METHOD 8330B

NITROAROMATICS, NITRAMINES, AND NITRATE ESTERS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is intended for the trace analysis of explosives and propellant residues by high performance liquid chromatography (HPLC) using a dual wavelength UV detector. The following RCRA compounds in a water, soil, or sediment matrix have been determined by this method:

Analyte	Abbreviation	CAS Number[a]
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4
1,3-Dinitrobenzene	1,3-DNB	99-65-0
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	2,4,6-TNT	118-96-7
4-Amino-2,6-dinitrotoluene	4-Am-DNT	19406-51-0
2-Amino-4,6-dinitrotoluene	2-Am-DNT	35572-78-2
2,4-Dinitrotoluene	2,4-DNT	121-14-2
2,6-Dinitrotoluene	2,6-DNT	606-20-2
2-Nitrotoluene	2-NT	88-72-2
3-Nitrotoluene	3-NT	99-08-1
4-Nitrotoluene	4-NT	99-99-0
Nitroglycerin	NG	55-63-0
Pentaerythritol tetranitrate	PETN	78-11-5
3,5-Dinitroaniline	3,5-DNA	618-87-1

[a] Chemical Abstract Service Registry Number

1.2 This method provides a direct injection procedure for high level water samples, an extraction procedure for soils and sediments as well as a low level method for the extraction of water samples. The use of solid-phase extraction, Method 3535, has been shown to provide equal or superior results and is preferred for low level aqueous samples.

1.3 All of these compounds are either used in the manufacture of explosives or propellants, are impurities in their manufacture, or they are the degradation products of compounds used for that purpose. Stock solutions for calibration are available through several commercial vendors.

1.4 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern. Analysts and samplers should also consult the method Appendix for more specific information on the best approaches to collect and process samples in order to obtain representative results.

In addition, analysts and data users are advised that, except where explicitly required in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by or under the supervision of analysts experienced in the use of HPLC, skilled in the interpretation of chromatograms, and experienced in handling explosive materials (see Sec. 5.0). Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain explosive and propellant residues in water, soil, and sediment. Prior to use of this method, appropriate sample preparation techniques must be used. (See Appendix A)

2.2 Solid-phase extraction method -- Aqueous samples may be preconcentrated using solid-phase extraction, as described in Method 3535 and then diluted with water as appropriate for the selected separations.

2.3 Low-level salting-out method with no evaporation -- Aqueous samples of low concentration may also be preconcentrated by a salting-out extraction procedure with acetonitrile and sodium chloride. The small volume of acetonitrile that remains undissolved above the salt water is drawn off and transferred to a smaller volumetric flask. It is back-extracted by vigorous stirring with a specific volume of salt water. After equilibration, the phases are allowed to separate and the small volume of acetonitrile residing in the narrow neck of the volumetric flask is removed using a Pasteur pipet. The concentrated extract is mixed

either 1:1 or 1:3 with reagent water (depending on the separations chosen). An aliquot is separated on a primary reversed-phase column (either C-18 or C-8 column), determined at 254 nm and 210 nm, and target analytes tentatively identified on the primary column are confirmed on a second reversed-phase column that provides a different order of analyte elution (CN or Phenylhexyl).

2.4 High-level direct injection method -- Aqueous samples of higher concentration can be diluted either 1:1 (v/v) or 1:3 v/v (depending on the selected separation) with methanol or acetonitrile, filtered, separated on a primary reversed-phase column, determined at 254 nm and 210 nm, and confirmed on a reversed-phase confirmation column. If HMX is an important target analyte, methanol is preferred.

2.5 Soil and sediment samples are extracted using acetonitrile in an ultrasonic bath, or shaker (See Ref. 13), filtered, diluted with water as appropriate, and analyzed as described in Sec. 2.4.

3.0 DEFINITIONS

Refer to Chapter One and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. HPLC grade solvents are preferred.

4.2 2,4-DNT and 2,6-DNT elute at similar retention times on C-18 columns using the separation conditions described in this method (retention time difference of 0.2 minutes). A large concentration of one isomer (generally 2,4-DNT) may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.

4.3 Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All aqueous samples expected to contain tetryl should be diluted with acetonitrile prior to filtration and acidified to pH <3 with aqueous sodium bisulfate. All samples expected to contain tetryl should not be exposed to temperatures above room temperature.

4.4 Degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak using the C18 separation. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-TNT.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A

reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Standard precautionary measures used for handling other organic compounds should be sufficient for the safe handling of the analytes targeted by this method. Extra caution should be taken if handling the analytical standard neat material for the explosives themselves and in rare cases where soil or waste samples are highly contaminated with the explosives. Heed the warning for drying the neat materials at ambient temperatures in Sec. 7.3.

5.3 It is advisable to screen soil or waste samples using Methods 8510 or 8515 to determine whether high concentrations of explosives are present. Soil samples containing as much as 2% of 2,4,6-TNT have been safely ground. Samples containing higher concentrations should not be ground in a mortar and pestle or a mechanical grinder. Method 8515 is for 2,4,6-TNT, but the other nitroaromatics will also cause a color to be developed and provide a rough estimation of their concentrations. Method 8510 is for RDX and HMX, but mixtures of RDX (and/or related compounds with 2,4,6-TNT will cause an orange color, rather than a pink color to form. Other screening methods may be used provided that they can be demonstrated to generate data that is applicable for its intended use (Ref. 15). Visual observation of a soil sample is also important when the sample is taken from a site expected to contain explosives. Lumps of material that have a chemical appearance should be suspect and not ground. Chunks of TNT-based explosives that have been exposed to light are generally reddish-brown to orange in color.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list common laboratory glassware (e.g., beakers and flasks).

6.1 HPLC system

6.1.1 HPLC -- Equipped with a pump capable of achieving 4000 psi, a 100-µL loop injector and a dual or multi-wavelength UV detector. For the low concentration option, the detector must be capable of maintaining a stable baseline at 0.001 absorbance units full scale.

6.1.2 Recommended primary columns

The columns listed in this section were the columns used to develop or update the method. The listing of these columns in this method is not intended to exclude the use of other columns that are available or that may be developed. Laboratories may use these columns or other columns provided that the laboratories document method performance data (e.g., chromatographic resolution, analyte breakdown, and sensitivity) that are appropriate for the intended application.

6.1.2.1 Primary column -- C-18 reversed-phase HPLC column, 25-cm x 4.6-mm (5 µm) (Supelco LC-18, or equivalent).

6.1.2.2 Primary column – C-8 reversed-phase HPLC, 25-cm x 4.6-mm (5 µm)

6.1.3 Recommended secondary columns

Secondary or confirmation columns should provide a separation that is substantially different from that obtained on the primary column.

6.1.3.1 Secondary column -- CN reversed-phase HPLC column, 25-cm x 4.6-mm (5 µm) (Supelco LC-CN, or equivalent).

6.1.3.2 Secondary column – Phenylhexyl reversed-phase HPLC column, 25-cm x 4.6-mm (5 µm)

6.1.4 Digital integrator or computerized data collection system

6.1.5 Autosampler

6.2 Other equipment

6.2.1 Temperature-controlled ultrasonic bath or platform shaker

6.2.2 Vortex mixer

6.2.3 Balance capable of weighing ± 0.0001 g

6.2.4 Magnetic stirrer equipped with PTFE stirring bars

6.2.5 Mortar and pestle, mechanical grinder, or ring puck mill

6.3 Materials

6.3.1 High-pressure injection syringe -- 500-µL (Hamilton liquid syringe, or equivalent).

6.3.2 Disposable cartridge filters -- 0.45-µm PTFE filter.

6.3.3 Pipets -- Class A, glass, appropriate sizes.

6.3.4 Pasteur pipets

6.3.5 Scintillation vials -- 20-mL, glass.

6.3.6 Vials -- 15-mL, glass, PTFE-lined cap.

6.3.7 Vials -- 40-mL, glass, PTFE-lined cap.

6.3.8 Disposable syringes -- Plastipak, 3-mL and 10-mL or equivalent.

6.3.9 Volumetric flasks -- 10-mL, 25-mL, 100-mL, and 1-L, fitted with ground-glass stoppers, Class A.

NOTE: The 100-mL and 1-L volumetric flasks used for magnetic stirrer extraction must be round.

6.3.10 Sieve -- 10-mesh

6.3.11 Graduated cylinders -- 10-mL, 25-mL, and 1-L.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination or introducing interferences. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

7.2 Solvents

The choice of solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent system is employed, *including* those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

All solvents should be HPLC-grade or equivalent. Solvents may be degassed prior to use.

7.2.1 Acetonitrile, CH_3CN -- HPLC-grade, or equivalent.

7.2.2 Methanol, CH_3OH -- HPLC-grade, or equivalent.

7.3 Calcium chloride, $CaCl_2$ -- Prepare an aqueous solution containing 5 g/L of calcium chloride.

7.4 Sodium chloride, NaCl, shipped in glass bottles.

7.5 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

7.6 Standard solutions

The following sections describe the preparation of stock, intermediate, and working standards for the compounds of interest. This discussion is provided as an example, and other approaches and concentrations of the target compounds may be used, as appropriate for the intended application. See Method 8000 for additional information on the preparation of calibration standards.

7.6.1 Stock standard solutions

Individual and mixed stock standards of the target analytes for this method are available from several commercial vendors, generally at a concentration of 1000 mg/L. The mixed standards are available as 8330 Mix 1 and 2 (or A and B). These standards do

not generally include NG, PETN, and 3,5-DNA, but stock standards of these individual compounds are also available. Stock standards should remain refrigerated when not in use.

7.6.2 Intermediate standard solutions

Two separate intermediate stock solutions (10 mg/L) are prepared from the two commercial stock standards by dilution with acetonitrile 1:100 in a volumetric flask. If NG, PETN, and 3,5-DNA are to be included, it is recommended that NG and PETN be added to Intermediate Standard 1 (or A) and 3,5-DNA be added to Intermediate Standard 2 (or B).

