UV sensitive compounds were found in this project. Battelle in published chromatograms (reference A) of actual ground-water samples also found some unidentified peaks. In actual analyses of ground-water samples for target explosives, chromatographic interferences will have to be carefully monitored.

C. PC Detector Performance.

1. The PC detector, first introduced in 1979 (reference D), is a less frequently used detector and consequently less has been published about its operating characteristics. The USAEHA found its PC detector to be very comparable to the unit used by Battelle in sensitivity and stability. The PC detector signal linearity appears to be somewhat less than that for the UV detector, based on a visual inspection of precertification/certification response versus target concentration graphs generated for NG and PETN.

2. The PC detector electronics and zinc lamp were kept on continually for day-to-day operations, and the stability of the detector was acceptable. Battelle specified that this procedure be followed in their current method SOP.

3. One early operational problem encountered with the PC detector was negative baseline drift (shown in Figure 5) during the chromatographic gradient. Since the chromatographic gradient used resulted in diminished amounts of water being introduced to the PC detector during the HPLC analytical run, the water was suspected to be the cause of the negative gradient. The PC detector unit separates the chromatographic column effluent into two equal parts, a reference stream and an analytical stream. The analytical stream is exposed to the zinc lamp radiation, while the reference stream is not irradiated. Any trace ionizable organic impurities in the deionized water would be detected by the PC, a conductivity cell. Negative baseline drift was theorized to be caused by reduced levels of trace organic impurities as less water is introduced into the detector during the solvent gradient.

4. The negative detector drift problem was solved by using only the highest quality, freshly prepared deionized water.

5. Another cperational problem with the PC detector was the appearance of occasional severe positive or negative detector signal spikes (shown in Figure 6). These spikes were found to occur when gas bubbles formed in the PC detector Teflon inlet tubing. Since the Teflon lines in the unit are thin-walled, the effluent at this point in the analysis is no longer at high pressure. Dissolved gases in the HPLC solvent will revaporize under these lowered pressure conditions and produce the observed spiking phenomena.

6. The gas bubble problem was minimized through exhaustive degassing of the HPLC solvents and a satisfactory procedure for solvent degassing was documented in an SOP. However, infrequent signal spikes were still occasionally encountered and the problem was never completely resolved.

7. The Tracor product specialist on the PC detector was not aware of other users encountering problems with gas bubble formation. It would, therefore, seem that this was an isolated problem with the particular detector system used in this study.

FIGURE 5

CHROMATOGRAM SHOWING NEGATIVE PHOTOCONDUCTIVITY DETECTOR DRIFT

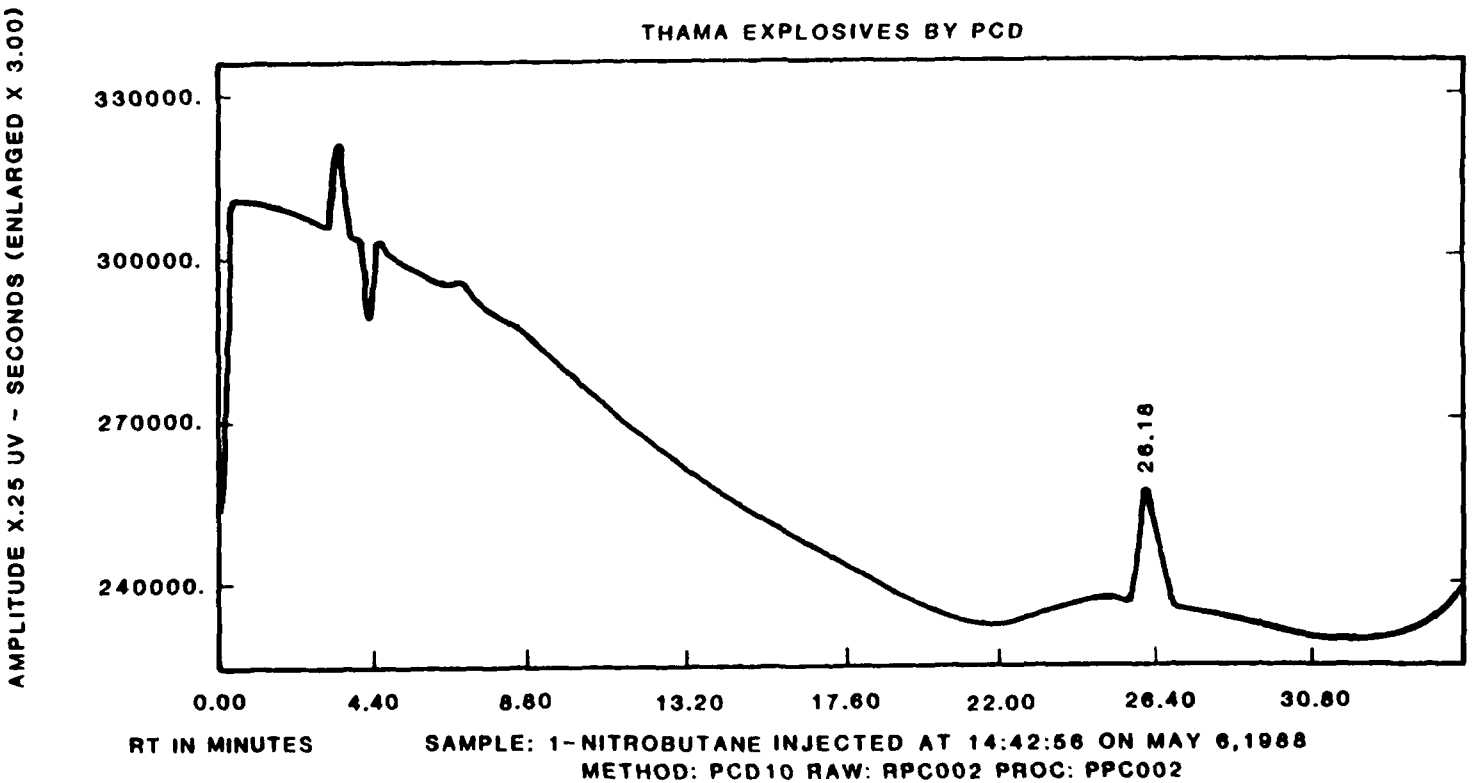
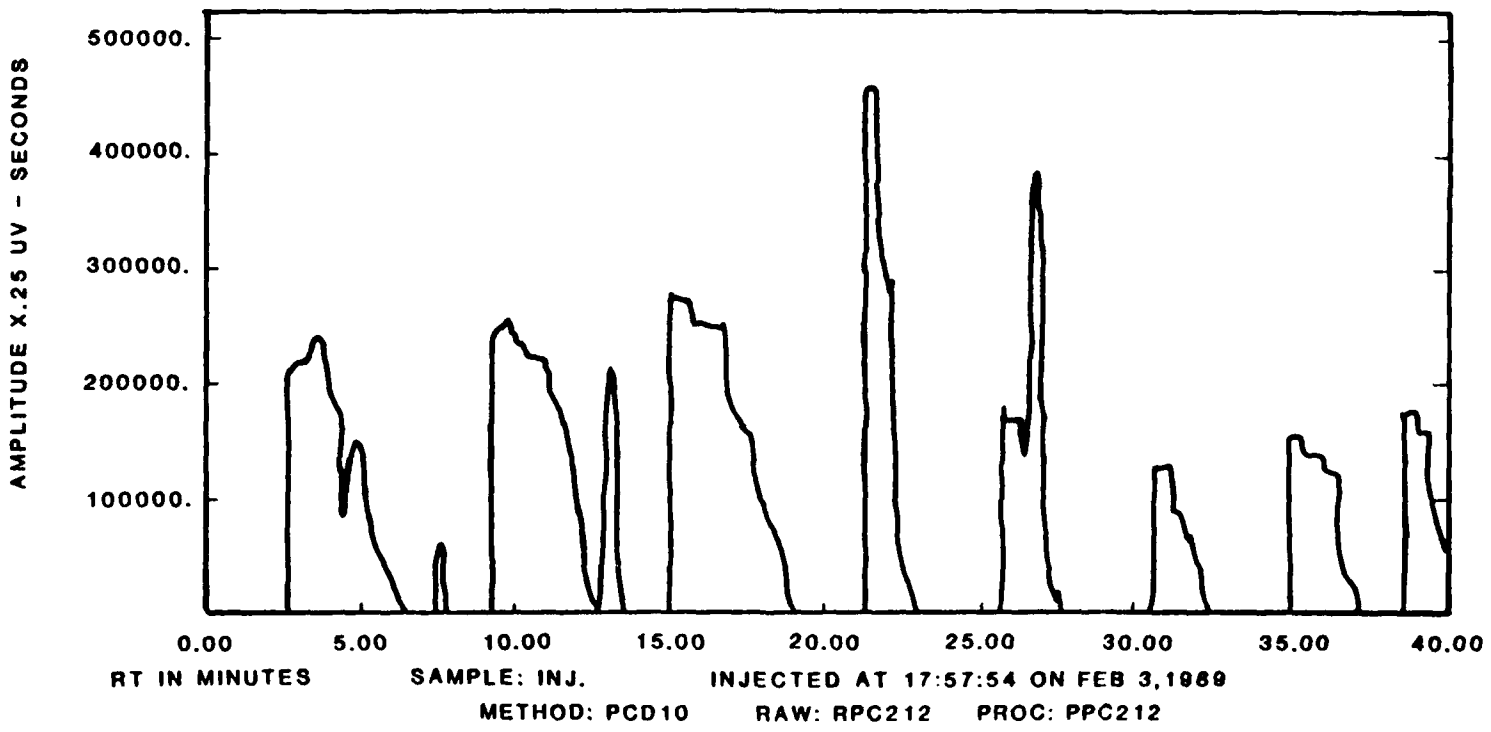


