METHOD 8510

COLORIMETRIC SCREENING PROCEDURE FOR RDX AND HMX IN SOIL

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 a colorimetric *screening* procedure that may be used to determine the presence of the following RCRA compounds in soil samples:

Compound	Abbreviation	CAS Number*
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0

* Chemical Abstracts Service Registry Number

Other chemically-related explosive and propellant compounds, including nitramine compounds and organonitrate esters, also react with the test reagents to form the pink-to-reddish color typical of this group of chemicals. Such compounds include nitroguanidine (NQ), nitroglycerine (NG), pentaerythritol tetranitrate (PETN), nitrocellulose (NC), and tetryl. This method does not measure trinitrotoluene (TNT) if it is found by itself. However, TNT does interfere if mixed with RDX or any of the other nitramines and nitrate esters listed above (see Sec. 4.2).

1.2 This screening procedure may be applicable for site remediation purposes when supported by data from other techniques such as HPLC, GC/MS, or other analytical methods capable of providing specific qualitative and quantitative analysis. It also may be used to determine the most appropriate sampling points for standard laboratory testing for the initial screening of a site that is expected to contain any of the explosives/propellants listed above. As with any screening procedure, the data may not be appropriate for regulatory compliance purposes.

1.3 This method is designed to provide results for RDX and HMX. If the history of the site shows that compounds other than RDX and HMX predominate, then analytical standards of the appropriate compounds may be utilized in the generic procedure. The commercial testing product is designed for RDX and HMX analysis only.

1.4 As written, this screening method may be used to identify those soil samples with RDX concentrations between 1 and 20 mg/kg. Extracts of samples with concentrations >20 mg/kg of RDX should be diluted and reanalyzed. The procedure is approximately three times less sensitive to HMX than to RDX. Therefore, for sites where HMX is the predominant explosive, HMX should be used as the analytical standard and extracts from soil samples with concentrations >60 mg/kg should be diluted and reanalyzed.

1.5 If TNT is to be determined using Method 8515, then a portion of the soil extract from that method may be used for the determination of RDX or HMX using this method.

1.6 This method may be performed using either a commercially-available testing product (see Sec. 6.1) or from equipment, supplies, reagents, and standards assembled from other sources. When using the commercially-available testing product, follow the manufacturer's instructions. Otherwise, follow the generic procedures described in Sec. 11.2 of this method.

1.7 Prior to employing this method, analysts are advised to consult the manufacturer's instructions 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 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.

In addition, analysts and data users are advised that, except where explicitly specified 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.

1.8 Use of this method is restricted to use by, or under the supervision of, personnel appropriately experienced and trained in the handling of environmental samples that may contain explosives. Each analyst must demonstrate the ability to generate acceptable results with this method.

NOTE: See Sec. 5.0 for additional information on safety.

2.0 SUMMARY OF METHOD

Soil samples may be screened for RDX or HMX using a commercially-available testing product and following the manufacturer's directions, or using materials assembled from other sources by following the generic procedures outlined in Sec. 11.2 of this method. The summary that follows applies to either approach.

2.1 Soil samples are extracted with acetone.

2.2 After extraction, extracts are taken through the steps in the subsections to follow.

2.2.1 If inorganic nitrates and/or nitrites are present, the extract is passed through an ion exchange resin to remove them.

2.2.2 The extract is then acidified and mixed with zinc dust, thereby forming nitrite through the reaction of the target analytes with the zinc dust.

2.2.3 A color is developed using a NitriVer 3 powder pillow. The color ranges from pink to a deep red, depending on the concentration of RDX, HMX, and/or related analytes. An orange-colored solution indicates that a mixture of TNT and RDX, HMX, and/or related analytes are present.

2.2.4 The absorbance of the treated extract is measured at the designated wavelength using a spectrophotometer. The concentration of RDX/HMX in an unknown sample is estimated by comparison to a known standard.

3.0 DEFINITIONS

3.1 Reagent spike -- An aliquot of acetone (the extraction solvent) which is spiked with the analytes of interest and carried through only the analysis portions of the procedure. The results of the reagent spike are compared to matrix spike results in order to separate analysis problems from extraction problems.

3.2 Refer to Chapter One, Chapter Four, 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 of 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.

4.2 Besides RDX and HMX, chemically-related explosives such as nitroguanidine (NQ), nitroglycerine (NG), pentaerythritol tetranitrate (PETN), nitrocellulose (NC), or tetryl will cause a pink color to develop if they are present in the sample.