7.6.3 Working standard solutions

Dilute the two concentrated (10 mg/L) intermediate stock solutions (Sec. 7.6.2), with the appropriate solvent, to prepare working standard solutions that typically cover the range of 50 - 10,000 µg/L. The intermediate solutions should be refrigerated between uses, and may be used for 1 year. However, these solutions must be replaced sooner, if a comparison with check standards indicates a problem.

7.6.4 Calibration standard solutions

Calibration standards at a minimum of five concentration levels should be prepared by the dilution of the intermediate standards solutions by either 1:1 or 1:3 (v/v) with reagent grade water, depending on the separation selected (Sec. 11.3). These solutions must be refrigerated and stored in the dark, and prepared fresh on the day of calibration.

For the low-level water method, the analyst must conduct a detection limit study and devise dilution series appropriate to the desired range. Standards for the low-level water method should be prepared immediately prior to use due to compound stability concerns at lower concentrations.

NOTE: The calibration verification standard prepared along with the low-level calibration standards will serve to ensure the compound stability over the course of the initial calibration sequence. Also note this stability phenomenon is less pronounced in the sample extracts as long as they remain refrigerated prior to analysis.

7.7 Surrogate spiking solution

The analyst should monitor the performance of the extraction and analytical system as well as the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and reagent water blank with one or two surrogates (e.g., analytes not expected to be present in the sample).

7.8 Matrix spiking solutions

Prepare matrix spiking solutions in acetonitrile or methanol. All target analytes should be included.

7.9 HPLC mobile phase

Prepare mobile phases by combining the appropriate volumes of the appropriate solvents (HPLC grade) and organic-free water for the separation selected.

7.10 Internal standards and surrogates

Commonly used chemicals for internal standards and surrogates are 3,4-dinitrotolune and 1,2-dinitrobenzene. These compounds have not been found in the environment associated with explosives or propellant contamination and are available from the same commercial vendors that provide standards for this analysis.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes" and the Appendix to this method to select sampling methods appropriate for the commonly encountered distribution of the target analytes of this method. In soil sampling, it is particularly important to understand that these analytes are often present in soil as fine particles and this influences the methods recommended for field sample collection and for laboratory processing and subsampling. (See Appendix A)

8.2 Samples and sample extracts should be stored in the dark at 4 °C, or lower. Holding times are the same as for semivolatile organics. After air-drying soil and sediment, the samples can be held at room temperature (22±4 °C) or cooler (See Ref.17).

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to Method 8000 for specific quality control (QC) procedures. Refer to Method 3500 for QC procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques. If an extract cleanup procedure is performed, refer to Method 3600 for the appropriate QC procedures. Any more specific QC procedures provided in this method will supersede those noted in Methods 8000, 3500, 3600, or 5000.

9.3 The quality control procedures necessary to validate the HPLC system operation are found in Method 8000 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation, cleanup, and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should

satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish a demonstration of proficiency.

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would prevent the determination of that analyte, determine the source and eliminate it, if possible, before processing samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, matrix spike, a matrix spike duplicate or unspiked duplicate, and a laboratory control sample (LCS) in each analytical batch, along with the addition of project-specific surrogates to each field sample and QC sample. Any method blanks, matrix spike samples, and replicate samples should be subjected to the same analytical procedure (Sec. 11.0) as those used on actual samples.

9.6.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

9.6.2 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

9.6.3 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.7 Surrogate recoveries

The laboratory should evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000 for information on evaluating surrogate data and developing and updating surrogate limits. Procedures for evaluating the recoveries of multiple surrogates and the associated corrective actions should be defined in an approved project plan.

9.8 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

10.0 CALIBRATION AND STANDARDIZATION

See Sec. 11.4 for information on calibration and standardization.

11.0 PROCEDURE

11.1 Sample preparation

This method addresses both aqueous and solid samples. There are three procedures that may be applied to aqueous samples, depending on the expected level of explosive residue in the sample and the available equipment. The procedure options include a low-level solid-phase extraction method for low concentration samples, an alternative salting-out extraction method, and a direct analysis method for high concentration samples. It is highly recommended that aqueous process waste samples be screened with the high-level method (1 - 50 mg/L) to determine if use of the low-level method (<1 mg/L) is necessary. Most groundwater samples should be processed by the solid-phase or the salting-out low-level methods. Of the two low-level methods, the solid-phase extraction method is generally preferred.

11.1.1 Aqueous Solid-phase extraction method

Aqueous samples containing nitroaromatics and nitramines are extracted using solid-phase extraction (SPE) in both disk and cartridge formats. See Method 3535 for the procedures to be employed and the apparatus and materials that are necessary. Generally, silica-based solid phases are not sufficiently sorptive for RDX and HMX and thus resin-based solid phases are preferred.

11.1.2 Aqueous low-level method (salting-out extraction)

11.1.2.1 Add 251.3 g of sodium chloride to a 1-L volumetric flask (round). Measure 770 mL of a water sample (using a 1-L graduated cylinder) and transfer it to the volumetric flask containing the salt. Add a stir bar and mix the contents at maximum speed on a magnetic stirrer until the salt is completely dissolved.

11.1.2.2 Add 164 mL of acetonitrile (measured with a 250-mL graduated cylinder) while the solution is being stirred and stir for an additional 15 min. Turn off the stirrer and allow the phases to separate for 10 min.

11.1.2.3 Remove the acetonitrile (upper) layer (about 8 mL) with a Pasteur pipet and transfer it to a 100-mL volumetric flask (with a round bottom). Add 10 mL of fresh acetonitrile to the water sample in the 1-L flask. Again stir the contents of the flask for 15 min followed by standing for 10 min for phase separation. Combine the second acetonitrile portion with the initial extract. The inclusion of a few drops of salt water at this point is unimportant.

11.1.2.4 Add 84 mL of salt water (325 g NaCl per 1000 mL of reagent water) to the acetonitrile extract in the 100-mL volumetric flask. Add a stir bar and stir the contents on a magnetic stirrer for 15 min, followed by standing for 10 min for phase separation. Carefully transfer the acetonitrile phase to a 10-mL graduated cylinder using a Pasteur pipet. At this stage, the amount of water transferred with the acetonitrile must be minimized. The water contains a high concentration of NaCl that produces a large peak at the beginning of the chromatogram, where it could interfere with the HMX determination.

11.1.2.5 Add an additional 1.0 mL of acetonitrile to the 100-mL volumetric flask. Again stir the contents of the flask for 15 min, followed by standing for 10 min for phase separation. Combine the second acetonitrile portion with the initial extract in the 10-mL graduated cylinder (transfer to a 25-mL graduated cylinder if the volume exceeds 5 mL). Record the total volume of acetonitrile extract to the nearest 0.1 mL. (Use this as the volume of total extract [V_t] in the calculation of concentration after converting to μL). The resulting extract, about 5 - 6 mL, is then diluted 1:1 with organic-free reagent water (with pH <3 if tetryl is a suspected analyte) prior to analysis.

11.1.2.6 If the diluted extract is turbid, filter it through a 0.45-μm PTFE filter using a disposable syringe. Discard the first 0.5 mL of filtrate, and retain the remainder in a PTFE-capped vial for RP-HPLC analysis in Sec. 11.5.

11.1.3 Aqueous high-level method

11.1.3.1 Sample filtration

Place a 5-mL aliquot of each water sample in a scintillation vial, add 5 mL of acetonitrile, shake thoroughly, and filter through a 0.45-μm PTFE filter using a disposable syringe.

11.1.3.2 Discard the first 3 mL of filtrate, and retain the remainder in a PTFE-capped vial for RP-HPLC analysis in Sec. 11.5. HMX quantitation can be improved with the use of methanol rather than acetonitrile for dilution before filtration.

11.1.4 Soil and sediment samples

11.1.4.1 Sample drying

Dry the entire soil sample in air at room temperature (or less) to a constant weight, being careful not to expose the samples to direct sunlight.

11.1.4.2 Sample grinding

11.1.4.2.1 Sample grinding for soil samples from ammunition plants and depots

Dried samples are ground thoroughly in an acetonitrile rinsed mortar and pestle to pass a 10-mesh sieve.

11.1.4.2.2 Sample grinding for soil samples from firing ranges

Remove the oversize fraction by passing it through a 10-mesh (2 mm) sieve. Weigh both fractions then pulverize the entire < 2 mm fraction in a ring puck mill or equivalent mechanical grinder. In a ring puck mill samples containing crystalline energetic residues (i.e., TNT, RDX, HMX and their breakdown products) can be adequately pulverized in 90 sec. In this same device sample containing polymeric residues (i.e., propellants and rocket fuel) can be adequately pulverized by 5 separate 60 sec grinding cycles. If the sample was ground in more than one portion (grinding bowls have a limited capacity) following this step the entire sample should be combined and thoroughly mixed. (See Appendix A, Sec. A.5.0 for soil agglomerate processing recommendations)

WARNING: Soil samples should be screened by Method 8510 and Method 8515 or other applicable methods prior to grinding if very high concentrations of target compounds are expected (see Sec. 5.3).

11.1.4.3 Subsampling

To obtain a subsample, the entire sample should be spread out on a clean surface so that it is only 1 or 2 cm thick and preferably in a fume hood designed to prevent the spread of dust and possible inhalation or residue losses. Then at least 30 different increments, i.e., portions (~0.3 g) should be obtained from randomly chosen locations by sampling the whole profile. (See Appendix A, Sec. A.5.0 for additional sampling processing recommendations)

11.1.4.4 Sample extraction

11.1.4.4.1 Place a 10-g subsample of each soil sample in a 2 oz wide mouth bottle. Add 20.0 mL of acetonitrile, cap with a PTFE-lined cap, vortex swirl for one min, and place either on a platform shaker or in a cooled (<30 °C) ultrasonic bath for 18 hr.

11.1.4.4.2 After extraction, allow sample to settle for 30 min. Using a 10-mL disposable syringe, remove 8.0 mL of supernatant and filter through a 0.45 µm PTFE filter, discarding the first mL. If solids remain suspended in the solvent phase, they can be centrifuged.

