The USACHPPM Gas Chromatographic Procedures for the Analysis of Waters and Soils for Energetics and Related Compounds

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Abstract

The procedures currently used by the U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM) for the analysis of energetics and related compounds in water and soils are presented. These procedures are based on the use of isoamyl acetate to extract the analytes of interest from their environmental matrices with subsequent analysis using gas chromatography with electron capture detection. The suite of compounds included are those that have been of environmental significance for years (such as 2,4,6-trinitrotoluene, hexahydro-1,3,5-trinitro-1,3,5-triazine, and dinitrotoluenes) and are the subject of several U.S. Environmental Protection Agency SW-846 methods. The procedures presented in this study are the product of years of development and refinement of methods used for the analysis of many real-world samples by the USACHPPM explosives analysis laboratory. The development, performance, advantages, and details of these procedures are described. The extension of these methods to the analysis of other media is also briefly discussed.

Introduction

The U.S. Army has been involved with the environmental monitoring of residual energetics and related compounds for over three decades. Concern for the health and safety of soldiers; civilian workers; the general population; and the environment near military bases, ammunition plants, and munitions testing centers led to this monitoring requirement. Energetic compounds and some of their breakdown products are of sufficient toxicity and thus are chemicals of concern when present in the environment (1–3). Methodology that can be used to analyze soil and water samples for nitroaromatics, nitramines, and nitrate esters was developed over the years by various army laboratories, many of them being internal unpublished methods. The U.S. Army Environmental Hygiene Agency (USAEHA) did begin to publish some of its procedures, however, starting in the 1970s (4–7). T. Jenkins et al. (8–13) at the U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory (CRREL) (Hanover, NH) have been regularly developing methods for analyzing munitions and making them public since the 1980s. The U.S. Environmental Protection Agency (USEPA) has included several of these methods into its SW-846 compendium of procedures (14). SW-846 Method 8330 is a high-performance liquid chromatographic (HPLC) technique for analyzing soil and water extracts for nitroaromatics and nitramines. It has been a popular procedure for more than a dozen years, especially for analyzing soil samples. Method 8332 is a variant on Method 8330 and is used for the analysis of nitroglycerin using a different UV wavelength. The more recent draft, Method 8095, was proposed in 1998; it employs gas chromatography (GC) with electron capture detection (ECD) to analyze sample extracts. Soils are prepared in a similar fashion as for Method 8330, but the waters are extracted using solid-phase extraction techniques.

The U.S. Army Center for Health Promotion and Preventive Medicine (USACHPPM), which was formerly the USAEHA, never adopted the water analysis portion of Method 8330, preferring its own water procedures. The very earliest GC procedures that USAEHA used for the determination of nitroaromatics in water are primitive by today's standards. Water samples were extracted using benzene, and the extracts were analyzed using GC with packed columns and flame ionization detection. The detection limit for trinitrotoluene (TNT) at the time was approximately 1 part per million, and nitramines could not be detected at all with the technique. Over the years, the procedure was modified to use toluene instead of benzene (for reasons of safety); toluene was satisfactory for the extraction of nitroaromatics, but not nitramines. A search for a more suitable solvent eventually led to isoamyl acetate, which was found to work well for nitroaromatics, nitramines, and nitroglycerin. Capillary columns (first glass, then fused silica) replaced packed columns and greatly improved the chromatography. ECD replaced flame ionization and significantly reduced detection limits. The suite of analytes was increased to

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mirror the Method 8330 list. Inert injection port liners and seals permitted the reliable analysis for the nitramine compounds. Thus, the method that is presented in this study is one that has evolved over several decades and has proven to be sensitive and dependable for the analysis of water samples. USEPA Region 3 has approved its use for the analysis of samples from specific sites within its region.

USACHPPM has used Method 8330 for many years for the analysis of soil samples and used its internal procedure equivalent to what has become draft Method 8095 to perform confirmatory analyses on the soil extracts and to analyze for nitroglycerin. The soil procedure that USACHPPM is now employing was developed out of the requirement to achieve lower detection limits than Method 8330 provides and the desire to use GC rather than HPLC. There have always been some difficulties with Method 8330 in terms of the detection of false positives with the UV detector used with the procedure because this detector is not very specific. Another problem we have faced with the HPLC procedure is the variability between columns in their ability to obtain separation of all the analytes. We have found that we must revise the operating conditions for each new column or whenever we store a column for any duration. These problems, coupled with our requirement to set up and perform rapid analyses for environmental contaminants in areas containing deployed soldiers, led us to pursue GC as the instrumental technique of choice for analyzing soil extracts. The GC draft Method 8095 has its advantages of sensitivity and selectivity over Method 8330. However, its use of acetonitrile as the solvent can sometimes be a problem with GC (as will be discussed). The USACHPPM soil procedure described in this study is, in many ways, a modification of the water procedure. It employs a similar chromatographic approach and it uses isoamyl acetate as an extraction solvent. It has been tested with various soil types and directly compared with Method 8095. The results have been favorable (as will be shown).