4.3 No color development was observed when the following compounds were present and when RDX, HMX, and related compounds were absent:

Trinitrotoluene	Dinitrobenzene	2,6-Dinitrotoluene
Trinitrobenzene	2,4-Dinitrotoluene	

However, an orange-colored solution is formed in samples containing mixtures of RDX (and/or related compounds) and TNT.

4.4 Some humic matter, a naturally occurring form of organic matter normally present in soil, can be extracted using the procedure and will result in a yellow-colored extract. Much of the humic matter precipitates following acidification, which causes the extract to turn cloudy and can interfere with the accurate determination of the absorbance. However, the humic matter precipitate can be removed by filtration.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The user 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 The target analytes for this method are explosive materials. Analysts must be trained in proper handling techniques for explosive-containing material in order to appropriately use this method, or be supervised by those who have received such training.

5.3 Extra caution is necessary when handling neat materials such as the analytical standards. Follow the directions in Sec. 7.3.1.2 regarding drying neat materials at ambient temperature.

5.4 Caution should be exercised during the sampling of possible explosive-contaminated material. Visual inspection 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. Explosives are generally a very finely ground grayish-white material.

5.5 Grinding solid samples containing explosives poses a significant risk to the analyst and should be avoided at all costs. During use of this method, it is **not** necessary to ground solid materials before extraction.

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 A commercial testing product, the EnSys RDX Soil Test System, is available from Strategic Diagnostic Inc. (SDI), Newark, DE. The commercial testing product will supply or specify the apparatus and materials necessary for successful completion of the test. Other equivalent testing products may be employed, if available. The procedure may also be performed using equipment and supplies assembled from other sources.

6.2 Some additional equipment and supplies are necessary when using either the testing product or the procedure described in this method. Those items include:

6.2.1 Field-portable, battery-operated UV/Vis spectrophotometer -- Hach DR/2000, or equivalent. If used in a fixed laboratory, any UV/Vis spectrophotometer capable of reading absorbance at 507 - 510 nm may be used.

6.2.2 Mechanical or top-loading balance -- For weighing samples to ± 0.1 g.

6.2.3 Two or more matched spectrophotometer cuvettes -- 25-mL and 2.5-cm path length, Hach or equivalent.

6.3 The following items are needed for the generic procedure outlined in Sec. 11.2 , but may not be needed if the commercial testing product is used.

6.3.1 Analytical balance -- For preparation of the calibration standards, if prepared from neat material

6.3.2 Wide-mouth bottles -- 125-mL, high density polypropylene (Nalgene 33-2189-0004 or equivalent).

6.3.3 Glass volumetric pipettes -- 0.5-mL, 1.0-mL, 2.0-mL, 3.0-mL, 5.0-mL, 10.0-mL, 25.0-mL.

6.3.4 Graduated cylinders -- 10- and 100-mL.

6.3.5 Glass volumetric flasks -- 100- and 250-mL.

6.3.6 Filter units -- 0.45- or 0.5-µm, (Millex SR or equivalent), 3 per sample.

6.3.7 Syringes -- 10-mL (2 per sample) and 30-mL (1 per sample) (BD Plastipak or equivalent).

6.3.8 Spatula.

6.3.9 Vacuum desiccator -- For preparing calibration standards in a fixed laboratory and for storage of zinc dust.

6.3.10 Ion exchange tubes -- Alumina-A, 3-mL (Supelclean, or equivalent, Supelco 5-7082).

6.3.11 Automatic pipet -- 500-µL equipped with tips (Eppendorf or equivalent).

6.3.12 Adapter for ion exchange tubes -- Supelco 5-7020, or equivalent.

6.3.13 Measuring spoon for zinc dust.

6.3.14 A platform or wrist action shaker -- For soil samples that need greater than a 3-min shake extraction.

6.3.15 Vials -- 40-mL amber glass, equipped with a solid cap (Supelco 2-7182 or equivalent).

7.0 REAGENTS AND STANDARDS

7.1 Each commercially-available testing product will supply or specify the reagents necessary for successful completion of the test, except for acetone and distilled or deionized water. Reagents should be labeled with appropriate expiration dates.

7.2 The following reagents are necessary for both the commercial testing product and the generic procedure in Sec 11.0.

7.2.1 Acetone, CH_3COCH_3 -- Any grade of acetone may be employed, including that available through hardware stores.

7.2.2 Distilled or deionized water -- Locally-purchased distilled or deionized water may be used.

7.3 The reagents listed in the subsections to follow are used in the generic procedure outlined in Sec. 11.2.

7.3.1 Analytical standards

It is highly recommended that commercially-prepared stock standard solutions be purchased rather than handling pure explosive and propellant material. However, if the laboratory routinely handles these types of compounds, then they may be prepared as follows.