11.2 Chromatographic columns (recommended)

Primary Columns:	C-18 reversed-phase HPLC column, 25-cm x 4.6-mm, 5 µm
	C8 Reversed-phase HPLC column, 15-cm x 3.9-mm, 4 µm
Secondary Columns:	CN reversed-phase HPLC column, 25-cm x 4.6-mm, 5 µm
	Phenyl-Hexyl Reversed-phase HPLC column, 25-cm x 4.6-mm, 5 µm

Injection Volume:	100-µL
UV Detector:	Dual 254 & 210 nm, or Photodiode array

11.3 Mobile phases

The recommended mobile phases are keyed to specific reversed-phase columns. For C-18, the mobile phase is 50:50 methanol:water; for C-8 it is 15:85 isopropanol:water; for CN it is 50:50 methanol: water or 65:12:23 water:methanol:acetonitrile (Ref. 18); and for the Phenyl-hexyl it is 50:50 methanol:water or a methanol:water gradient from 50:50 to 70:30.

11.4 Calibration of HPLC

11.4.1 Allow all electronic equipment to warm up for 30 min. During this period, pass at least 15 void volumes of mobile phase through the column (approximately 20 min at 1.5 mL/min) and continue until the baseline is level at the UV detector's greatest sensitivity.

11.4.2 Initial calibration -- Sequentially inject each of at least five calibration standards over the concentration range of interest into the HPLC in an appropriate order. Peak heights or peak areas are obtained for each analyte. Employ one of the linear calibration options described in Method 8000.

11.4.3 The initial calibration function for each target analyte should be checked immediately after the first occurrence in the region of the middle of the calibration range with a standard from a source different from that used for the initial calibration. The value determined from the second source check should be within 30% of the expected concentration. An alternative recovery limit may be appropriate based on the desired project-specific data quality objectives. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification. However, analyses may continue for those analytes that fail the criteria with an understanding that these results could be used for screening purposes and would be considered estimated values.

11.4.4 Calibration verification -- Analyze one mid-point calibration standard, at a minimum, at the beginning of the day, and after every 20 sample extracts (*recommended* after every 10, in order to minimize the number of samples that may be affected by a failing standard), and after the last sample of the day. Calculate the calibration factor for each analyte from the peak height or peak area and compare it with the mean calibration factor obtained for the initial calibration, as described in Method 8000. The calibration factor for the calibration verification must agree within ± 20% of the mean calibration factor of the initial calibration. If this criterion is not met corrective action to identify the cause is recommended prior to a calibration verification reanalysis. Should the reanalysis fail for the majority of target analytes, a new initial calibration should be performed. In instances were only a few target analytes fail the verification criteria, sample analyses may proceed with an understanding the sample data associated with these compounds needs to be qualified as estimated.

11.5 HPLC analysis

11.5.1 Analyze the samples using optimized chromatographic conditions. Use the conditions given in Sec. 11.2 either directly or as a basis for the optimization. Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Confirmation is necessary when the sample composition is not well characterized. All positive measurements observed on the primary column should be confirmed by injection onto the secondary column, or by another appropriate technique, e.g., diode array or mass spectral detection.

When results are confirmed using a second HPLC column of dissimilar stationary phase, such as the CN column, the analyst should check the agreement between the quantitative results on both columns once the identification has been confirmed. See Method 8000 for a discussion of such a comparison and appropriate data reporting approaches.

11.5.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 20 samples in the analysis sequence. If column temperature control is not employed, special care must be taken to ensure that temperature shifts do not cause peak misidentification.

11.5.3 Table 1 summarizes the estimated retention times on both C-18 and CN columns for a number of analytes analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1. The retention times listed in Table 1 are provided for illustrative purposes only. Each laboratory must determine retention times and retention time widows for their specific application of the method.

11.5.4 Record the resulting peak sizes in peak heights or area units. The use of peak heights is recommended to improve reproducibility of low level samples.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 See Method 8000 for information regarding data analysis and calculations.

12.2 Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. <u>These performance data are not intended to be and must not be used as absolute QC acceptance for purposes of laboratory accreditation.</u>

13.2 Table 2 provides the single-laboratory precision based on data from the analysis of blind duplicates of four spiked soil samples and four field-contaminated samples analyzed by seven laboratories. These data are provided for guidance purposes only.

13.3 Table 3 provides the multi-laboratory error based on data from the analysis of blind duplicates of four spiked soil samples and four field-contaminated samples analyzed by seven laboratories. These data are provided for guidance purposes only.

13.4 Table 4 provides the multi-laboratory variance of the high-level method for water based on data from nine laboratories. These data are provided for guidance purposes only.

13.5 Table 5 provides multi-laboratory recovery data from the analysis of spiked soil samples by seven laboratories. These data are provided for guidance purposes only.

13.6 Table 6 provides a comparison of method accuracy for soil and aqueous samples (high-level method). These data are provided for guidance purposes only.

13.7 Table 7 provides precision and accuracy data for the salting-out extraction method. These data are provided for guidance purposes only.

13.8 Table 8 provides data from a comparison of direct injection of groundwater samples with both the salting-out extraction and the solid-phase extraction techniques. These data are provided for guidance purposes only.

13.9 Table 9 provides data comparing the precision of duplicate samples analyzed by direct injection of groundwater samples with both the salting-out extraction and the solid-phase extraction techniques. These data are provided for guidance purposes only.

13.10 Table 10 provides a comparison of recovery data for spiked samples analyzed by direct injection of groundwater samples with both the salting-out extraction and the solid-phase extraction techniques. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables and figure referenced by this method.

TABLE 1

EXAMPLE ESTIMATED RETENTION TIMES AND CAPACITY FACTORS
ON LC-18 AND LC-CN COLUMNS

	Retention Time (min)			
Analyte	LC-18	LC-CN	LC-8	Phenyl-hexyl
HMX	2.44	8.35	1.41	7.11
RDX	3.73	6.15	2.67	9.30
1,3,5-TNB	5.11	4.05	2.28	17.58
1,3-DNB	6.16	4.18	4.22	14.79
3,5-DNA	6.90		7.23	
Tetryl	6.93	7.36	5.77	23.25
NB	7.23	3.81	6.61	11.47
NG	7.74	6.00	7.90	
2,4,6-TNT	8.42	5.00	4.95	23.54
4-Am-DNT	8.88	5.10	14.59	17.19
2-Am-DNT	9.12	5.65	13.08	18.10
2,6-DNT	9.82	4.61	11.54	19.09
2,4-DNT	10.05	4.87	9.56	19.51
2-NT	12.26	4.37	16.48	15.78
4-NT	13.26	4.41	16.10	15.98
PETN	14.10	10.10	16.34	
3-NT	14.23	4.45	18.40	16.91

Retention times are provided for guidance purposes only. Each laboratory must determine retention times and retention time widows for their specific application of the method.

TABLE 2

SINGLE LABORATORY PRECISION OF METHOD FOR SOIL SAMPLES

	Spiked Soils			Field-Contaminated Soils		
Analyte	Mean Conc. (mg/kg)	SD	%RSD	Mean Conc. (mg/kg)	SD	%RSD
HMX	46	1.7	3.7	14	1.8	12.8
				153	21.6	14.1
RDX	60	1.4	2.3	104	12	11.5
				877	29.6	3.4
1,3,5-TNB	8.6	0.4	4.6	2.8	0.2	7.1
	46	1.9	4.1	72	6.0	8.3
2,4,6-TNT	40	1.4	3.5	7.0	0.61	9.0
				669	55	8.2
1,3-DNB	3.5	0.14	4.0	1.1	0.11	9.8
2,4-DNT	5.0	0.17	3.4	1.0	0.44	42.3
Tetryl	17	3.1	17.9	2.3	0.41	18.0

Source: Ref. 1.
These data are provided for guidance purposes only.

TABLE 3

MULTI-LABORATORY ERROR OF METHOD FOR SOIL SAMPLES

	Spiked Soils			Field-Contaminated Soils		
Analyte	Mean Conc. (mg/kg)	SD	%RSD	Mean Conc. (mg/kg)	SD	%RSD
HMX	46	2.6	5.7	14	3.7	26.0
				153	37.3	24.0
RDX	60	2.6	4.4	104	17.4	17.0
				877	67.3	7.7
1,3,5-TNB	8.6	0.61	7.1	2.8	0.23	8.2
	46	2.97	6.5	72	8.8	12.2
2,4,6-TNT	40	1.88	4.7	7.0	1.27	18.0
				669	63.4	9.5
1,3-DNB	3.5	0.24	6.9	1.1	0.16	14.5
2,4-DNT	5.0	0.22	4.4	1.0	0.74	74.0
Tetryl	17	5.22	30.7	2.3	0.49	21.3

Source: Ref. 1.
These data are provided for guidance purposes only.

TABLE 4

MULTI-LABORATORY VARIANCE OF METHOD FOR WATER SAMPLES[a]

Analyte	Mean Conc. (μg/L)	SD	%RSD
HMX	203	14.8	7.3
RDX	274	20.8	7.6
2,4-DNT	107	7.7	7.2
2,4,6-TNT	107	11.1	10.4

[a] Nine Laboratories
These data are provided for guidance purposes only.

TABLE 5

MULTI-LABORATORY RECOVERY DATA FOR SPIKED SOIL SAMPLES

	Concentration (mg/kg)						
Laboratory	HMX	RDX	1,3,5-TNB	1,3-DNB	Tetryl	2,4,6-TNT	2,4-DNT
1	44.97	48.78	48.99	49.94	32.48	49.73	51.05
3	50.25	48.50	45.85	45.96	47.91	46.25	48.37
4	42.40	44.00	43.40	49.50	31.60	53.50	50.90
5	46.50	48.40	46.90	48.80	32.10	55.80	49.60
6	56.20	55.00	41.60	46.30	13.20	56.80	45.70
7	41.50	41.50	38.00	44.50	2.60	36.00	43.50
8	52.70	52.20	48.00	48.30	44.80	51.30	49.10
True Conc	50.35	50.20	50.15	50.05	50.35	50.65	50.05
Mean Conc	47.79	48.34	44.68	47.67	29.24	49.91	48.32
Std. Dev.	5.46	4.57	3.91	2.09	16.24	7.11	2.78
% RSD	11.42	9.45	8.75	4.39	55.53	14.26	5.76
% Diff.*	5.08	3.71	10.91	4.76	41.93	1.46	3.46
Mean % Recovery	95	96	89	95	58	98	96

* Between true value and mean determined value.
Source: Ref. 1.
These data are provided for guidance purposes only.