It should also be noted that GC–mass spectrometry (MS) has been proposed as an alternative to GC–ECD (15). Our laboratory does use it as a tool for confirming positive sample results, especially in samples containing significant interferences. For this study, however, GC–MS (or GC–MS–MS) has not yet been proven to be as economical or practical to use for the routine quantitation of the suite of analytes that are analyzed by the other methods.

The chromatographic methodologies used for water and soil have also been incorporated into the USACHPPM procedures for atmospheric sampling, as described elsewhere (16). They have also been used for the analysis of a variety of munitions destruction process waste samples. This particular application is briefly described in this study.

Experimental

Preparation of water samples and standards

Water samples were extracted within seven days of their collection, and kept refrigerated at 4ºC ± 2ºC until time of extraction. The extraction was conducted in a 100-mL screw-top volumetric flask with a Teflon-lined screw cap. The flask was filled with sample beyond the meniscus mark and then allowed to stand until the water reached room temperature. The excess water was withdrawn to bring the water level to the mark. Forty microliters of 3,4-dinitrotoluene (DNT) at 0.30 µg/mL in acetonitrile was added to the flask as a surrogate compound. One milliliter of isoamyl acetate (anhydrous, 99+%) (Aldrich, Milwaukee, WI) was then added to the flask and the flask capped and placed on a rotary shaker for 30 min. The sample was shaken at a speed of approximately 15 rpm. At the end of that time, the sample was removed from the shaker and allowed to stand until the isoamyl acetate and water layers separated. The isoamyl acetate portion was transferred with a Pasteur pipette to an autosampler vial for GC analysis. Usually a standard 2-mL autosampler vial is satisfactory, but if a sample has a severe emulsion then a limited insert vial may be required. A laboratory deionized water blank, laboratory control sample(s), matrix spikes, and the standards to be analyzed were prepared using this same procedure.

The standards were made by injecting varying amounts of a mixed component spiking solution into six flasks, each containing 100 mL deionized water. The spiking solution was prepared in acetonitrile by the dilution of 1.0-mg/mL individual standards of Method 8330 compounds from AccuStandard (New Haven, CT), 3,4-DNT (Aldrich), and nitroglycerin from Cerilliant (Austin, TX) up to 50 mL. The spiking solution contained nitrobenzene, 2,4,6-TNT, and 1,3,5-trinitrobenzene at 0.60 µg/mL (using 30 µL); 1,3-dinitrobenzene, nitroglycerin, and the nitrotoluene isomers at 1.8 µg/mL (using 90 µL); 2,4-DNT at 0.40 µg/mL (using 20 µL); 2,6-DNT at 0.20 µg/mL (using 10 µL); 3,4-DNT at 0.30 µg/mL (using 15 µL); 4-amino-2,6-DNT, 2-amino-4,6-DNT, and tetryl at 3.0 µg/mL (using 150 µL); hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) at 2.4 µg/mL (using 120 µL); and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) at 48.0 µg/mL (using 2.4 mL). This solution was added to the 6 flasks using 2.5, 5.0, 10.0, 25.0, 50.0, and 100 µL, respectively. The low standard was equivalent to one-half of the reporting limit for most of the analytes. Finally, the same spiking solution was used for matrix spiking in water samples (using 40 µL).

Preparation of soil samples

Soil (and sediment) samples were extracted within 14 days of their collection and kept refrigerated at 4ºC ± 2ºC until time of processing. An aliquot of sample (at least 10 g) was placed in a disposable aluminum weighing pan and air dried to a constant weight (generally overnight). The dried soil was carefully ground (if necessary) in a clean mortar, homogenized, and sieved to pass through a 40-mesh sieve. A subsample of this sieved fraction was placed in a 40-mL amber glass vial with a Teflon-lined screw cap. Generally, a 2.0-g portion of sample was taken for analysis, but up to a 5.0-g sample may be used when lower reporting limits are desired. Twenty milliliters of deionized water were added to the vial and 10 µL of 3,4-DNT at 0.50 µg/µL in isoamyl acetate were injected into the soil as a surrogate compound. Finally, 5.0 mL of isoamyl acetate was added to the vial. The vial was capped and set into an ultrasonic bath for a minimum of 12 h and then on a rotary shaker for two more hours. The sample was removed from the shaker and allowed to stand until the isoamyl acetate and water layers separated. It has been found that placing the vial in a refrigerator for several hours usually helps to produce a very clear