7.3.1.1 RDX and HMX analytical standards

Prepare a standard of the predominant explosive component at the site.

7.3.1.2 Stock standard solution

Dry solid RDX and HMX to a constant weight in a vacuum desiccator in the dark at ambient temperature. Weigh about 0.1 g, to the nearest 0.0001 g, transfer to a 250-mL volumetric flask and dilute to volume with acetone. The analyte concentration of this stock standard is about 400 mg/L. This stock standard should be prepared in the laboratory before going to the field. Prepare each analyte in an individual solution.

WARNING: RDX and HMX are explosives and the neat material should be handled carefully. Both RDX and HMX neat materials are shipped under water. Drying at ambient temperature in a vacuum dessicator takes several days. DO NOT DRY AT ELEVATED TEMPERATURES!

7.3.2 Working standard solution

Prepare a working stock standard of RDX by diluting 25.0 mL of the stock standard to 250 mL in a glass volumetric flask and bringing to volume with acetone. The concentration of the RDX working stock standard is about 40 mg/L. For HMX, dilute 75.0 mL of the stock standard to 250 mL in a glass volumetric flask and bring to volume with acetone. The concentration of the HMX working stock standard is about 120 mg/L. Commercially-prepared stock standard solutions at other concentrations may be used. If the concentration is different, adjust the aliquot size and final volume to provide a working standard for RDX at 40 mg/L or for HMX at 120 mg/L.

7.3.3 Calibration solutions

Prepare calibration solutions as described in Table 1. Use glass volumetric pipettes to dispense the working stock standard and water, and use a 100-mL graduated cylinder to add the acetone. Prepare each solution in a 125-mL polypropylene bottle.

7.3.4 Acetic acid (glacial), CH_3CO_2H.

7.3.5 Zinc dust, 325-mesh (Aldrich 20,99808 or equivalent).

7.3.6 Hach NitriVer 3 powder pillow (1 per sample), or equivalent.

7.3.7 Acetone with 3% added water -- Add 114 mL of water (see Sec. 7.2.2) to one gallon of acetone.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Four, "Organic Analytes."

8.2 Soil samples may be contaminated with explosives and/or propellants, and should therefore be considered hazardous and handled accordingly. See Sec. 5.0 for additional safety considerations.

8.3 When testing is conducted in the field, store samples, sample extracts, and testing product reagents out of direct sunlight. When testing is conducted in a fixed laboratory, it is recommended that samples be shipped to the laboratory on ice, at #6 EC. Once at the laboratory, samples and sample extracts be stored in the dark at #6 EC. No formal holding times have been established for the analysis of solid samples containing explosives.

9.0 QUALITY CONTROL

9.1 Secs. 9.2 through 9.5 address quality control guidance for both a commercial testing product and the generic procedure addressed by Sec. 11.2. Also, refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols that may be applicable. 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.

This method is intended for either on-site (field) or laboratory use. The appropriate level of quality assurance/quality control should accompany the application of this method to document data quality.

9.2 Quality control considerations for the use of a commercial testing product

9.2.1 Follow the manufacturer's instructions for the quality control procedures specific to the commercial testing product being used.

9.2.2 The use of replicate analyses, particularly when results are near the action level, is recommended to refine the information gathered with the testing product.

9.2.3 Do not use commercial testing products past their expiration dates.

9.2.4 Use the commercial testing products within their storage temperature and operating temperature limits.

9.2.5 Verify operation of the colorimeter/spectrophotometer through the use of appropriate standards.

9.2.6 Analyze a laboratory control sample (LCS) at the frequency recommended by the manufacturer, using the reagents and standards provided by the manufacturer for this purpose.

9.3. Initial demonstration of proficiency

Because this is a screening procedure designed for on-site use, the quality control requirements are significantly less stringent than those employed for quantitative trace analyses. However, each analyst that utilizes this method should analyze a blank and four replicates of a spiked reference matrix to demonstrate proficiency with the method.

NOTE: The initial demonstration applies to *both* the use of the commercial testing product and the generic procedure described in Sec. 11.0 of this method.

9.3.1. The matrix used for spiking should be dried soil or sand that has been demonstrated to be free of anything that would result in color development (see Sec. 4.0).