TABLE 6

COMPARISON OF METHOD ACCURACY FOR SOIL AND AQUEOUS SAMPLES
(HIGH CONCENTRATION METHOD)

	Recovery (%)	
Analyte	Soil Method*	Aqueous Method**
2,4-DNT	96.0	98.6
2,4,6-TNT	96.8	94.4
RDX	96.8	99.6
HMX	95.4	95.5

* Data from Ref. 1.

** Data from Ref. 3.

These data are provided for guidance purposes only.

TABLE 7

EXAMPLE PRECISION AND ACCURACY DATA
FOR THE SALTING-OUT EXTRACTION METHOD

Analyte	# Samples	%RSD	Mean Recovery (%)	Highest Concentration Tested (mg/L)
HMX	20	10.5	106	1.14
RDX	20	8.7	106	1.04
1,3,5-TNB	20	7.6	119	0.82
1,3-DNB	20	6.6	102	1.04
Tetryl	20	16.4	93	0.93
2,4,6-TNT	20	7.6	105	0.98
2-Am-DNT	20	9.1	102	1.04
2,4-DNT	20	5.8	101	1.01
1,2-NT	20	9.1	102	1.07
1,4-NT	20	18.1	96	1.06
1,3-NT	20	12.4	97	1.23

All tests were performed in reagent water.
Source: Ref. 6.
These data are provided for guidance purposes only.

TABLE 8

COMPARISON OF DIRECT ANALYSIS OF GROUNDWATER SAMPLES CONTAINING NITROAROMATICS WITH SALTING-OUT AND SOLID-PHASE EXTRACTION TECHNIQUES

		Analyte Concentration (μg/L)								
Sample	Technique	HMX	RDX	TNB	DNB	DNA	TNT	24D	4A	2A
1	Direct									
	Salting-out	1.04	2.45				0.47		0.36	0.32
	SPE-Cart.	1.00	1.33				0.44		0.29	0.30
	SPE-Disk	0.93	1.35				0.57		0.28	0.56
2	Direct	94	79							
	Salting-out	54.2	63.8			0.3	0.33		3.08	1.36
	SPE-Cart.	64.0	83.1			0.3	0.34		3.34	2.27
	SPE-Disk	57.1	71.8			0.3	0.29		2.89	2.05
3	Direct	93	91							
	Salting-out	85.7	75.3			0.2	0.19		2.43	1.31
	SPE-Cart.	93.1	88.8			0.2	0.17		2.49	1.65
	SPE-Disk	78.9	74.7			0.2	0.13		1.99	1.89
4	Direct	45	14							
	Salting-out	45.7	16.4		0.17	0.3	0.13		2.18	1.21
	SPE-Cart.	48.0	21.6			0.2	0.19		2.31	1.42
	SPE-Disk	40.8	18.9			0.2	0.13		2.07	1.64
5	Direct									
	Salting-out	0.76	5.77						0.13	0.05
	SPE-Cart.	1.16	6.48						0.16	0.05
	SPE-Disk	1.19	6.11						0.16	0.14
6	Direct									
	Salting-out	10.5	6.17				0.10		0.71	0.33

Table 8 cont.

		Analyte Concentration (μg/L)								
Sample	Technique	HMX	RDX	TNB	DNB	DNA	TNT	24D	4A	2A
	SPE-Cart.	11.5	7.03				0.10		0.79	0.40
	SPE-Disk	10.3	6.34				0.07		0.82	0.70
7	Direct	134	365							
	Salting-out	75.4	202				0.98		8.12	1.80
	SPE-Cart.	115	308				1.51		11.3	3.44
	SPE-Disk	109	291				1.41		9.81	3.30
8	Direct									
	Salting-out	0.61	10.9							
	SPE-Cart.	0.64	11.9							
	SPE-Disk	0.64	11.0							
9	Direct	25	13							
	Salting-out	30.2	12.1						1.14	0.56
	SPE-Cart.	31.2	12.7						1.50	0.79
	SPE-Disk	27.5	11.0						1.34	0.79
10	Direct									
	Salting-out	0.33	7.12							
	SPE-Cart.	0.62	8.23							
	SPE-Disk	0.26	7.60							
14	Direct		13							
	Salting-out		5.98							
	SPE-Cart.		12.0							
	SPE-Disk		11.6							
16	Direct		40							
	Salting-out	0.58	28.7			0.04			0.39	0.13

Table 8 cont.

		Analyte Concentration (μg/L)								
Sample	Technique	HMX	RDX	TNB	DNB	DNA	TNT	24D	4A	2A
	SPE-Cart.	0.77	33.8			0.03			0.43	0.17
	SPE-Disk	0.66	32.7			0.03			0.44	0.22
18	Direct	165	58						9	7
	Salting-out	141	39.1			0.80	0.96		8.5	5.62
	SPE-Cart.	152	44.4			0.93	0.88		9.5	7.01
	SPE-Disk	138	40.9			0.90	0.99		9.3	6.03
19	Direct	173	76				17		59	54
	Salting-out	172	69.5			2.6	23.1	1.20	65.2	56.4
	SPE-Cart.	142	75.6		0.11	2.5	20.9	1.08	57.7	50.5
	SPE-Disk	136	72.7		0.11	2.4	20.3	1.23	55.0	48.0
21	Direct	252	157	5			110		47	65
	Salting-out	227	132	6.62	0.30		102		42.6	56.5
	SPE-Cart.	238	146	6.90	0.33		104		48.0	63.5
	SPE-Disk	226	141	6.45	0.31		102		47.0	61.8
22	Direct	218	40							
	Salting-out	201	35.9						2.20	1.90
	SPE-Cart.	203	36.5						2.74	2.24
	SPE-Disk	199	35.8						2.78	2.08
24	Direct									
	Salting-out	2.15	7.54							
	SPE-Cart.	2.47	8.91							
	SPE-Disk	2.34	8.84							
25	Direct									

Table 8 cont.

Sample	Technique	Analyte Concentration (μg/L) HMX	RDX	TNB	DNB	DNA	TNT	24D	4A	2A
	Salting-out									
	SPE-Cart.		0.59							
	SPE-Disk		0.63							
27	Direct	112	608	8			180		10	8
	Salting-out	82.8	429	4.45	0.79		137		7.71	6.20
	SPE-Cart.	91.0	510	9.53	0.90		149		8.25	7.67
	SPE-Disk	77.3	445	7.37	0.79		128		8.16	6.33
28	Direct	325	102				14		51	40
	Salting-out	290	87.5	0.37	0.10		13.9		42.3	33.5
	SPE-Cart.	319	109	0.87	0.17		22.0		56.2	45.0
	SPE-Disk	249	85.7	0.65	0.13		17.2		43.0	34.5
29	Direct									
	Salting-out									
	SPE-Cart.		0.43							
	SPE-Disk		0.28							
31	Direct									
	Salting-out									
	SPE-Cart.		0.21							
	SPE-Disk		0.23							
32	Direct									
	Salting-out									
	SPE-Cart.									
	SPE-Disk	0.38								

An additional 11 samples (11, 12, 13, 15, 17, 20, 23, 26, 30, 31, and 33) were analyzed in which none of the analytes were detected by any of the techniques. Therefore, the non-detect results are not shown here. Similarly, for those samples that are shown here, the fields are left blank for the analytes that were not detected.

All data are taken from Ref. 10.

These data are provided for guidance purposes only.

TABLE 9

EXAMPLE RELATIVE PERCENT DIFFERENCE BETWEEN DUPLICATE SAMPLE ANALYSES

		Relative Percent Difference (%)								
Sample	Technique	HMX	RDX	TNB	DNB	DNA	TNT	24D	4A	2A
4	Direct	0	24							
	Salting-out	0	15		6	100	8		18	11
	SPE-Cart.	1	12			0	45		8	5
	SPE-Disk	3	8			0	17		2	1
29	Direct									
	Salting-out									
	SPE-Cart.		26							
	SPE-Disk		7							
LCS	Direct	1	0	0			1	1		
	Salting-out	4	4	4			3	3		
	SPE-Cart.	6	1	7			6	6		
	SPE-Disk	5	7	7			13	6		

All data are taken from Ref. 10.
These data are provided for guidance purposes only.