isoamyl acetate phase, requiring no filtration or centrifugation. A portion of the isoamyl acetate extract was transferred with a Pasteur pipette to an autosampler vial for GC analysis. A laboratory blank soil, laboratory spiked control soil, and matrix spikes were prepared by using the same procedure with the spiking done directly into the soils prior to the addition of water.

Standards for the soil's analysis, such as were used for these studies, were prepared by the serial dilution in isoamyl acetate of a 1.0-mg/mL mix of Method 8330 compounds, a 1.0-mg/mL individual HMX solution, a 1.0-mg/mL standard of 3,4-DNT from Aldrich, and a 1.0-mg/mL sample of nitroglycerin from Cerilliant. Standards were made at 2.0, 1.0, 0.5, 0.2, 0.1, 0.02, and 0.01 µg/mL of all the compounds except HMX, which was twice the concentration of the others. The Method 8330 mix and nitroglycerin were also used for matrix spiking; they were first diluted together 1/10 in isoamyl acetate and 50 µL used per spike.

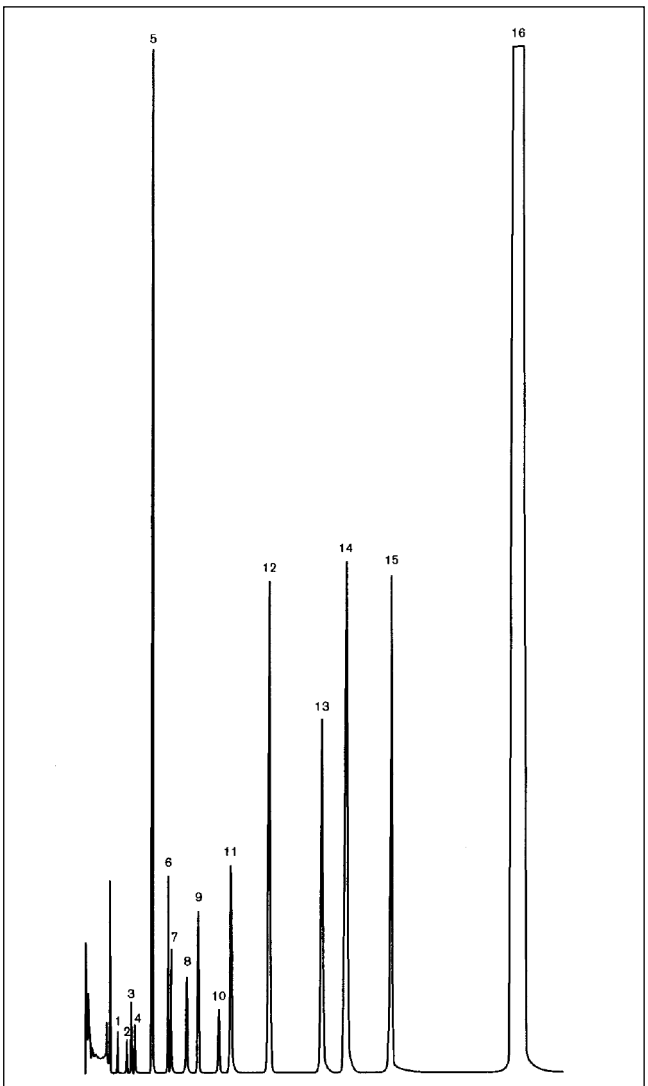

Figure 1. Chromatogram for energetics analysis in water on a 7-m, 0.53-mm-i.d., 1.0-µm-film dimethylpolysiloxane column with ECD. Temperature programmed in steps from 80°C to 200°C, and He carrier pressure programmed from 2.0 to 4.0 psig. The respective components peaks had the following retention time values: nitrobenzene (1), 1.57; 2-nitrotoluene (2), 2.03; 3-nitrotoluene (3), 2.29; 4-nitrotoluene (4), 2.41; nitroglycerin (5), 3.26; 1,3-dinitrobenzene (6), 3.97; 2,6-dinitrotoluene (7), 4.13; 2,4-dinitrotoluene (8), 4.84; 3,4-dinitrotoluene (9), 5.37; 1,3,5-trinitrobenzene (10), 6.32; 2,4,6-trinitrotoluene (11), 6.88; RDX (12), 8.62; 4-amino-2,6-dinitrotoluene (13), 11.04; 2-amino-4,6-dinitrotoluene (14), 12.14; tetryl (15), 13.80; and HMX (16), 19.56.