FIGURE 6

CHROMATOGRAM SHOWING PHOTOCONDUCTIVITY DETECTOR SIGNAL SPIKES



D. HAYESEP R TREATMENT.

1. The Hayesep R procedure developed by Battelle worked well in this study. Blank Hayesep R cartridges, after the prerinse procedure defined by Battelle, were free of chromatographic impurities in every case. No interferences were introduced through use of these cartridges.

2. Manipulations described by Battelle for processing Hayesep R cartridges were followed, with one minor variation. Two mL volumetric flasks rather than the 2 mL concentrator tubes described in the Battelle method SOP in order to better measure the 2 mL final volume.

3. It is important to make sure that acetone is completely removed during the final solvent concentration to 0.5 mL because residual acetone in the extract will yield a UV positive peak eluting before HMX. If high levels of acetone remain in the final extract, HMX detection may actually be masked by the acetone peak.

4. Tetryl was the one compound showing evidence of chemical decomposition out of all of the explosives studied. Harsh conditions during the Hayesep R treatment (probably the solvent blowdown step) will most likely be reflected in reduced recoveries for this compound.

5. The manifold (Supelco, Inc.) used for the manipulations involved in the Hayesep R procedure worked best when six samples were processed in a batch. Two batches per day are achievable with the system. The 6 samples per batch are recommended over a single batch of 12 samples because of space limitations.

X. CONCLUSIONS.

A. The USAEHA and Battelle performance of the HPLC method under investigation was nearly identical.

1. Equivalent detector responses were achieved.

2. Comparable Certified Reporting Levels were generated.

3. Chromatographic performances were very similar.

4. Hayesep R quantitatively collected the explosives from water.

5. The explosives were quantitatively desorbed from the Hayesep R.

B. The photoconductivity detector was a relatively stable, satisfactory detector for NG and PETN determination.

C. Some potential method interferences were found in interference testing:

1. Bromacil and 2-nitrophenol coeluted with Tetryl.

2. Nitrobenzene eluted in the TNT chromatographic region.

3. 4,6-dinitro-o-toluidine was an interferant in TNT monitoring.

4. Hayesep R treatment did not remove any interferants other than partially reducing nitrobenzene levels.

D. The TNT/3,4-DNT separation is a critical consideration for proper chromatographic method performance if one plans to monitor this series of explosives with a UV detector.

XI. RECOMMENDATIONS.

A. Consider the Use of a Second Column for Explosives Confirmation.

1. Initial detection of explosives using this procedure should be considered tentative. Many potential interfering compounds can be present in complex environmental samples which can elute in a chromatographic region assigned to an explosive of interest. The limited interference studies conducted, in addition to some actual ground-water chromatograms shown by Battelle, demonstrate that significant extraneous peaks might be present, especially in the UV detector trace. In addition, several explosive precursors/degradation products are projected to be potential method interferants.

2. A second chromatographic column should be developed and used to confirm the presence of explosives in actual samples. The use of a confirmation column is part of the method protocol in a recent USATHAMA funded explosives analysis project by Jenkins, et. al. (reference E). One of the columns used by Jenkins would appear to satisfy the confirmation requirement.

B. Replace 3,4-DNT as the UV Detector Internal Standard.

1. The most critical separation in the current procedure is the separation of TNT from 3,4-DNT, which is the UV absorbance internal standard. During the project work TNT/3,4-DNT separation was unsatisfactory on several occasions and method work was temporarily suspended as a result. The separation

between these two species was also shown to be incomplete in the Battelle work (reference A).

2. Because of the critical nature of the TNT/3,4-DNT separation, an alternative internal standard for 3,4-DNT should be employed in the future. The use of an internal standard which elutes in a region of the chromatogram where no explosives of interest also elute is desirable to eliminate the critical separation requirement. Eliminating 3,4-DNT would also have the likely effect of lowering the CRL for TNT, since no interfering material would be in the TNT chromatographic window.