TABLE 10

EXAMPLE RECOVERY OF ANALYTES FROM SPIKED SAMPLES

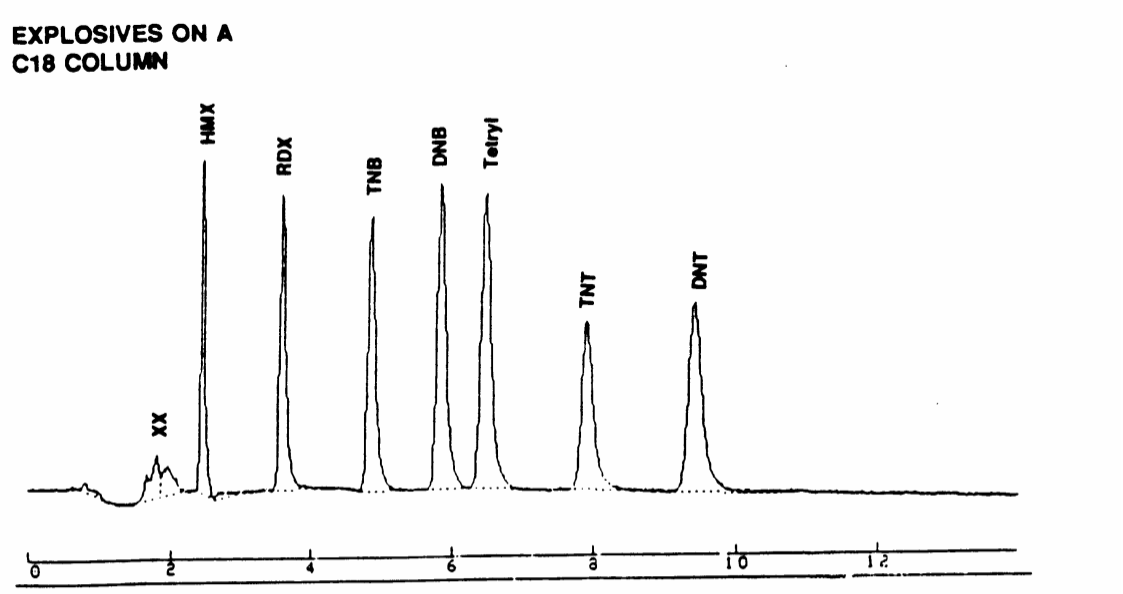
		Percent Recovery (%)				
Sample	Technique	HMX	RDX	TNB	TNT	24D
LCS1	Direct	99.5	98.5	95.6	96.5	98.1
	Salting-out	94.2	91.2	92.9	83.2	92.1
	SPE-Cart.	99.0	101.0	96.6	94.1	95.1
	SPE-Disk	92.5	95.6	89.3	88.6	86.9
LCS2	Direct	98.8	98.2	95.9	97.2	99.2
	Salting-out	91.0	95.0	89.0	81.0	89.0
	SPE-Cart.	93.5	100.0	83.0	89.1	89.3
	SPE-Disk	88.0	102.0	83.0	78.0	82.0
29	Direct	95.0	95.5	95.2	92.8	93.0
	Salting-out	107.0	89.0	85.0	89.0	65.0
	SPE-Cart.	103.0	107.0	104.0	05.0	102.0
	SPE-Disk	80.0	78.0	76.0	78.0	77.0
4	Direct	105.5	105.0	103.0	104.0	105.0
	Salting-out	23*	191*	76.0	83.0	76.0
	SPE-Cart.	351*	95*	92.2	91.1	93.7
	SPE-Disk	308*	49.5*	87.4	85.6	90.8

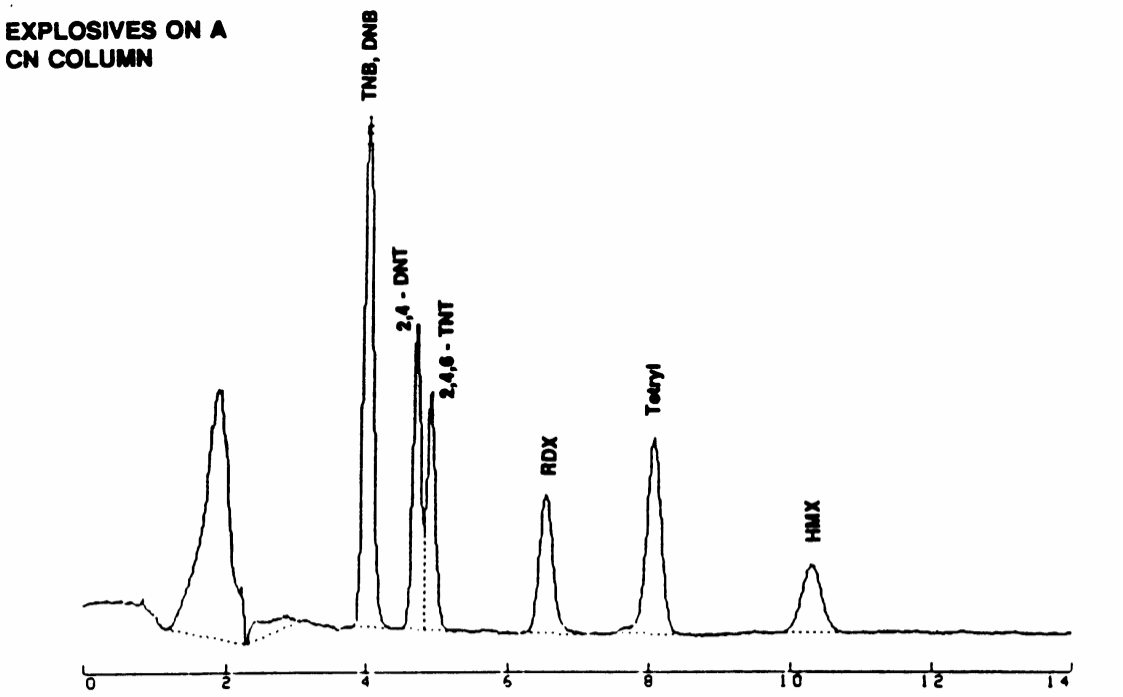
All data are taken from Ref. 10.

* Results for these analytes in Sample 4 are believed to result from spiking levels that are very similar to the background concentrations of these analytes in this sample (see Ref. 10).

These data are provided for guidance purposes only.

FIGURE 1
EXAMPLE CHROMATOGRAMS





APPENDIX A

COLLECTING AND PROCESSING OF REPRESENTATIVE SAMPLES FOR ENERGETIC RESIDUES IN SOLID MATRICES FROM MILITARY TRAINING RANGES

FORWARD

The information provided in this Appendix is based on EPA's evaluation of currently available data and technology as applied to the most appropriate sample collection, handling and processing procedures to determine representative concentrations of energetic material residues in solid matrices, such as soils, solid waste, or sediments. These procedures are designed to minimize the random error associated with heterogeneity of constituents that are distributed as particles into the environment. The intended users of this Appendix guidance are those individuals and organizations involved in the collection and preparation of samples for energetic material residue analysis during the characterization of solid materials under the Resource Conservation and Recovery Act (RCRA). The procedures and techniques described in this Appendix are not presented in any preferential order nor do they represent EPA requirements, but rather they are intended solely as guidance and should be selected and utilized based on the stated project-specific data quality objectives.

This Method 8330 Appendix was developed under the direction of Mr. Barry Lesnik, U.S. EPA, Office of Solid Waste (OSW), Methods Team in collaboration with Mr. Alan Hewitt, Dr. Thomas Jenkins, Marianne Walsh, and Jay Clausen of U.S. Army ERDC-CRREL, Charles Ramsey of EnviroStat, Inc., and the SW-846 Organic Methods Workgroup Members. The Methods Team is the focal point within OSW for expertise in analytical chemistry and characteristic testing methodologies, environmental sampling and monitoring, and quality assurance. The Methods Team provides technical support to other OSW Divisions, EPA Program Offices and Regions, state regulatory agencies, and the regulated community.

DISCLAIMER

The U.S. Environmental Protection Agency's Office of Solid Waste (EPA or the Agency) has prepared this Method 8330 Appendix to provide guidance to those individuals involved in the collection and preparation of samples for energetic material residue analysis during the characterization of solid materials under the Resource Conservation and Recovery Act (RCRA). This Appendix provides guidance for selecting an appropriate sample collection, handling, and laboratory processing techniques that are suitable for residues of secondary explosives and propellants in order to meet the data quality requirements or objectives for the intended use of the results.

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CONTENTS

A.1.0 PURPOSE AND OVERVIEW

This appendix provides guidance for the collection and processing of samples for characterization of secondary explosive and propellant residues in solid matrices, such as soils, solid wastes, and sediment obtained on military training ranges. Analysis of subsample extracts can be by High Performance Liquid Chromatography (HPLC), by Gas Chromatography (GC) Electron Capture (EC) or with other appropriate analytical techniques.

A.1.1 What are energetic material residues?

Energetic material residues are unreacted explosives and propellant compounds that remain after firing or the detonation of munitions. Energetic compounds are used by the military in the formulation of propellants, explosives, and pyrotechnics (PEP). Explosives are classified as 'primary' or 'secondary' based on their susceptibility to initiation. Secondary explosives are present in much greater quantities within military munitions than primary explosives and are far more prevalent among the energetic residues dispersed at military testing and training facilities. Secondary explosives include 2,4,6-trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), octrahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), 2,4,6-trinitro-phenylmethylnitramine (tetryl) and ammonium picrate (AP). Secondary explosives can also be classified according to their chemical structure. For example, TNT and picric acid/ammonium picrate are classified as nitroaromatics, whereas RDX and HMX are nitramines. Primary explosives, which include lead azide, lead styphnate, and mercury fulminate are highly susceptible to ignition and are often referred to as initiating explosives. Other energetic materials present at military facilities include 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), nitroglycerin (NG), perchlorate, nitrocellulose (NC), nitroguanidine (NQ), and pentaerythritol tetranitrate (PETN). NC, NG, DNT, NQ and perchlorate are used in several different types of artillery, mortar and rocket propellants, in the form of single base (NC/2,4-DNT), double base (NC/NG), triple base (NC/NG/NQ), and composite (ammonium perchlorate containing) propellants (Refs. 59, 2, and 13). PETN is the major component of detonation cord and blasting caps, often used during demolition activities.

Examples of pyrotechnics and smokes are white and red phosphorous, potassium perchlorate, hexachloroethane-zinc (HC), and metal nitrates (Refs. 12, 9 and 2).

White phosphorus is pyrophoric and will auto ignite when exposed to air, however is persistent in anaerobic sediments (Ref. 72). For this reason, white phosphorus is not compatible with processing protocols where the sample needs to be air-dried, and thus cannot be processed by the laboratory protocols described in this appendix. In addition, the laboratory protocols described herein have not been evaluated with compounds classified as primary explosives and pyrotechnics. The occurrence of residues of primary explosives on military training ranges is believed to be very infrequent. The protocols covered in this appendix are currently being evaluated for use with perchlorate residues.

TNT and RDX constitute the largest quantity of secondary explosives used in military applications, since they are major ingredients in nearly every formulation used for high explosive munitions (Table A-1-1, Ref. 70). In addition to the chemicals developed for secondary explosive formulations, production impurities or decomposition by-products have been detected. For example, military grade TNT often contains a number of impurities, including 2,4-DNT and other isomers of dinitrotoluene and trinitrotoluene (Ref. 40). In addition, TNT is susceptible to photo and microbial degradation from which a variety of transformation products have been identified (Ref. 71). The major impurity in production grade RDX is HMX, which can be present at concentrations as high as 12% (Ref. 66).