9.3.2 Add 0.5 mL of the stock solution from Sec. 7.3.1.2 to a 20-g aliquot of clean soil or sand contained in a 125-mL polypropylene bottle (or other suitable container supplied by the manufacturer of the commercial testing product), resulting in a concentration of 10 mg/kg of RDX or 30 mg/kg of HMX (depending on the predominant analyte of interest). Prepare a total of four such aliquots and analyze them following either the commercial testing product procedure in Sec. 11.1 or the generic procedure in Sec. 11.2.

9.3.3 Calculate the concentration of RDX or HMX in each of the four aliquots, as well as the mean concentration, the standard deviation, and the relative standard deviation, using the equations below.

$$\text{mean concentration} = \frac{\sum_{i=1}^{n} \text{Concentration}_i}{n}$$

$$SD_{\text{concentration}} = \sqrt{\frac{\sum_{i=1}^{n} (\text{concentration}_i - \text{mean concentration})^2}{n-1}}$$

$$RSD = \frac{SD}{\text{mean concentration}} \times 100$$

where n = 4 and the RSD is expressed as a percentage (%).

9.3.4 Unless otherwise specified in an approved project plan, in order to be acceptable for use as a screening method, the mean concentration for the four aliquots

should be within 40% of the test concentration (i.e., 6 - 14 ppm of RDX or 18 - 42 ppm of HMX), and the RSD should be less than or equal to 30%.

9.3.5 Records of this demonstration should be retained on file.

9.4 Routine quality control considerations

Routine quality control procedures for a screening method generally include the periodic analyses of method blanks and laboratory control samples. When employing a commercial testing product, follow the manufacturer's instructions regarding quality control. If none are given, then follow the guidance given below for the generic procedure described in Sec. 11.2.

9.4.1 Analyze a method blank and an LCS on each day that samples are analyzed. The method blank and LCS aliquots are prepared from clean soil or sand. Prepare the LCS as described in Sec. 9.3.2, but only prepare one aliquot. Begin the analysis starting with the extraction step in Sec. 11.2.4, but add 99 mL of acetone with 3% added water (Sec. 7.3.7), rather than 100 mL.

9.4.2 Analyze a reagent spike that is only taken through the analysis procedure. The reagent spike is prepared by adding 0.5 mL of the working standard (Sec. 7.3.2) to 4.5 mL of acetone in a 10-mL graduated cylinder. Begin the analysis with the addition of glacial acetic acid (Sec. 11.2.5.4). The recovery should be between 60 and 140%. After 10 such spikes have been analyzed, calculate the standard deviation and establish control limits as the mean recovery ± 2 standard deviations.

9.4.3 It may also be useful to prepare and analyze a matrix spike sample consisting of soil from the specific site, rather than the clean sand or soil used to prepare the LCS. One purpose of the matrix spike analysis is to determine that there are no nitrates or nitrites in the soil from other sources such as fertilizers that will result in a positive response in the screening test.

NOTE: Given that this is a screening procedure, no acceptance criteria have been applied to the matrix spike or LCS results. Analysts should employ professional judgement in determining if interferences are a likely problem and should report all results, including the LCS and matrix spike data, to the data user.

9.5 The reagent blank should be clear and colorless. If any contamination is noted, review the glassware cleaning procedures or other possible sources of contamination.

10.0 CALIBRATION AND STANDARDIZATION

The calibration procedures for this method depend on whether the commercial testing product or the generic procedure is used. Use the calibration approach described for the procedure that is used to analyze samples. See Secs. 11.1.1 and 11.2.2 for information on calibration and standardization.

11.0 PROCEDURE

The actual procedures used to analyze samples differ slightly between the commercial testing product and the generic procedure. Either approach will yield acceptable screening results. The commercial testing product approach may provide advantages in terms of ease of use and the self-contained nature of the testing product. The generic procedure offers the

ability to tailor the analysis to site-specific conditions to some degree through the optimization of the sample extraction time, the ability to change the calibration range, and the ability to use the predominant explosive at the site for calibration.

11.1 Commercial testing product

11.1.1 Calibration

If the commercial testing product is utilized, follow the manufacturer's instructions for calibration. The commercial testing product employs the subtraction of a constant background absorbance and a predetermined constant calibration factor that relates the response to the concentration of RDX. When combined with the various quality control checks specified by the manufacturer, this calibration approach will produce results of an acceptable quality for a screening method.

11.1.2 Sample analysis

Follow the manufacturer's instructions.