3. The USAEHA has studied the behavior of about 40 compounds relative to method performance and, based on evaluations of these compounds, recommends that one of the following three materials be substituted for 3,4-DNT:

a. 2-methyl phenol (o cresol).

b. 3-methyl phenol (m cresol).

c. 4-methyl phenol (p cresol).

Each of the above phenols exhibits a strong UV absorbance, slightly differing retention times, and elutes between RDX and Tetryl (where there is an approximate 10-minute gap between elution of these explosives). Figure 7 shows the chromatogram obtained in substituting 2-methyl phenol for 3,4-DNT as the method internal standard. Each of the methyl phenols are stable compounds available in high purity from EPA or commercial vendors. While the ideal internal standard would be one compound which is detectable by both UV and PC detectors, of those compounds studied in this project, only atrazine responded in this way and it eluted late in the chromatographic run.

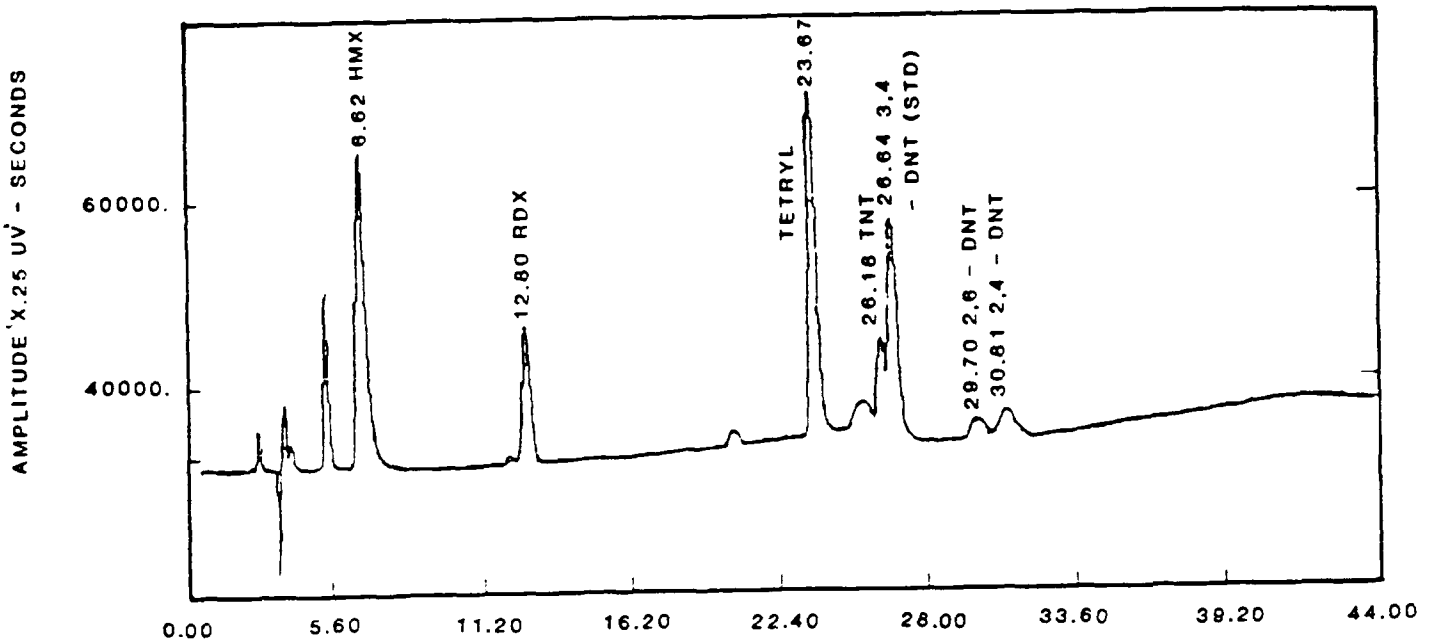
4. A mixing of stock portions of the PC detector internal standard (1-nitrobutane) and the UV detector internal standard (to be selected) before addition to the actual test extract would also eliminate the less efficient addition of two separate standards to samples. This would have the effect of minimizing procedural steps in the analysis, thereby reducing operator errors and increasing method accuracy.

C. Use a Surrogate Material to Monitor Extraction Adequacy.

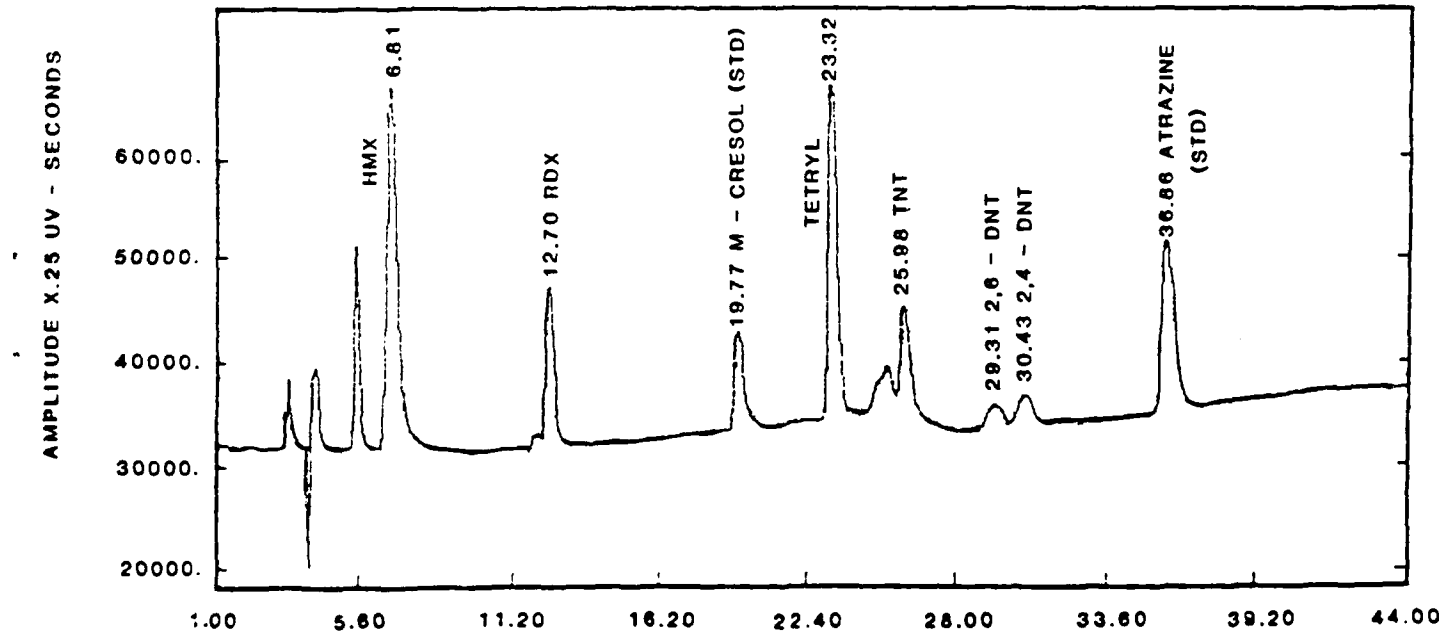
1. Many state-of-the-art environmental methods now being developed by the EPA make use of surrogate standard materials to document the extraction efficiency of the particular method for each sample assayed. The use of surrogate standards allows an evaluation of whether the extraction procedures (extraction, concentration, manipulative losses, etc.) were satisfactory for the particular sample. These materials are routinely used in most EPA organics monitoring methods.