Table A-1-1. Common Secondary Explosives

Name	Composition	Common Use
Composition A	91% RDX: 9% wax	Grenades and Projectiles
Composition B	60% RDX: 39% TNT: 1% Wax	Projectiles, Shells, Grenades, E
Composition C-4	91% RDX: 9% plasticizer	Demolition Explosive
Explosive D “Yellow D”	Ammonium Picrate, Picric Acid	Bombs and Projectiles
Octol	70/75% HMX: 30/25% TNT	Shaped and Bursting Charges
TNT	100% TNT	Projectiles and Shells
Tritonal	80% TNT: 20% Aluminum	Bombs and Projectiles
H6	80% Composition B: 20% Aluminu	Bombs and Projectiles

A.1.2 How are energetic compounds dispersed on military training ranges?

Energetic material residues are heterogeneously distributed as particulates of various sizes, shapes, and compositions over large areas (> 100 m^2) at firing points, around targets, and around individual detonation events (Refs. 24-28, 31-33, 36, 56, 76, 55, 18, 43-47, and 8). Most of the energetic material residue deposition on DoD training ranges occurs as particles of pure or mixtures of secondary explosive compounds and as fibers or particles of gun propellants and solid-rocket fuels or motor grains. The highest concentrations of energetic material residues have been found on or close to the ground surface at firing points, and around targets where rounds have ruptured (low-order detonation or casing breach), where Unexploded Ordnance (UXO) or Discarded Military Munitions (DMM) have been blown-in-place (BIP) as part of a range clearance activity, and on demolition ranges used for open burn/open detonation (OB/OD) disposal of munitions. Gun and rocket propellant residues are dispersed at firing points, and in the case of rocket motors, down range around targets. Propellant residues at firing points are typically smaller than 2-mm nominal dimension. Residues of propellants around targets vary in size up to several cm nominal dimensions depending on the amount of unconsumed solid rocket fuel present at the detonation site. Residues of secondary explosives are found in locations where munitions detonate. Low-order (or partial) detonations are munitions that have breached the casing because of impact with hardened surfaces or rupture by shrapnel; these can release particles in a variety of sizes up to several cm nominal dimension. High-order detonations (detonation as designed, normal detonation train of fuse, booster, secondary explosive with a sealed casing) produce very fine micron and sub-micron sized particles.

The sample processing protocol in this appendix addresses only those energetic material residues of secondary explosives and propellants that fall within the size classification of soil (< 2 mm). Particles of energetic material residues larger than 2 mm should not be included in any sample sent off-site for processing and analysis. When residues of secondary explosives and propellants greater than 2-mm nominal dimension are observed, they should be gathered and weighed in the field by military explosive ordnance disposal (EOD) personnel or contractor UXO technicians.

A.1.3 What constitutes a representative energetic material residue sample?

A representative sample is one that answers a question about a decision unit with an acceptable level of confidence. This requires a complete understanding of the data quality objective (DQO) process, selecting the appropriate sampling design and strategy, and including proper quality controls to assess sample representativeness (Ref. 50). For example, if a representative mean concentration is desired for a given area, then the sample(s) collected should contain the same proportion of energetic residue particles as exists within the area and depth selected for sampling. The most efficient means to achieve this goal is to collect a multi-increment sample with an appropriate mass and number of increments to address the compositional and distributional heterogeneity (Refs. 49, 76, 77, and 34). To estimate the total uncertainty associated with a given sampling strategy and design, replicate samples must be collected.

A.1.4 Who is the intended audience for this Appendix?

This appendix is designed for people who need to characterize ranges to sustain training range activities or to transfer property under the Base Realignment and Closure Act (BRAC) and Formerly Used Defense Site (FUDS) programs. Users of the guidance in this Appendix are individuals involved the collection, preparation and analysis of solid samples collected on the surface of operational or non-operational Military Training Facility. This may include:

- Field sampling personnel
- Laboratory analysts
- Environmental project managers
- Federal, state, and local regulators
- Quality assurance personnel
- Data quality assessors

A.1.5 What does this guidance <u>not</u> cover?

This appendix does not provide guidance on how samples containing either primary explosives or pyrotechnics compounds should be processed for laboratory

analysis. In addition, very little information is known about the physical and distributional characteristics of perchlorate residues on military training ranges from pyrotechnics and composite propellant use and disposal; therefore, this guidance may not be applicable. Guidance on the analysis of secondary explosives and propellant residues will address some of the new instrumentation and separations that have been achieved with new columns; however, it will not duplicate the information covered in Methods 8330 and 8095.

A.1.6 What equipment is needed?

Surface sampling can be performed with hardened plastic or metal scoops, spoons, or corers. In cases where surface vegetation is present, coring tools aid in the collection of surface samples with minimal surface disturbance, and help to avoid inadequate (biased) sampling, i.e., sampling only the exposed soil surfaces (Ref. 79). The Expray kit (Plexus Scientific, Silver Spring, MD) may be practical for screening large pieces of materials believed to be chunks of energetic materials prior to sample collection, provided that it can be demonstrated to generate data that is applicable for its intended use (see Sec. A.3.0).

In the laboratory, the entire sample should be processed, including organic material such as vegetation (moss, grass, roots, etc.). Furthermore, to help ensure that representative subsamples can be removed from the portion of the sample that is consistent with the classification of soil (< 2 mm) a particle size reduction step is necessary (Refs. 75 and 76). It may be necessary to acquire large trays, storage racks, #10 (2 mm) sieves and a mechanical grinder to meet the recommendations within this appendix.

A.2.0 **PROJECT PLANNING** – Data Quality Objectives

The EPA's Data Quality Objectives (DQO) seven-step process provides guidance for the development of a scientific plan for data collection (Ref. 64). This systematic planning process helps to define the type, quantity, and quality of environmental data needed for a specified decision. Two very critical components of the DQO process are a

Quality Assurance Project Plan (QAPP) and a Field Sampling Plan (FSP), both of which comprise a site-specific Sampling and Analysis Plan (SAP). Refer to Guidance for the Data Quality Objectives Process (G-4) (August 2000, EPA/600/R-96/055), Guidance for Quality Assurance Project Plans (G-5) (February 1998, EPA/600/R-98/018) and RCRA Waste Sampling Draft Technical Guidance (August, 2002, EPA530-D-02-002)

The EPA's support of the performance-based measurement systems (PBMS) eliminates the requirement that only standard or consensus methods be used for sample collection and preparation. However, standard methods may have a long history of performance that should be considered when selecting the appropriate analytical method(s) for use on a site-specific basis. The EPA defines the PBMS process as "a set of processes wherein the data quality needs, mandates or limitations of a program or project are specified, and serve as criteria for selecting appropriate methods to meet those needs in a cost effective manner." Moreover, the use of PBMS requires that the project generate initial and sufficient continuing method performance data to demonstrate the appropriateness of the selected methods.

Paramount to all environmental samples is the desire that the resulting data be representative of the environmental media subject to investigation. The aerial extent of the media that needs to be sampled typically is dependent on whether risk is driven by an acute (short term, higher level) or chronic (longer term, lower level) exposure scenario. In both cases, the data obtained should represent the mean concentration of the constituents of concern, or a statistically valid upper confidence limit, such as the 95% UCL. Simply stated, the portion of the sample taken for analysis should contain the constituents of concern in the same proportions as the bulk sample of the media, which in turn should have the same proportions as present within the area (decision unit) under investigation. In the absence of the acquisition and analysis of the entire media area under investigation, the only scientifically defensible supporting evidence that can address this criterion is reproducibility. That is, does the repeatability of data from replicate field samples meet the DQOs? "If evidence for representativeness is not presented, then the data cannot be characterized as effective for project decision-making (Ref. 11)."

A.3.0 **SAFETY** – Collection, shipping, and screening.

A site visit to a location where energetic residues may be present should occur only after reviewing all the historical information and attending a safety briefing that addresses how to recognize and avoid military munitions. The reason for the briefing is that most military firing ranges contain unexploded ordnance (UXO) or discarded military munitions (DMM) on and below the ground surface. Therefore, all sample collecting activities must occur under the direct supervision of military EOD personnel or qualified contractor UXO technicians. Clearance provided by EOD personnel or UXO technicians is mandatory for areas where UXO/DMM are present or may exist. Safety clearances on military testing and training ranges can be performed at three different levels. Level one clearance consists of identifying and/or removing surface UXOs. Level two clearance consists of identifying and/or removing surface UXOs and screening the top 30-45 cm of soil for detected metallic anomalies (i.e., potential UXO/DMM) with the use of a hand held analog magnetometer. Level three clearance involves completely clearing the site of UXO/DMM in the area where work will be performed, normally based on a detailed digitally recorded geophysical mapping survey. As a minimum, surface UXOs and near-surface potential UXO/DMM should be marked for avoidance and all sampling areas or locations should receive level two clearances prior to initiating any surface or near-surface sampling activity.

Extreme care must also be taken in areas where energetic material residues are visible. Secondary explosives in excess of 12% w/w can propagate a detonation throughout the mass, if sufficient initiating force is placed on the material (Refs. 39, 53, and 59). In general, secondary explosives can violently detonate, deflagrate, or burn if exposed to heat, shock, impact, friction, or an electrostatic discharge. Shipping soils that contain reactive levels (> 12%) of energetic material residues using domestic carriers is prohibited. It should be noted that concentrations as high as 120,000 mg/kg of explosives material residues are rarely encountered. However, these high levels could exist around ruptured (low-ordered or breached) munitions and in areas where the operation of open burning / open detonation (OB/OD) of off-specification, obsolete, or excess energetic materials has been performed. When these high concentrations have been encountered, large pieces of pure crystalline energetic materials (e.g., “chunks”) were present.

When chunks of energetic material residues need to be verified, field analytical or screening techniques can be applied. These tests can be performed on-site to provide immediate information with respect to any potential risks (Refs. 57 and 10). The field analytical methods approved by the Environmental Protection Agency are colorimetric SW-846 Methods 8510 and 8515 and immunoassay Methods 4050 and 4051 (Refs. 63 and 60-62). Other screening methods, such as the Expray kit, may be used provided that they can be demonstrated to generate data that is applicable for its intended use. However, the Expray Kit, which has not yet been formally validated by EPA for inclusion in SW-846, provides qualitative and semi-quantitative (screening level) results, is very economical and is the easiest to use and transport. This screening tool is based on colorimetric products and uses chemical reactions similar to those in Methods 8510 and 8515 (Ref. 16).