Chromatography

Analyses for the Method 8330 target list of compounds, nitroglycerin, and the surrogate compound have been conducted using Agilent Technologies (Palo Alto, CA) (formerly Hewlett Packard) Model 6890 GCs equipped with ECDs. Although the standards concentrations differed between the water and soil analyses, the chromatography was similar between the two methods. It will generally vary according to the individual GC used and the nature of the samples, but the basic column types and conditions used in our laboratory are as follows.

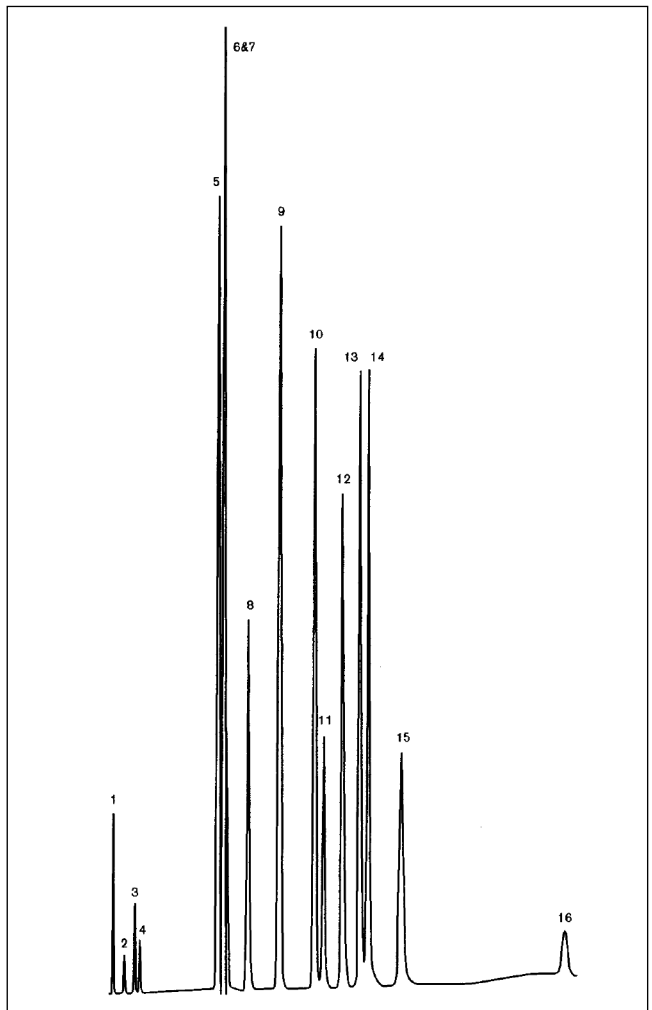

Figure 2. Chromatogram for energetics verification analysis on a 7–8-m, 0.53-mm-i.d., 1.0-µm-film 50% trifluoropropyl–methylpolysiloxane column with ECD. Temperature programmed from 80°C to 225°C, and H_2 carrier pressure programmed from 3.0 to 9.0 psig. The respective components peaks had the following retention time values: nitrobenzene (1), 1.58; 2-nitrotoluene (2), 1.86; 3-nitrotoluene (3), 2.12; 4-nitrotoluene (4), 2.25; 2,6-dinitrotoluene (5), 4.17; nitroglycerin (6), 4.31; 1,3-dinitrobenzene (7), 4.39; 2,4-dinitrotoluene (8), 4.89; 3,4-dinitrotoluene (9), 5.66; 2,4,6-trinitrotoluene (10), 6.53; 1,3,5-trinitrobenzene (11), 6.75; 4-amino-2,6-dinitrotoluene (12), 7.21; 2-amino-4,6-dinitrotoluene (13), 7.65; RDX (14), 7.86; tetryl (15), 8.68; and HMX (16), 12.67.