FIGURE 7

CHROMATOGRAMS OF A 10XTRL STANDARD WITH CURRENT AND RECOMMENDED STANDARDS ADDED - ULTRAVIOLET DETECTOR



CURRENT STANDARDS



REMCOMMENDED STANDARDS

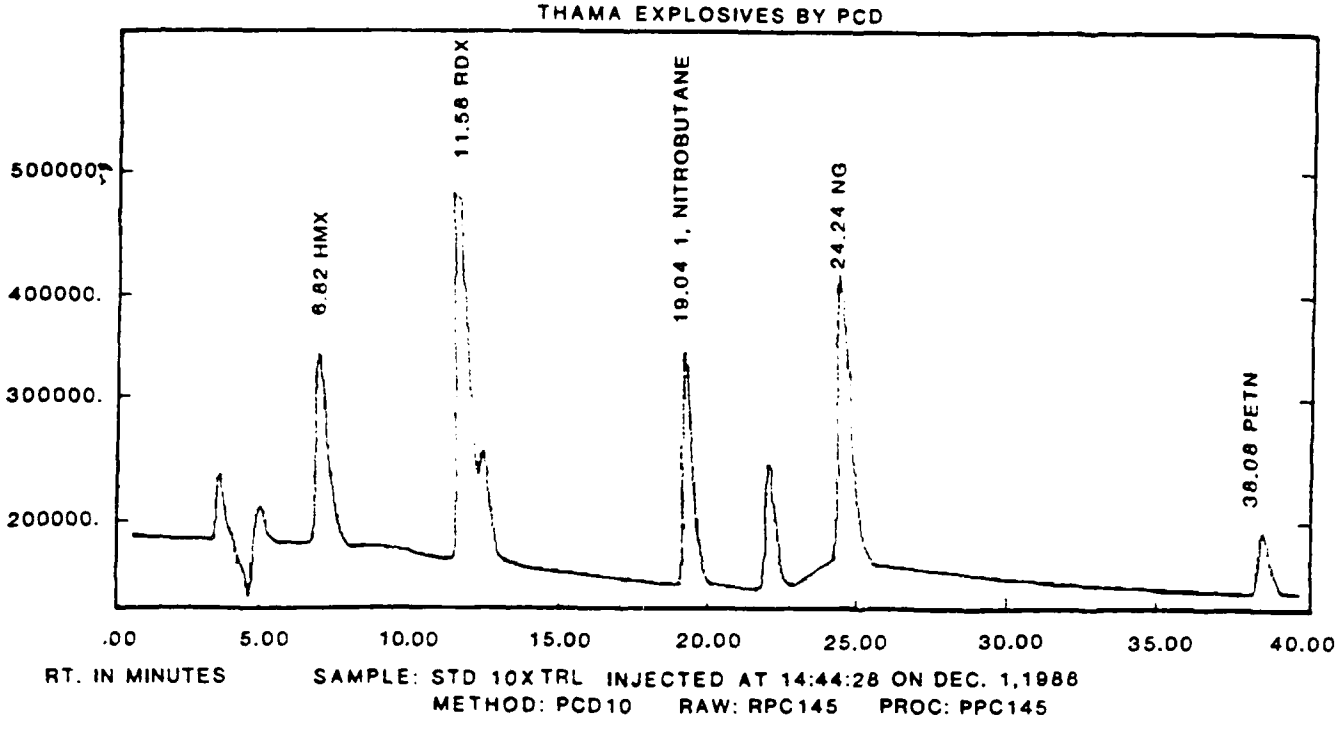
2. The USAEHA recommends using such a material in this procedure when it is implemented for explosives monitoring. Atrazine appears to be an excellent surrogate material for this purpose. Atrazine gives excellent response on both UV and PC detectors and elutes in a region of the chromatogram (after all explosives monitored) where little chemical interference has been noted to date. Figure 7 shows the retention behavior of atrazine in the UV detector chromatographic trace, and Figure 8 shows the corresponding PC detector chromatogram. Note that atrazine appears to be quantitatively recovered through the Hayesep R treatment. Atrazine is available in high purity from EPA.

3. Use of a surrogate standard such as atrazine would also indirectly monitor the presence of unknown chemical interferences affecting either the internal standards and/or the sample chromatography.