The lightweight (less than 1.4 Kg) Expray Kit contains analysis paper, quality assurance test strips, and three aerosol cans of chemical reagents. To analyze hardened surfaces the first step is to wipe (rub) the exposed surfaces with a white sheet of analysis paper. Soil samples can be prepared for analysis by first extracting with acetone (hardware store grade is acceptable) for a couple of minutes then transferring a small volume (5 μL) of extract to an analysis sheet. If needed, several (6 to 12) sample extracts can be screened simultaneously by carefully placing multiple aliquots on one analysis sheet. The next step is to spray the surface of the analysis sheet following the kit instructions. If a color appears after spraying with the first aerosol, then polynitroaromatics (e.g. TNT, TNB, DNT, Picric acid, tetryl, etc.) are present. The appearance of a pink color after spray from the second aerosol can indicates the presence of nitramines or nitrate esters (e.g., RDX, HMX, NG, PETN, NC, NQ, and tetryl). If the first two aerosols have produced no color, the analysis sheet is sprayed with the third aerosol can. Formation of a pink color after applying the third aerosol indicates presence of an inorganic nitrate (ammonium, potassium, sodium, barium, and strontium nitrates). To estimate the explosives concentrations in the soil sample extracts, a visual calibration scale can be prepared with 10, 100, and 1000 mg/L standards of TNT and RDX (Ref. 6).

If energetic material residues are present within an order of magnitude of 12%

w/w in a soil sample, it should be blended with background soil or Ottawa sand. This dilution is not a remedial action by itself, but a safety measure that will allow the safe handling, storing and shipping of samples. Blending should be carried out precisely in order to calculate the initial concentration present in the sample. If the soil was not diluted, transport of the samples with 12% w/w secondary explosives would require the same safety waiver (manifested as a RCRA characteristic hazardous material due to reactivity and shipped according to DOT and EPA requirements for waste explosives) as that required for transporting pure secondary explosive material (Ref. 1).

A.4.0 SECONDARY EXPLOSIVES AND PROPELLANT RESIDUES – Guidance on the sampling strategy, design, and tools for collecting representative samples.

Energetic material residues often exist at detectable levels in heavily impacted areas (i.e., around targets), at firing positions, and where repeated demolition activities (e.g., OB/OD) occur (Refs. 28, 31-34, 36, 43, 47, 75, 76, and 8). The mass loading of energetic residues in these locations could potentially serve as a source for dissolved constituents in surface water runoff or ground water and present a potential risk to human health and ecological receptors. When characterizing the mass loading of energetic residues, the size of the decision unit selected for sampling can be based on several factors: the area influenced by a single event, the area influenced by an activity, or the area of concern for human health or ecological exposure (habitat).

Studies using fresh snow-covered ranges as a collection template for energetic material residues have been performed at artillery and mortar firing positions, and for live-fire and blow-in-place detonations. The results showed that energetic material residues were spread over large areas, typically on the order of hundreds of square meters (Refs. 29, 19, 80 and 81). With the exception of the explosives safety risk posed by UXO/DMM, the ecological risk associated with energetic material residues is usually a chronic exposure scenario (Ref. 42), for which the mean concentration, or statistically valid upper confidence interval, over the exposure area of concern is the most appropriate descriptor (Refs. 34, 35 and 44). Risk to ground water should be based on a representative evaluation of surface mass loading, which – similar to chronic exposure –

should be based on the best estimate of the mean concentration for the potential source zone, and the fate and transport of energetic residues from the source area(s). This information coupled with range records, munitions properties, range function and design, and surface conditions should all be considered when developing the conceptual site model to guide the sampling activities (Refs. 67, 33 and 37).

The selected sampling depth can strongly influence the concentration of energetic material residues in samples. Most energetic material residue deposition on DoD training ranges is at the surface and occurs as particles of pure or mixtures of explosive compounds and as fibers and particles of gun and rocket propellants (Refs. 75, 76, 55, and 33). Profile samples collected where particles of energetic material residue have accumulated on the surface near firing and detonation events have shown that soil concentrations drop off rapidly with depth, often by one or two orders of magnitude within the top 10 cm (Refs. 45, 47, 48, and 18). Two notable exceptions are hand grenade and demolition ranges where the filling of craters is common maintenance practice. On these two types of ranges energetic residues often are distributed over greater depths (Ref. 37). Moreover, because of the limited solubility of energetic compounds and the low moisture content of most solid media, it is seldom practical to measure these constituents in soil pore waters without isolating the aqueous phase and performing a pre-concentration step.

A sampling plan to assess energetic material residues should stratify the following from the remainder of the range: 1) firing points, 2) target locations, and 3) locations where OB/OD demolition activities have occurred. Moreover, the sampling plans should have the flexibility to further stratify areas where ruptured munitions or other visual evidence of chunk explosives and propellants are encountered. These areas could be stratified separately from the remainder of the decision unit because they are potential point sources for migration of energetic residues into surface or ground water.

Sampling performed near chunks of energetic residues has resulted in concentrations of energetic compounds in excess of 100 and even 1000 mg/kg in the < 2 mm surface soil fraction (Refs. 28, 31, 32, 43-47, and 20). The decision unit for sampling around a ruptured munition item should encompass all of the visible residue

chunks and any surface discolorations. When chunks are present, they should be gathered and removed by EOD personnel or UXO technicians, so they are not inadvertently sampled. To prevent cross contamination, samples collected where chunk residues were present just prior to sampling should be segregated from other samples during storage, transportation, and laboratory processing. The Expray kit (Plexus Scientific, Silver Spring, MD) may be applicable to identify chunk residues as energetic compounds prior to sample collection (See Sec. A.3.0). Energetic chunk material > 2 mm in diameter should not be included in the sample.

The sampling strategy for acquiring a representative sample must address compositional and distribution heterogeneity of the constituents of concern. Compositional heterogeneity exists because not all particles within a population have the same concentration of target analytes. This heterogeneity is at a maximum when the target analyte is present as a few discrete particles of pure material. Error due to compositional heterogeneity is called the fundamental error and is inversely related to the sample mass. Distributional heterogeneity is due to contaminant particles being scattered across the site unevenly. Error associated with distributional heterogeneity is inversely related to the number of individual increments used to build the sample. This type of error is at a maximum when a single discrete sample is used to estimate the mean for a larger decision unit. To reduce the influence of these sources of error in the estimate of the mean concentration for a decision unit, the collection of a 1 kg or larger sample comprised of 30 or more evenly spaced soil aliquots (i.e. increments) of the top 2.5 to 5.0 cm of the ground surface is recommended (Refs. 31, 32, 34, 77, and 18). The collection of several discrete samples is discouraged because of the large amount of uncertainty that will be associated with the estimation of mean concentrations (Refs 33 and 34).

Collecting a multi-increment sample at evenly spaced positions within the decision unit creates a sample that is much more reproducible than a discrete or small set of discrete samples (Ref. 34). Therefore, with respect to energetic material residues, a multi-increment sample is much more likely to contain the same proportional number of particles of different sizes (< 2 mm), composition (e.g. Tritonal, Composition B, octol, etc.), and configuration (e.g. crystalline spheres or elongated fibers) as exists within the

decision unit. A square or rectangular decision unit is recommended for ease of planning and implementing this task. The decision unit size is typically from 25 to 10,000 m^2. The choice of size depends on how residues are dispersed or on the size of the exposure or remediation decision unit, or the habitat for the ecological indicator of concern (Ref. 37). Sample increments should be collected while walking side-to-side and moving from one end to the other of the 25-m^2 or 10,000-m^2 area. The ability to obtain mean energetic material residue concentrations with a low level of uncertainty cannot be predetermined. Past sampling activities using this approach have shown that percent relative standard deviation (RSD) is inversely related to concentration and that, in general, lower RSDs ($n = 3$; < 30% RSD) are more frequently obtained at firing points than in impact areas (Refs. 76, 77, 31, 32, 34, 20, and 48). To establish the sampling uncertainty for estimating mean concentrations of energetic material residues, triplicate multi-increment samples should be collected for each type of activity under investigation. To avoid collecting co-located samples and to be random, each replicate of multi-increment samples should be collected starting at different corners of the decision unit or different random start locations within the same starting corner. If replicate samples are not included in a sampling plan, sampling error cannot be estimated.

Surface sampling can be performed with hardened plastic or metal scoops, spoons, or coring tools. Scoops and spoons are necessary for non-cohesive soils and heavily cobbled surfaces. Coring tools are recommended for cohesive surface soils with and without vegetation. Coring tools minimize surface disturbance, help maintain the consistently of the sampled surface area and depth, and can help eliminate the tendency to remove increments only from areas with no vegetation (Ref. 79). The sampling tool does not need to be cleaned between increments, since within a decision unit individual increments are part of the same sample. Tools should be cleaned between the collection of replicate samples and between decision units. The cleaning process involves first removing all adhering soil, then rinsing the sampling head with clean water. The final cleaning step is a rinse with acetone.

Multi-increment samples should be stored in clean plastic bags or clean large mouth glass bottles for off-site shipment. Splitting the sample in the field to reduce the volume sent for laboratory analysis or for QA purposes is not recommended (Refs. 75

and 76). When the samples cannot be air-dried on site, they should be stored and shipped on ice. Once samples have been air-dried, it is only necessary to maintain them at room temperature (25°C) or below during shipping and storage.

A.5.0 LABORATORY PROTOCOL FOR SOLID MATRICES CONTAINING SECONDARY EXPLOSIVES AND PROPELLENT RESIDUES – Guidance on the handling and processing of whole samples for representative subsampling and analysis.

It is well recognized that inadequate sample processing causes poor subsampling, which results in highly variable and biased analytical results (Ref. 65). No explicit guidance is presently available for environmental laboratories to follow regarding how to process large samples properly, particularly those that may contain vegetative detritus, grasses, mosses, and plant roots. Currently, when analyzing for energetic material residues, laboratories often only remove a small (< 50 g) portion of soil from the top of the sample container to dry, sieve, and grind using a mortar and pestle, prior to subsampling. Laboratory studies of this approach, and several others, all have shown that anything short of processing the whole sample introduces a large amount of uncertainty (Refs. 75, 76, and 17).