Primary runs were typically made using a dimethylpolysiloxane column (0.53-mm i.d., 1.0-µm film thickness) cut to 7 m in length (see Figure 1 for an example of the chromatography). The GC oven was temperature programmed from 80ºC at 15º/min to 140ºC, then at 3ºC/min to 170ºC, and finally at 5.0ºC/min to 200ºC (held 3.0 min). The helium carrier gas was programmed from 2.0 psig (held 13.0 min) to 4.0 psig at a rate of 150 psig/min and then held. The dilution gas was nitrogen set at 30 mL/min. The injection port temperature was set at 225ºC; the injection port liner was a silanized glass 4-mm liner or a Silcosleeve (Restek, Bellefonte, PA) with a Silcosteel seal used in splitless mode. The Ni-63 ECD temperature was 250ºC. Data processing was done using TotalChrom (PE Nelson, Shelton, CT). An Agilent Model 7673A autosampler was used to make the injections; the injection volume was 1.0 µL for the soil extracts and 2.0 µL for water extracts.

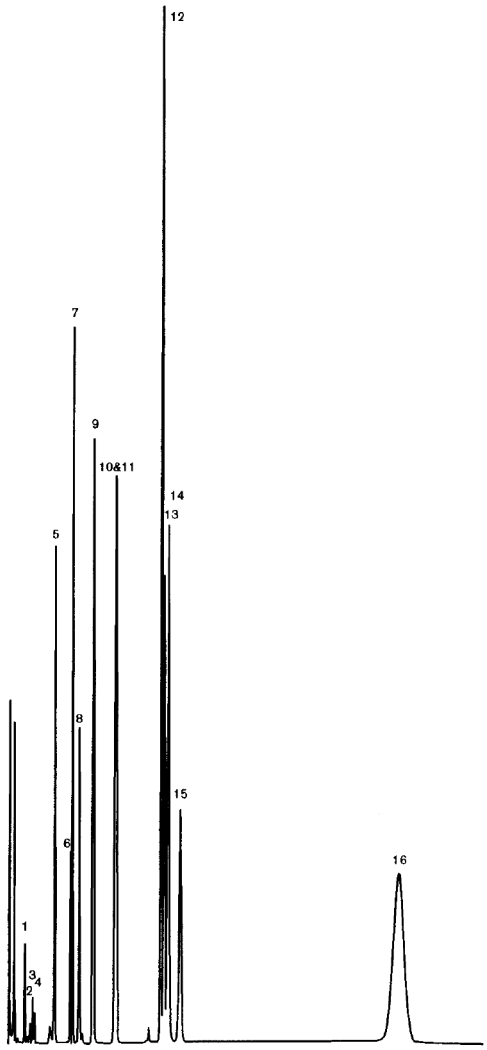

Figure 3. Chromatogram for energetics verification analysis on a 10-m, 0.53-mm-i.d., 1.0-µm-film 50% phenyl–methylpolysiloxane column with ECD. Temperature programmed from 80°C to 200°C, and He carrier pressure programmed from 2.0 to 6.0 psig. The respective components peaks had the following retention time values: nitrobenzene (1), 0.67; 2-nitrotoluene (2), 0.84; 3-nitrotoluene (3), 1.11; 4-nitrotoluene (4), 1.25; nitroglycerin (5), 2.25; 1,3-dinitrobenzene (6), 3.01; 2,6-dinitrotoluene (7), 3.09; 2,4-dinitrotoluene (8), 3.56; 3,4-dinitrotoluene (9), 4.07; 2,4,6-trinitrotoluene (10), 5.12; 1,3,5-trinitrobenzene (11), 5.12; RDX (12), 7.30; 4-amino-2,6-dinitrotoluene (13), 7.50; 2-amino-4,6-dinitrotoluene (14), 7.62; tetryl (15), 8.18; and HMX (16), 18.50.

Confirmation column analyses were done on all positive samples. Columns that have proven useful for this contain 50% trifluoropropyl–methylpolysiloxane or 50% phenyl–methylpolysiloxane liquid phases. Figures 2 and 3 provide chromatographic examples. The 50% trifluoropropyl–methylpolysiloxane column was 0.53-mm i.d. and 1.0-µm film thickness cut to 7–8 m in length; it was temperature programmed from 80ºC at 15º/min to 225ºC and held for 7 min. It used hydrogen carrier pressure programmed from 3.0 to 9.0 psig at a rate of 10.0 psig/min and held

Table I. Method Detection and Reporting Limits for the USACHPPM Water and Soils Procedures