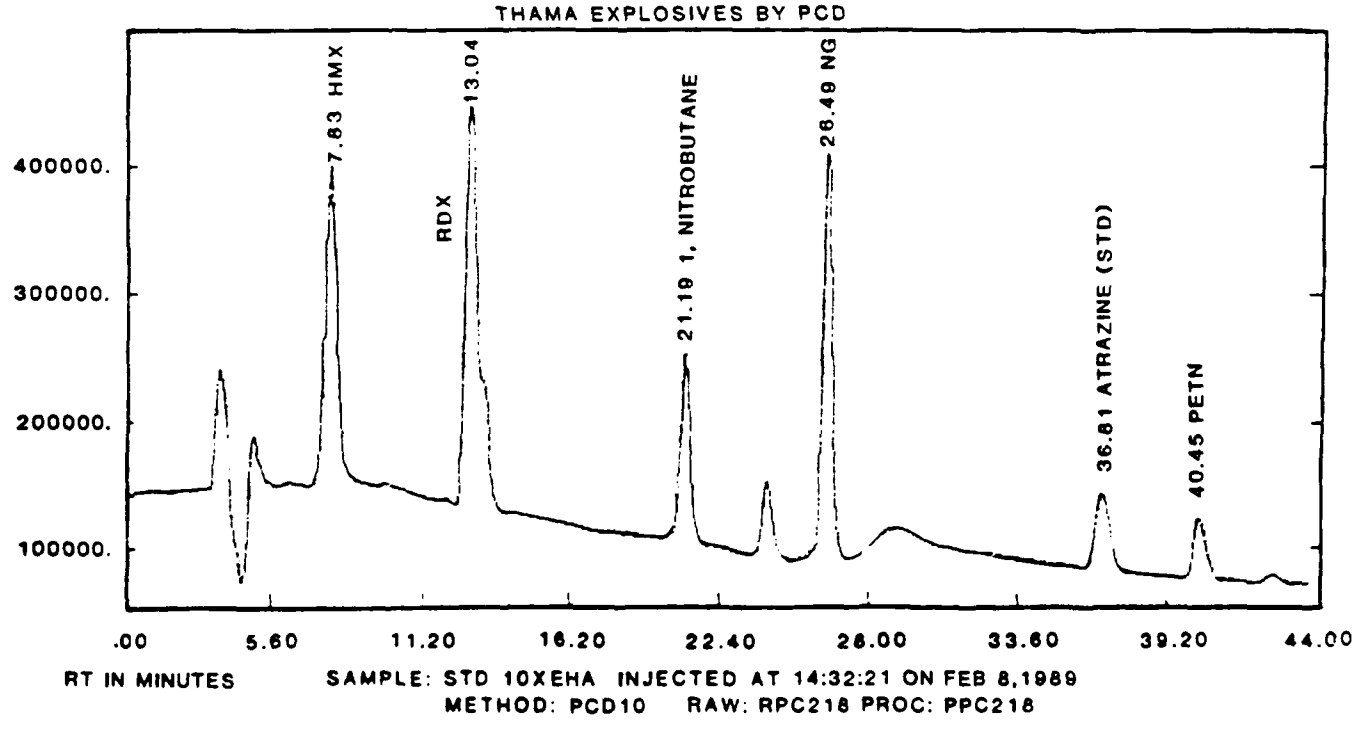
4. Proper method performance would depend on the recovery of atrazine within the method specified recovery windows for each compound with each detector. Actual recovery windows would be established through continual evaluations of method performance by USATHAMA on contractor-supplied data.

FIGURE 8

CHROMATOGRAMS OF A 10XTRL STANDARD WITH CURRENT AND RECOMMENDED STANDARDS ADDED - PHOTOCONDUCTIVITY DETECTOR



CURRENT STANDARDS



RECOMMENDED STANDARDS

APPENDIX

STANDING OPERATING PROCEDURE FOR HPLC DETERMINATION OF EIGHT EXPLOSIVES IN GROUND WATER

I. REFERENCES.

A. Evaluation of Solid Sorbent and Detector Technology for Determination of Explosives in Water. M.K.L. Bicking and S.J. Summer, February 1988.

B. U.S. Army Toxic and Hazardous Materials Agency Contract No. DAAL03-86-D-0001 Delivery Order 0620.

C. USATHAMA Installation Restoration Quality Assurance Program, December 1985 (2d Edition, March 1987). U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland.

II. SUMMARY.

A. Analytes.

The following analytes may be determined by this method:

Cyclotetramethylenetetranitramine (HMX);
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX);
N-methyl-N,2,4,6-tetranitroaniline (Tetryl);
Nitroglycerin (NG);
2,4,6-trinitrotoluene (TNT);
2,6-dinitrotoluene (2,6-DNT);
2,4-dinitrotoluene (2,4-DNT)
Pentaerythritoltetranitrate (PETN).

B. Matrix. This method is applicable to ground water. ASTM TYPE II water, containing 100 mg/L each of sulfate and chloride, is used for certification work as a simulant for ground water. The ASTM Type II water is made in the following manner:

1. 1.48 g of reagent grade anhydrous sodium sulfate is weighed into a 1-liter volumetric flask and diluted to the mark with ASTM TYPE I water.

2. 1.65 g of reagent grade anhydrous sodium chloride is weighed into a 1 -liter volumetric flask and diluted to the mark with ASTM TYPE 1 water.

3. 100 mL of each solution prepared in (1) and (2) is pipetted into a 1-liter volumetric flask and diluted to volume with ASTM TYPE I water.

C. General Method.

1. A 500 mL aliquot of ground water (or ASTM TYPE II water spiked with one of the explosives test concentrations) is passed through a pretreated solid sorbent cartridge packed with Hayesep R at approximately 10 mL/min (pretreatment of cartridges includes passing 100 mL of acetone followed by 100 mL ASTM TYPE I water at 10 mL/min through the cartridge before introducing sample).

2. After removal of excess water, the cartridge is eluted with 10 mL acetone into a 12 mL vortex tube, after which the acetone is evaporated under nitrogen to a volume of about 0.5 mL (primarily residual water). A commercially available heater assembly maintained at 42 to 47 degrees Centigrade is used to accelerate acetone evaporation. The 0.5 mL concentrate, after addition of both internal standards, is quantitatively transferred to a 2 mL volumetric flask and diluted to volume with 50/50 methanol/water. The sample is analyzed by reverse phase high pressure liquid chromatography (HPLC) using a methanol/water mobile phase gradient. Explosives detected are quantified by a dual detector system consisting of an ultraviolet (UV) absorbance detector set to 254 nm and a photoconductivity detector equipped with a zinc photoionization source.

III. APPLICATION.

A. Tested Concentration Range (ug/L).

HMX:	2.5 - 50;
RDX:	2.5 - 50;
Tetryl:	2.5 - 50;
NG:	5 - 100;
TNT:	0.5 - 10;
2,6-DNT:	0.25 - 5;
2,4-DNT:	0.25 - 5;
PETN:	2.5 - 50.

B. Sensitivity. This method employs a concentration factor of 250 (500 mL sample, 2.00 mL final volume). The mean response for each analyte, relative to the respective internal standard peak area, at the TRL should be approximately:

Compound	CRL	Detector
HMX	0.065	Absorbance
RDX	0.092	Absorbance
Tetryl	0.18	Absorbance
TNT	0.028	Absorbance
2,6-DNT	0.012	Absorbance
2,4-DNT	0.031	Absorbance
NG	0.11	Photoconductivity
PETN	0.068	Photoconductivity

C. Reporting Limit (ug/L).

Compound	TRL	CRL
HMX	5.0	5.1
RDX	5.0	7.5
Tetryl	5.0	14.
NG	10.	22.
TNT	1.0	1.3
2,6-DNT	0.5	2.7
2,4-DNT	0.5	0.79
PETN	5.0	6.3

D. Interferences. Trinitrotoluene separation from 3,4-dinitrotoluene (3,4-DNT), the UV detector internal standard, is the critical chromatographic separation in the analysis and system performance can be measured by separation of these constituents. An alternative standard to 3,4-DNT is suggested to lessen analytical performance requirements. Tetryl is unstable and decomposition products may interfere with the determination of HMX. Nitroglycerin and TNT may elute in the same time window with some columns; these analytes must be determined in separate experiments in such situations.

E. Analysis Rate. Using this procedure, a maximum of 12 samples may be analyzed in one day after instrument calibration. This estimate assumes that all instrument calibration data pass appropriate statistical tests.