To facilitate air-drying of large samples and limit the amount of floor or bench space occupied, the use of large trays and racks is recommended. Once air-dried, the entire sample, less large pebbles and sticks, should be sieved. Care must be exercised not to eliminate soil agglomerates during this step. This is critical for clay soils. There are several ways to disaggregate soil agglomerates. The moist soil can be broken into small pieces with a gloved hand prior to drying coupled with applying pressure with a gloved hand or another instrument (e.g. spoon) to the dried material on top of the 2 mm screen. If this approach is used care must be taken not to damage the screen or force legitimate > 2mm material through. Another option is to break apart the dried agglomerates with a mortar and pestle.

The particle size cutoff for energetic residues should include those that fall within the classification of soil (< 2 mm) to comply with risk models for ecological exposure and to encompass those particles that can be readily dissolved (Refs. 46 and 20). In

addition, mosses and other types of fine vegetation should be physically shredded while sieving to release entrapped crystalline or fibrous residues. Including vegetation and increasing the size cutoff from the currently recommended <0.6 mm to < 2-mm (Methods 8330 and 8095) to eliminate extraneous environmental materials such as pebbles, twigs, and shrapnel often results in more representative estimates of energetic residue concentrations. In other words, using the current method, which excludes energetic residue fibers and particles between 2 and 0.6 mm, produces analyte concentrations that can be biased low, particularly for propellant residues (Refs. 46 and 77).

Within the < 2-mm soil size class, particles of energetic material residues exist as a variety of sizes, shapes and compositions. Therefore, either the entire sample must be extracted or it must be processed further prior to the removal of subsamples for analysis (Refs 75 and 76). Grinding the < 2-mm fraction in quantities of between 200 and 500 g for 60 seconds on a LabTech Essa LM-2 Ring Mill equipped with a B800 bowl reduces the particle size to less than 75 microns. This particle size reduction prior to subsampling reduces subsampling error to acceptable levels (n = 3; < 10 %RSD) for samples containing crystalline secondary explosives (Refs. 75 and 77). For samples containing NC based propellant residues, five 60-second grinding intervals are needed to adequately pulverize the same quantities of soil. Furthermore, to prevent the ring mill from warming to temperatures where more volatile energetic compounds may be lost, a 2-minute or longer cool down period is recommended between the grind cycles. When handling and processing samples from areas where chunk energetic material existed, the samples should be screened prior to mechanical grinding (see Section A.3.0).

To further reduce the uncertainty among subsamples, a 10-g subsample size is recommended for analysis instead of a 2.0-g subsample as currently cited in Methods 8330 and 8095. The entire ground sample should be mixed, spread out on a clean surface, and 30 or more randomly located increments removed from the entire depth to form this 10-g subsample. Moreover, to lower the detection limits of Methods 8330 and 8095 and minimize the consumption of solvent, the 10-g subsample of soil should be extracted with 20 ml of acetonitrile, instead of the 1:5 ratio cited in Methods 8330 and 8095 (Ref. 77). Extraction of energetic compounds from soils can either be performed using an ultrasonic bath or a platform shaker table (Ref. 78). To assess if the grinding,

mixing, and subsampling adequately addressed the compositional and distribution heterogeneity in the sample, triplicate subsamples should be removed and analyzed for every 5 to 20 samples processed.

A.6.0 ANALYSIS – Overview of analytical equipment and energetic compounds of concern.

Since the development of Method 8330 in the late 1980s (Refs. 21, 22 and 23), several additional RP-HPLC separations have been recognized as providing adequate resolution for the Method 8330 target analyte list (Table A-6-1). Analysts must be aware, however, that solvent strengths for extracts may need to be adjusted to be similar to the solvent strength of the mobile phase used for separation. If that is not done, peak shapes will be degraded and resolution reduced. There have also been improvements in the stability of the UV detectors allowing for improvements in the detection limits quoted in the method, and more importantly, dual and multi-wavelength detectors are now available.

Table A-6-1. RP-HPLC columns for the analysis of energetic residues.

Primary Columns	C-18 reversed-phase HPLC column, 25-cm x 4.6-mm, 5 µm C8 reversed-phase HPLC column, 15-cm x 3.9-mm, 4 µm
Secondary Columns	CN reversed-phase HPLC column, 25-cm x 4.6-mm, 5 µm Luna Phenyl-Hexyl reversed-phase HPLC column, 25-cm x 3.0-mm, 5 µm

GC-ECD methods for explosives were first developed in the 1970s and later were improved for routine commercial laboratory applications (Refs. 3, 15, 73, 74, and 5). Walsh and Ranney (Refs. 73 and 74) developed GC-ECD methods for both soil and aqueous media that were complementary to Method 8330, i.e., the same solvent extraction protocol for soils and the use of solid phase extraction for water samples (Method 3535). Hable et al. (Ref. 15) has successfully demonstrated the use of isoamyl acetate to extract nitroaromatics, nitramines and nitrate esters from both soils and water

samples.

The detection limits for the GC-ECD methods are one to two orders of magnitude lower than those for RP-HPLC. For some applications, this improved detection capability may be important to achieving project goals. However, all GC methods must deal with the thermal instability of some of the energetic compounds. Specifically, tetryl, RDX and HMX can be problematic in this regard. Method 8095 requires a much more rigorous QA program in order to maintain the same high quality of data as provided by RP-HPLC, and therefore, has not been adopted by many commercial laboratories.

Methods 8330 and 8095, respectively, contain target lists of 14 and 17 compounds. These lists include secondary high explosives (TNT, RDX, HMX, Tetryl), TNT manufacturing impurities (2,4-DNT; 2,6-DNT; 1,3-DNB), environmental transformation products of TNT (1,3,5-TNB; 2-amino-4,6-dinitrotoluene; 4-amino-2,6-dinitrotoluene; 3,5-DNA), gun propellant additives (nitrogylcerin (NG), 2,4-DNT), pentaerythritol tetranitrate (PETN), and several mononitroaromatics. The mononitroaromatics (nitrobenzene NB, ortho, para, and meta-nitrotoluene, o-NT, p-NT, and m-NT) were presumed to be present because of incomplete nitration in the production of TNT and 2,4-DNT. Analysis of many thousands of samples indicates that the major energetic-related compounds found in soil samples from manufacturing facilities, load and pack plants, and depots were TNT, RDX, 1,3,5-TNB; 2,4-DNT; 1,3-DNB; 2-ADNT, 4-ADNT, HMX, and tetryl (Ref. 70). NB and the NTs were only detected in manufacturer's effluent (Ref. 54). Subsequent analyses of samples from over 25 military training ranges throughout the United States and Canada indicate that the most commonly encountered energetic compounds are TNT, RDX, HMX, NG, 2,4-DNT; 2-ADNT and 4-ADNT, with most of the other target analytes detected occasionally. NB and the NT's have not been detected in samples from military training ranges; therefore, they could potentially be eliminated from the analyte list for range investigations.

NG and PETN are not target analytes in Method 8330. The major reason for this is that these compounds do not absorb strongly at 254 nm, the recommended wavelength for Method 8330. NG and PETN can be determined at much lower concentrations using Method 8332, since the recommended wavelength is 214 nm. With the advent of HPLC systems with either a dual wavelength detector or a diode array

detector, all the analytes originally recognized by Methods 8330 and 8095 and have been frequently detected can be determined in a single analysis.

Some laboratories using Method 8330 have relied on spectral matching with a diode array detector instead of recommended second column confirmation. In most cases, either approach would be acceptable, but specific samples may prove troublesome. This is particularly true when concentrations are near analytical detection limits. At lower concentrations, a successful approach is to conduct primary analysis by RP-HPLC (Method 8330), then confirm the results using GC-ECD (Method 8095).

On a case-by-case basis, several other energetic compounds associated with secondary explosives and propellants may be included in a scope of work for a training range investigation (Table A-6-2). Picric acid (PA)/Ammonium Picrate (AP) is an example of a secondary explosive used in some older munitions such as armor piercing naval gun projectiles. The compounds 2,4-diamino-6-nitrotoluene and 2,6-diamino-4-nitrotoluene are by-products of TNT following the reduction of a second nitro-group from 2-amino,-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene isomers. Hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX), hexahydro-1,3-dinitroso-5-dinitro-1,3,5-triazine (DNX), and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) are intermediate environmental reduction products of RDX. Nitrocellulose (NC), nitroguanidine (NQ), diphenylamine (DPA), nitro- and dinitro-diphenylamines, n-nitrosodiphenylamine (NDPA), and ethyl centralite (EC) are examples of energetic residues in propellants (Refs. 82, 83, 66, and 13). Some of these compounds and perhaps others not listed in Table A-6-2 may be of greater interest in the future once information on their fate and transport becomes available. Toxicity values for several of these compounds can be found on the EPA IRIS database (www.epa.gov/iris). Table A-6-2 provides references to published methods of analysis for these different energetic residues.

Table A-6-2. Energetic compounds not currently target analytes of Methods 8330 and 8095.	
Energetic Compound	**References**
picric acid (PA)/Ammonium picrate (AP)	58
2,4-diamino-6-nitrotoluene	69, 74
2,6-diamino-4-nitrotoluene	69, 74
hexanitro-hexaazaisowurtzitane (CL-20)	30
1,3,3-trinitroazetidine (TNAZ)	30
hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX)	14, 51, 52, 4, 7
hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine (DNX)	14, 51, 52, 4, 7
hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX)	14, 51, 52, 4 ,7
nitrocellulose (NC)	41
nitroguanidine (NQ)	68
diphenylamine (DPA)	84
n-nitroso-diphenylamine (NDPA)	82, 66, 13
2-nitrodiphenylamine	40, 87, 69
4-nitrodiphenylamine	84, 66
2,4-dinitrodiphenylamine	38, 84, 66
ethyl centralite (EC)	82, 83
n-nitroso-2-nitrodiphenylamine	38, 66

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