	Water (µg/L)		Soil* (µg/g)	
Compound	MDL	MRL	MDL	MRL
2,6-DNT	0.001	0.01	0.004	0.01
2,4-DNT	0.003	0.02	0.006	0.02
2,4,6-TNT	0.004	0.03	0.007	0.01
RDX	0.016	0.10	0.006	0.01
HMX	0.58	3.0	0.023	0.05
2-Nitrotoluene	0.016	0.09	0.006	0.02
3-Nitrotoluene	0.044	0.09	0.005	0.02
4-Nitrotoluene	0.035	0.09	0.006	0.02
Nitrobenzene	0.004	0.03	0.005	0.02
1,3-Dinitrobenzene	0.011	0.09	0.005	0.02
1,3,5-TNT	0.004	0.03	0.006	0.02
4-Amino-2,6-DNT	0.023	0.10	0.026	0.05
2-Amino-4,6-DNT	0.026	0.10	0.009	0.02
Tetryl	0.023	0.50	0.012	0.02
Nitroglycerin	0.015	0.09	0.025	0.05

* Soil data based on a 5.0-g sample.

Table II. Precision and Accuracy Data for the USACHPPM Water Method*

Compound	%Recovery	%RSD†	Concentration range (µg/L)
2,6-DNT	98.8	3.49	0.03–0.08
2,4-DNT	99.4	3.21	0.06–0.16
2,4,6-TNT	88.5	9.60	0.09–0.24
RDX	96.2	4.67	0.36–0.96
HMX	97.0	5.18	6.0–20
2-Nitrotoluene	97.7	6.08	0.27–0.72
3-Nitrotoluene	100.0	9.97	0.27–0.72
4-Nitrotoluene	99.8	8.91	0.27–0.72
Nitrobenzene	97.4	5.94	0.09–0.24
1,3-Dinitrobenzene	98.5	4.17	0.27–0.72
1,3,5-Trinitrobenzene	98.4	9.88	0.09–0.24
4-Amino-2,6-DNT	90.5	18.7	0.3–0.8
2-Amino-4,6-DNT	95.5	12.2	0.3–0.8
Tetryl	96.5	8.82	0.47–1.2
Nitroglycerin	90.3	10.2	0.27–0.72

* Data compiled from 27 controls analyzed during 2000–2002.
† RSD, relative standard deviation.

and nitrogen diluted at 40 mL/min. Other conditions were the same as described previously. The 50% phenyl–methylpolysiloxane column was 0.53-mm i.d., 1.0-µm film thickness, and cut to 10 m in length; it was temperature programmed from 80ºC at 20º/min to 140ºC and then at 6ºC/min to 200ºC and held for 10 min. It used helium carrier pressure programmed from 2.0 to 6.0 psig at a rate of 150 psig/min and held and nitrogen diluted set to 30 mL/min. Other conditions were the same as described previously.

Method detection limit (MDL) studies have been conducted on both methods using the 40CFR part 136 EPA procedure (17). Results for recent MDL determinations are provided in Table I, as well as the method reporting limits (MRLs) USACHPPM uses. The MRLs were conservatively set to be the equivalent of or above the lowest standard run with the method because these can reliably be obtained with most instrumentation and for most samples. Precision and accuracy data for both methods are shown in Tables II and III; these data were compiled from numerous spiked controls analyzed over the past year. Finally, Tables IV and V provide some comparison data on actual contaminated soils analyzed by both the USACHPPM and draft Method 8095 or Method 8330 soil procedures.

Table III. Precision and Accuracy Data for the USACHPPM Soil Method*

Compound	%Recovery	%RSD†	Concentration range (µg/g)
2,6-DNT	101.7	7.4	1.2–6.0
2,4-DNT	89.5	10.2	1.2–6.0
2,4,6-TNT	86.5	12.8	1.2–6.0
RDX	94.8	7.0	1.2–6.0
HMX	105.6	19.1	1.2–6.0
2-Nitrotoluene	104.1	8.3	1.2–6.0
3-Nitrotoluene	102.1	8.2	1.2–6.0
4-Nitrotoluene	101.4	8.6	1.2–6.0
Nitrobenzene	97.6	6.8	1.2–6.0
1,3-Dinitrobenzene	94.9	10.4	1.2–6.0
1,3,5-Trinitrobenzene	76.9	14.0	1.2–6.0
4-Amino-2,6-DNT	83.8	10.2	1.2–6.0
2-Amino-4,6-DNT	92.4	8.0	1.2–6.0
Tetryl	103.4	11.4	1.2–6.0
Nitroglycerin‡	97.4	16.2	1.2–6.0

* Data compiled from 21 controls analyzed during 2001–2002.
† RSD, relative standard deviation.
‡ The data for nitroglycerin was calculated from 17 controls.