F. Safety Information. The pure standards should be considered explosive and stored only in an approved manner. One of the analytes (2,6-DNT) is a carcinogen; no other unusual precautions are necessary for the stock solutions. Storage in a refrigerator at 4 degrees Centigrade is recommended. The usual laboratory precautions should be observed in handling toxic and flammable solvents such as acetone and methanol.

IV. APPARATUS AND CHEMICALS.

A. Glassware/Hardware.

1. Glassware.

a. 1 L volumetric flask.

b. 500 mL volumetric flask.

c. 10 mL graduated pipet.

d. 100 mL graduated cylinder.

e. 12 mL vortex tubes, graduated to 0.05 mL.

f. 2 mL volumetric flask.

g. disposable pasteur pipet, borosilicate glass.

2. Hardware.

a. Vacuum manifold, equipped for simultaneous sampling of at least six sorbent tubes (Supelco or equivalent).

b. Vacuum source.

c. Omni-Fit connectors.

d. Teflon tubing, 1/4 inch.

e. Sorbent tubes packed with 600 mg Hayesep R (Supelco).

f. Tube heater, with adaptor to handle 12 mL vortex tubes, Kontes (or equivalent).

B. Instrumentation.

1. Liquid Chromatograph.

Gradient high pressure system, equipped with autosampler and column heater jacket (Perkin Elmer Series 4 with Perkin Elmer Autosampler ISS-100 or equivalent).

Injector with 20 uL loop (Rheodyne Model 7125).

Reverse phase column (Zorbax ODS, 5 um, 250 x 4.6 mm). The column should be maintained at 35 degrees Centigrade.

Mobile Phase: Linear gradient from methanol/water (35/65) to (70/30) in 35 minutes at a flow of 0.7 mL/min. Each mobile phase reservoir contains 1 ppm tetramethylammonium chloride (TMAC). Minimum equilibration time is 15 minutes.

2. Detectors.

Absorbance (Tracor Model 970A or equivalent) - Wavelength: 254 nm.

Photoconductivity (Tracor Model 965) - Source: Zinc
Range: 10. The detector should be allowed to warm-up at least 2 hours before samples are analyzed. The photoionization source should be left on continuously to provide a more stable baseline. Prior to analysis, balance the flow

rates through each flow outlet (sample and reference) to within 2 percent. Balance the conductivity cells using procedures described in the Operator's manual. When not in use, the detector should be rinsed with methanol/water which does not contain TMAC. Do not allow TMAC-containing solutions to stand in the detector cells.

3. Chromatography data system. Hewlett-Packard Model 3357, Laboratory Automation System including CPLOT software. Real time data displayed on identical Hewlett Packard Model 3390A integrator/recorders. Any system capable of measuring retention time and reporting peak height and peak area ratios using the method of internal standards can be substituted for the above.

a. Retention times (based on 4 chromatograms) for 10X TRL standards during precertification:

Analyte	Mean Retention Time (min)	Window (min)
HMX	5.7	0.3
RDX	10.9	0.7
Tetryl	20.5	1.5
NG	23.8	1.9
TNT	23.5	1.9
2,6-DNT	27.5	1.3
2,4-DNT	28.4	1.1
PETN	35.7	0.2
3,4-DNT (I.S.)	24.2	1.9
1-Nitrobutane (I.S.)	18.7	1.0

These retention time data were obtained using a 4.6 x 250 mm Zorbax ODS column and the specified mobile phase. However, reproduction of these exact retention times may be difficult due to variations in the chromatographic performance of individual HPLC systems and columns. The analyst may adjust the volumetric composition of the mobile phase components in order to obtain resolution of analytes equivalent to that described here. If this adjustment results in a change in mobile phase composition of greater that 15 percent from the specified value, the analyst should contact USATHAMA immediately before proceeding.

b. The width of the retention time window used to make identification should be based upon measurements of actual retention time variations of standards over the course of the day. Three times the standard deviation of the retention time for a compound is used to calculate the window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatograms.

C. Analytes.

HMX
RDX
Tetryl
NG
TNT
2,6-DNT
2,4-DNT
PETN

D. Reagents and SARMS

1. Reagents.

a. Water (ASTM TYPE I).

b. Methanol (HPLC grade).

c. Acetone (HPLC grade).

2. Interim Reference Materials (IRMS).

a. 1-Nitrobutane (99 percent)
Fluka Chemical Company catalog no. 73250, or equivalent.

b. 3,4-DNT (99 percent)
Phaltz and Bauer catalog no. D48080, or equivalent.

c. Tetramethylammonium chloride (98 percent)
Fluka Chemical Company catalog no. 87720, or equivalent.

3. SARMs.

HMX:	Lot 1217	
RDX:	Lot 1130	
Tetryl:	Lot 1149	
NG:	Lot 1150	(Solution)
TNT:	Lot 1129	
2,6-DNT:	Lot 1148	
2,4-DNT:	Lot 1147	
PETN:	Lot 1151	(Solution)

V. CALIBRATION.

A. Initial Calibration.

1. Preparation of Standards.

a. Concentrated Stock Solutions.

HMX (0.5 mg/mL):	25 mg in 50 mL ethyl acetate/methanol(50/50);
RDX (1 mg/mL):	50 mg in 50 mL methanol;
Tetryl (1 mg/mL):	50 mg in 50 mL methanol;
NG (2 mg/mL):	200 mg in 100 mL methanol;
TNT (1 mg/mL):	50 mg in 50 mL methanol;
2,6-DNT (1 mg/mL):	50 mg in 50 mL methanol;
2,4-DNT (1 mg/mL):	50 mg in 50 mL methanol;
PETN (2 mg/mL):	200 mg in 100 mL methanol.

b. Composite Mixture (Stock A). Dilute the following volumes (mL) to 100 mL with methanol:

HMX:	10
RDX:	5.0
Tetryl:	5.0
NG:	5.0
TNT:	1.0
2,6-DNT:	0.50
2,4-DNT:	0.50
PETN:	2.50

If resolution between any of the analytes is not acceptable, two composite mixtures may be prepared.

c. Internal Standard Solution. Prepare a 400 ug/mL solution of the absorbance internal standard (3,4-DNT) in methanol. Prepare a 4,000 ug/mL solution of the PCD internal standard (1-nitrobutane) in methanol.

d. Calibration Standards/Spiking Solutions at Multiples of the TRL.

20X TRL	1.000 mL
10X TRL	0.500 mL
5X TRL	0.250 mL
2X TRL	0.100 mL
1X TRL	0.050 mL
0.5X TRL	0.025 mL
0.4X TRL	0.020 mL

Preparation of calibration standards: To prepare calibration standards at a desired multiple of the reporting limit, add 250 uL of the absorbance internal standard solution, 500 uL of the PCD internal solution and the appropriate amount of the composite mixture to a 10 mL graduated flask and dilute to volume with methanol/water (50/50).