Table IV. Comparison Data for Soils Analyzed by the USACHPPM and 8095 Methods*

Site	Compound	USACHPPM	Draft 8095
4935005	HMX	1.3	0.66
	RDX	0.86	0.53
	2,4,6-TNT	0.29	0.28
4935007	HMX	1.3	0.61
	RDX	0.18	0.24
	2,4,6-TNT	0.063	0.024
5005034	HMX	0.32	< 0.1
	RDX	0.40	0.38
	2,4,6-TNT	0.065	0.038
5005035	HMX	0.28	< 0.1
	RDX	0.23	0.28
	2,4,6-TNT	0.014	0.018
5005037	HMX	< 0.05	< 0.1
	RDX	0.15	0.15

* Field samples collected during 2002 and analyzed by USACHPPM (µg/g).

Results and Discussion

The data shown in Tables I–III indicate that the USACHPPM water and soil methods were both sensitive and capable of good precision and accuracy. The precision and accuracy data were the results of controls run with samples over the time these particular procedures have been used. The comparison data between the USACHPPM soils and draft Method 8095 showed good agreement. Similarly, the data for the field samples analyzed by the USACHPPM and HPLC soil procedures compared favorably.

One of the advantages of the USACHPPM procedures over the EPA SW846 energetics procedure lies in the preparation procedures used. The water extraction technique is very simple and quick to perform because there are no solvent concentration steps involved; a person can routinely process dozens of samples a day. There are infrequent problems with emulsions forming at the water–isoamyl acetate interface, but when they do occur they

Table V. Comparison Data for Soils Analyzed by the USACHPPM and HPLC Methods*

Site	Compound	USACHPPM	HPLC data
WHG1	HMX	0.49	0.38
	RDX	0.91	0.78
	2,4,6-TNT	0.04	0.02
	TNB	0.02	0.02
WHG2	HMX	0.82	0.73
	RDX	2.7	2.4
	2,4,6-TNT	0.20	0.13
	TNB	0.04	0.03
WHG5	HMX	3.9	3.5
	RDX	19	23
	2,4,6-TNT	2.6	2.2
	TNB	0.32	0.41
LMW5	HMX	1.1	1.2
	RDX	4.0	4.9
	2,4,6-TNT	0.94	1.9
	TNB	0.27	0.24
L33+2	2,4,6-TNT	0.1	0.1
L34+2	RDX	0.02	0.03
	2,4,6-TNT	0.3	0.3
	TNB	0.02	0.01
L35+2	RDX	0.01	0.02
	2,4,6-TNT	0.04	0.05
C-Line	HMX	380	341
	RDX	2300	2400
	2,4,6-TNT	110	120

* Field samples and HPLC data provided by CRREL (µg/g).

can easily be overcome using techniques such as the addition of a little sodium sulfate or centrifugation. This problem sometimes occurs during the analysis of surface waters. The standards for the water analyses are extracted from water rather than prepared directly in isoamyl acetate. This was instituted many years ago when there was a question as to the extraction efficiencies for some of the compounds at the varying concentrations. In reality, nonextracted standards would probably be acceptable in most cases, but we have not pursued this. The varying amounts of the compounds in the standards were based on the variability in required reporting levels of the compounds in water plus the variability in the ECD response.

The preparation of the soils was also simple to perform. The ultrasonic bath was used to produce good soil–water interaction; it may not be necessary to do it for a full 12 h, but that was the time selected out of convenience. The shaking step accomplished the actual extraction of the analytes into the isoamyl acetate. Unlike water, the standards for the soil analyses were not extracted because it was not practical being that the soils were so variable in composition. The compounds, with the exception of HMX, were present at equal concentrations because there have been no required reporting limits in soil based on health concerns (unlike the situation with water).

The soil data presented in this study were all gathered from soils extracted using the described procedure. Recent tests were made on some of the same soils whereby the extraction vials were laid on their sides on a platform shaker and shaken for 3 h. The results were comparable to the ultrasonic bath–rotary shaker technique, indicating that this may be a further simplified procedure for soil extractions.

Several GC issues must be addressed in order to obtain good chromatography with these procedures. The nonpolar (dimethylpolysiloxane) primary column used for energetics analysis was capable of separating all the analytes of interest in a relatively short time. However, there were occasionally background interferences with the peaks for the early eluting nitrotoluene isomers depending on the lot of isoamyl acetate used. The isoamyl acetate must be of high purity. A column containing a different liquid phase was used to quantitate compounds that could not be determined with the primary column. Secondary column analysis was also routinely done to verify positive detections on the primary column. Polar (50% trifluoropropyl–methylpolysiloxane) or intermediate polarity (50% phenyl–methylpolysiloxane) columns were useful for this purpose. Chromatographic conditions can be varied, but a short column is required if HMX verification is required. HMX is very reactive; a fast flow rate and temperature program is required to get it through the polar column before peak degradation begins to occur.

Another important factor that must be considered when performing GC analyses for energetic compounds is the use of a clean, properly silanized injection port liner and inert injection port seal. Commercially prepared liners and seals are recommended. Peaks for the more reactive compounds, especially HMX and the aminodinitrotoluene isomers, will show distorted peak shapes or disappear entirely if the liner or seal is dirty or not silanized. Oncolumn injections are not recommended with this analysis because nonvolatile compounds deposited at the head of the column produce problems with sensitivity and reproducibility.

It should be noted that the compound that was identified as "tetryl" by GC is actually not tetryl but probably a thermal transformation product, possibly *N*-methyl picramide (18). Because the transformation appeared to be complete, it was a satisfactory measure of the amount of tetryl in a sample.

A major difference between draft Method 8095 and the USACHPPM soil method involves the extraction solvents used. Method 8095 uses acetonitrile for extraction and injection into a GC. Acetonitrile is a good extraction solvent and is quite appropriate for HPLC usage (19), but it is not necessarily the best for use with GC systems. For example, it is not recommended for use with Agilent GC–MSD systems because it is corrosive. As mentioned previously, our laboratory has used variants of draft Method 8095 for some time to confirm HPLC soil results, but found some problems with reproducibility and rapid deterioration of column performance. These difficulties have not been present since we began to use isoamyl acetate, and we have observed higher recoveries for some compounds with the use of this solvent.

The information presented in this study concerns the analyses of environmental samples for the suite of Method 8330 compounds plus nitroglycerin. However, the USACHPPM laboratory also performed analyses for the same compounds recently in several thousand samples of considerably different matrices. This was done from 1999 until early 2002 in support of the U.S. Army's Assembled Chemical Weapons Assessment project, which investigated different techniques for the demilitarization of chemical munitions. The samples ranged from highly caustic to highly acidic aqueous solutions, biofeedstock solutions, and sludges to air samples collected on XAD-2 resin and in impingers containing water. The basic methodologies described previously were successfully modified to permit the analyses of these samples. Liquid samples were pH adjusted to be slightly acidic and extracted in the same way as water samples, and sludges were done in much the same manner as the soils procedure. Air samples were also extracted with isoamyl acetate. The chromatographic procedure was virtually the same as described previously, although admittedly much more difficult. Many sample dilutions and alternate column injections had to be made because of interferences or high levels of target analytes. The important fact to consider, however, is that the analytical approach described in this study worked well, even with these most difficult of matrices. Table VI displays the synopsis of the results from the matrix spikes run on caustic hydrolysates during 1999–2001 for the surrogate and the two key analytes from the energetic feed material.

Table VI. Recovery Data for Spikes into Caustic Hydrolysate Samples*

	RDX	2,4,6-TNT	3,4-DNT
Mean recovery	110	103	99
Standard deviation	10.5	7.8	15.8
No. of spikes	53	61	58

* Data compiled from samples analyzed during 1999–2001. The concentration range was 0.1–1.0 mg/L for all analytes and analyzed by variation of the USACHPPM water method.

Conclusion

The primary procedures that the USACHPPM uses for the analyses of energetics and related compounds have been described in this article. These procedures have been tested and refined over the past few years to the point in which we believe they are acceptable alternates to any methods currently available for this purpose. The procedures are relatively easy to perform in both sample preparation and the chromatographic analytical approach. The test data supports the conclusion that the methodology can provide sensitive and accurate analytical data for water and soil matrices and can be modified to accommodate other, more complex types of samples. It is hoped that the information provided will add to the arsenal of methods for those analysts tasked with measuring nitroaromatics, nitramines, and nitroglycerin in the environment.

Acknowledgments

The authors wish to express their appreciation to both Thomas F. Jenkins and Marianne E. Walsh of CRREL (Hanover, NH). Their advice, support, and assistance over the course of our years of explosives analyses and methods development have been extremely helpful.

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Manuscript accepted December 30, 2002.