2. Instrument Calibration. Prepare duplicate composite calibration standards as described in paragraph V.A.1.d. Prepare duplicate blanks using a 250 uL aliquot of the absorbance internal standard solution, 500 uL of the PCD internal standard solution, and dilute to 10.00 mL with methanol/water (50/50). Analyze all calibration standard solutions using reverse phase liquid chromatography as described in paragraph IV.B.

3. Analysis of Calibration Data. Submit calculated amount ratio data for lack-of-fit and zero intercept tests. If both tests are accepted, proceed with daily calibration as described in paragraph V.B. below. If tests are not accepted, follow procedures as described in the USATHAMA QA Program Manual.

B. Daily Calibration.

1. Preparation of Standards. Prepare calibration standards as described in paragraph V.A.1.d for the 10X TRL standard. Prepare a blank as described in paragraph IV.A.2.

2. Instrument Calibration. Use the same operating parameters and procedures used to obtain initial calibration. Analyze the daily calibration solution and recalibrate before any samples are tested.

3. Acceptance criteria are described in detail in the USATHAMA QA Program Manual. The 10X TRL standard is used for daily calibration. All standards are analyzed according to that calibration. Another 10X TRL standard tested at the end of the standard series must agree within 25 percent of the initial response for each analyte. If the daily calibration is not within the required percentage of the mean response, follow the corrective procedures described in the USATHAMA QA Manual.

4. Calibration Checks. No calibration check standards are available at this time.

VI. CERTIFICATION TESTING. See Tables attached labeled CERTIFICATION ANALYSIS DATA and DAILY CALIBRATION DATA FOR 10X TRL STANDARD for values obtained by USAEHA in certification of this method.

VII. SAMPLING HANDLING AND STORAGE.

A. Sample Procedure.

1. Sorbent cartridges are cleaned by passing 100 mL of acetone through each cartridge at approximately 10 mL/min using the vacuum manifold. The cartridge is then rinsed with 100 mL of reagent water. The sorbent should not be allowed to dry out at this stage. Cartridges are capped tightly until they are used. A 500 mL aliquot of the sample is measured into an volumetric flask. If suspended solids are visible, filter the sample through filter paper. Connect the cartridges to the Teflon tubing using the Omni-fit connectors. Place the Teflon tubing into the volumetric flask containing the sample. The sample is drawn through the sorbent tube at a rate of approximately 10 mL/min.

2. After the entire sample has passed through the cartridge, the sorbent is dried by allowing air to pass through the cartridge for several minutes. The cartridges are capped tightly until extraction.

B. Containers. Glass containers must be used for samples and standards.

C. Storage Conditions and Holding Time Limits. If water samples are not extracted at the sampling site, they may be stored at 4 degrees Centigrade for no more than 7 days before extraction. The sorbent must be extracted and analyzed within 40 days.

D. Solution Verification. For the first seven calibrations, the response of the 10X TRL standard must agree within 25 percent with a mean response for the same concentration, as determined in the precertification calibration. If the daily calibration is not within the required percent or two standard deviations of the mean response, follow the procedure as described in the USATHAMA QA Program Manual.

VIII. PROCEDURE.

A. Separations. Critical separations in the HPLC analysis are the separation of TNT/3,4-DNT as well as 2,4-DNT/2,6-DNT. Reduced chromatographic resolution will bring merging of the TNT/3,4-DNT analytes and inability to detect TRL quantities of TNT. Also, the 2,6-DNT/2,4-DNT separation could deteriorate to the point of incomplete separation of these analytes. A guard column is suggested to protect and maintain chromatographic column efficiency.

B. Chemical Reactions. Tetryl is unstable and decomposition products may interfere with the determination of HMX.

C. Instrumental Analysis. Analyze all samples by HPLC using instrumental procedures recommended by the manufacturer. When available, an autosampler may be used. The photoconductivity detector is a very sensitive detector of ionic impurities. Use of freshly prepared deionized water of the highest quality (> 17 megohm/cm) attainable keeps the detector drift to a minimal, acceptable level. Also, gas bubbles can form in the PCD cell and cause severe PCD signal spikes to occur. Scrupulous degassing of the HPLC solvents should eliminate the problem. This may be accomplished by sonicating the solvent containers under vacuum.

IX. CALCULATIONS.

A. The peak areas for all analytes are determined in the same manner as the calibration standards. All peak areas are ratioed to the peak area for the appropriate internal standard for the detector. The concentration of each analyte is then determined from the most recent instrument calibration data, provided that daily calibration meets acceptable performance criteria. The concentration may be calculated using either the actual concentration or a multiple of the detection limit. However, all results must be reported in terms of the concentration of analyte in the original sample.

B. Three analytes (HMX, RDX, and Tetryl) may be quantified using either the absorbance detector of the PCD. However, use of the ultraviolet absorbance detector is recommended due to its greater stability. For these analytes, the PCD data may then be used as secondary confirmation of identity and quantitation of analyte levels.

X. DATA. See attached data tables.

TABLE A1
RAW AREA COUNTS VERSUS CONCENTRATIONS OF EXPLOSIVES

SPIKE LEVEL (X TRL)	HMX	RDX	Tetryl	NG	TNT	2,6-DNT	2,4-DNT	PETN
	316523	395393	629933	5379626	170451	61054	121818	2614546
20	323391	434564	729037	7216672	166203	59088	125032	3024466
	171235	192526	338759	2057992	83777	31350	64827	1070374
10	165333	230311	356503	2364964	78735	31287	60476	1187420
	81301	90700	162926	812222	36386	14530	28863	439190
5	77725	114219	180310	1015992	33753	13426	30454	524115
	31694	38947	63304	293964	13613	5651	11580	167473
2	32168	48881	70126	371654	14445	6003	10812	193537
	13974	19049	35146	113772	6207	2855	6443	73991
1	15603	23095	45669	174556	6491	2561	7729	102021
	7877	10173	19331	45254	2311	ND*	7770	38484
0.5	8350	11076	22189	108764	3628	ND	6822	46038
	5291	8675	14021	15736	ND	ND	4099	26375
0.4	6733	9029	26506	50800	2197	2078	2523	36600
	2599	ND	4706	ND	ND	ND	2814	ND
0	ND	ND	ND	ND	ND	ND	ND	ND

*ND - None Detected

TABLE A2
CALCULATED AMOUNTS FOR INITIAL CALIBRATION CURVE

SPIKE LEVEL (X TRL)	HMX	RDX	Tetryl	NG	TNT	2,6-DNT	2,4-DNT	PETN
	23.916	25.922	23.049	66.639	5.178	2.429	2.435	31.600
20	24.396	23.564	25.294	90.530	4.751	2.445	2.441	31.918
	12.725	12.413	12.190	24.787	2.503	1.227	1.274	12.579
10	12.645	12.662	12.540	29.760	2.282	1.313	1.197	12.570
	6.933	6.711	6.728	10.417	1.248	0.652	0.651	5.496
5	6.203	6.552	6.618	10.425	1.021	0.588	0.629	5.188
	2.488	2.652	2.406	3.840	0.430	0.234	0.240	2.134
2	2.420	2.644	2.427	4.483	0.412	0.248	0.211	1.964
	1.089	1.288	1.326	1.478	0.194	0.117	0.133	0.938
1	1.206	1.283	1.623	2.075	0.190	0.109	0.155	1.020
	0.617	0.691	0.733	0.587	0.073	ND	0.161	0.487
0.5	0.634	0.604	0.755	1.300	0.104	ND	0.134	0.463
	0.415	0.591	0.533	0.205	ND	ND	0.085	0.335
0.4	0.501	0.483	0.907	0.608	0.062	0.085	0.049	0.368
	ND	0.182	0.184	ND	ND	ND	0.060	ND
0	ND	ND	ND	ND	ND	ND	ND	ND
Target Reporting Limit ug/mL STD	1.25	1.25	1.25	2.5	0.25	0.125	0.125	1.25

TABLE A3
DAILY PEAK AREA DATA FOR 10X TRL STANDARD

ACTIVITY	HMX	RDX	Tetryl	NG	TNT	2,6-DNT	2,4-DNT	PETN	3,4-DNT	1-NB
10X TRL-DAY1-CAL	168785	194530	348548	2132193	83958	32059	63801	1092650	239860	1244074
10X TRL-DAY2-CAL	162080	225487	352415	2011208	85548	29551	62635	1195354	228592	1420986
10X TLR-DAY1-DATA	171235	192526	338759	2057992	83777	31350	64827	1070374	239045	1211076
10X TRL-DAY2-DATA	165333	230311	356503	2364964	78735	31287	60476	1187420	230497	1403664
10X TRL-DAY2-FINAL	163430	233057	354552	2596402	79491	26798	55056	1345758	241377	1520476

TABLE A4

DAILY CALIBRATION DATA FOR 10X TRL STANDARD

		Peak Area							
Activity	Days	HMX	RDX	TETRYL	NG	TNT	2,6-DNT	2,4-DNT	PETN
Initial Calibration		171235	192526	338759	2057992	83777	31350	64827	1070374
		165333	230311	356503	2364964	78735	31287	60476	1187420
Certification Days	1	184563	212500	396334	3326616	85646	31814	62041	1721100
	2	178595	197028	368047	2171304	94620	25412	56162	1205858
	3	174250	244237	366673	2382718	75145	31629	62568	1281646
	4	170542	103593	400528	2651958	77660	27074	59006	508324

TABLE A5

CERTIFICATION ANALYSIS DATA

Multiple of TRL	Replicate	Concentration Found, ug/L							
		HMX	RDX	TETRYL	NG	TNT	2,6-DNT	2,4-DNT	PETN
10	1	41.8	47.7	40.0	93.9	8.78	4.35	4.64	45.2
	2	51.9	52.3	37.8	96.4	7.64	5.67	5.40	28.1
	3	48.8	45.9	43.7	87.4	7.59	4.28	4.65	43.2
	4	51.0	61.7	38.1	98.3	9.70	5.82	5.30	56.8
5	1	27.1	25.9	9.52	44.6	4.30	2.03	2.15	20.4
	2	27.7	28.3	16.7	44.1	3.79	2.83	2.87	16.9
	3	21.3	21.3	15.9	23.1	3.46	.672	1.57	12.6
	4	23.7	28.6	22.7	42.6	4.50	3.16	2.46	33.4
2	1	12.4	11.8	7.07	15.5	1.42	.882	.970	8.36
	2	9.41	10.7	7.30	16.5	1.34	1.64	1.31	8.47
	3	9.02	8.38	8.35	5.95	1.26	.177	.679	6.12
	4	10.4	13.6	1.85	12.2	1.63	1.18	1.22	11.6
1	1	6.98	6.56	4.06	7.54	.435	.374	.484	4.36
	2	5.85	7.04	3.99	10.6	.585	.397	.401	3.51
	3	4.29	4.56	3.75	2.18	.609	.442	.405	3.42
	4	5.25	5.90	4.57	5.15	ND	.472	.580	5.92
0.5	1	4.49	4.83	2.59	4.04	ND	.278	.177	1.78
	2	2.84	3.20	3.77	1.67	ND	ND	ND	1.60
	3	2.76	2.31	2.76	ND	ND	ND	.249	2.14
	4	3.90	5.64	1.66	1.13	.270	ND	ND	3.74
0	1	ND	1.18	.530	ND	ND	ND	.299	2.22
	2	ND	ND	ND	ND	ND	ND	.251	ND
	3	ND	.870	ND	ND	ND	ND	ND	ND
	4	3.55	5.86	.927	ND	ND	.200	ND	ND
Target Reporting Limit, ug/L		5	5	5	10	1	0.5	0.5	5

SOP 32.1
DATE: 14 JUNE 88

PROCEDURE FOR OBTAINING ASTM TYPE I WATER

PURPOSE: To obtain ASTM Type I water for laboratory operations.

The deionized water system (DI) is located in laboratory room 2200. It is a Millipore Milli-Q system. Cartridges are changed every 3 months to obtain the required quality of water.

PROCEDURE:

1. Turn on the building E2100 deionized water valve at the sink.

2. Turn on the Recirculator Pump on the Milli-Q system (a toggle switch located at the left side of the system).

3. Let the system run until the meter (above turn-on switch) reads 17 megohm/cm or better (ASTM Type I).

4. Flush about 6 liters of water into a flask (the valve is located to the far right of system) and dump.

5. Collect the required deionized water volumes while watching the quality meter and making sure the meter reads greater than or equal to 17 megohm/cm.

6. After collection is completed, turn off the system in the following sequence:

   a. Turn off the output valve.

   b. Turn off power to the recirculating pump.

   c. Turn off the building E2100 deionized water valve.

Initiated By JAB Reviewed By RJV Authorized By [illegible]

SOP C06
DATE: 18 AUG 88

PROCEDURE FOR DEGASSING SOLVENTS FOR HPLC

PURPOSE: To provide gas-free solvents to prevent out-gassing in the Photoconductivity detector.

PROCEDURE:

1. Follow procedure for filtering solvents for HPLC (SOP C05) except for item #5.

2. After pouring solvent into resevoir bottles attach to a vacuum supply and place bottle in sonic bath for 10 minutes.

3. Stop sonic bath and continue vacuuming for an additional 5 minutes.

Initiated By JAB Reviewed By _____ Authorized By _____