11.2 Generic procedure

11.2.1 Calibration

When the generic procedure is employed, the method should be calibrated using the predominant explosive or propellant compound found at the site. The approach described below mirrors that used for quantitative trace analysis by other methods in this manual, but the linearity criteria have been relaxed because this procedure remains a *screening* method. Once an acceptable multi-point calibration has been demonstrated, a single-point calibration may be employed on subsequent days, provided that all other quality control criteria have been met (see Sec. 11.2.2).

11.2.1.1 The initial calibration involves calibration of the spectrophotometer using a reagent blank and a series of five standards of the analyte of interest. Example concentrations of RDX and HMX standards are shown in Table 1. Other concentrations may be employed at the discretion of the analyst, provided that they are appropriate for the specific application. The reagent blank and each standard are prepared using the procedures described below.

11.2.1.2 Firmly attach a Millex-SR, or equivalent, filter unit to a 10-mL syringe and place approximately 0.2 g of zinc dust into the barrel of the syringe. Prepare one such syringe for each calibration standard and one for the reagent blank (i.e., six syringes total).

11.2.1.3 For each standard, add 20 mL of distilled or deionized water to a separate 40-mL vial. Tear open a NitriVer 3 powder pillow and add the contents to the 20 mL of water in the vial. Shake the contents of the vial until the powder is completely dissolved. Allow each vial to stand for at least 5 min but no longer than 10 min.

11.2.1.4 While the solutions in Sec.11.2.1.3 are allowed to stand, mix a 5.0-mL aliquot of each calibration standard from Sec. 7.3.3. with 0.5 mL of glacial acetic acid in separate 10-mL graduated cylinders.

11.2.1.5 Tap the syringes from Sec. 11.2.1.2 so that all zinc dust is at the bottom of the syringe. Pour each acidified calibration solution into the barrel of a separate 10-mL syringe.

11.2.1.6 For each syringe, insert the syringe plunger into the barrel of the syringe and invert the syringe once to mix the reagents. After 10 sec, filter each of the solutions into the separate vials from Sec. 11.2.1.3 containing 20 mL of water and the contents of the NitriVer 3 powder pillow.

CAUTION: The reaction of the acidified extract with the zinc dust is the most crucial step in obtaining consistent and correct results. This step should be done as quickly and consistently as possible (taking at most 15 sec). Longer contact between the solution and the zinc will result in a decrease in color development. The reaction is also somewhat temperature dependent and should be performed at an ambient temperature between 65 °F to 80 °F (18 EC to 27 EC).

11.2.1.7 Shake each vial to mix the contents and let it stand for 15 - 30 min. A pink-to-rose colored solution is indicative of the presence of RDX or HMX. After color development, transfer the solutions into clean 30-mL syringes with filters attached.

11.2.1.8 Establish the zero absorbance setting of the spectrophotometer using a filtered mixture of 5 mL of acetone and 20 mL of deionized water containing the contents of a NitriVer 3 powder pillow and mixed in a 40-mL vial. Transfer this reagent blank to a 25-mL reference cuvette and measure the absorbance at 507 nm. Record the absorbance.

11.2.1.9 Transfer each of the other calibration standards to separate 25-mL cuvettes and measure the absorbance at 507 nm, recording each result.

11.2.1.10 Calculate the calibration factor (CF) using the equation below.

$$CF = \frac{\text{absorbance units}}{\text{concentration in mg/kg}}$$

The absorbance readings for solutions A through F in Table 1 should range from 0.0 to 0.7 absorbance units. If so, the response should be linear with respect to the RDX or HMX concentration for soil samples (based on wet weight).

NOTE: No other linearity criteria have been applied to the calibration factors because this method is a *screening* procedure.

11.2.2 Calibration verification

Verify the instrument calibration daily using solution E of Table 1 and following the procedure as outlined in Sec. 11.2.1. The calibration verification standard absorbance should fall between 0.5 and 0.8 absorbance units. Calculate a calibration factor as described above and use this CF for the calculation of sample concentrations in Sec. 11.3.

The calibration verification solution may be taken through the analysis procedure along with the first set of samples for the day.

NOTE: The use of a single-point calibration is a departure from the calibration approach used for the 8000 series methods and is appropriate in the case of a *screening* method.

11.2.3 Determination of the extraction time

The time necessary to adequately extract the analytes of interest varies depends on the soil composition at each site. The results from this screening method will improve if the extraction time is optimized. Even at a given site, soil composition may vary from area to area and also by depth.

NOTE: Typically, the heaviest soil and/or the soil with the highest organic content will be the hardest to extract. If different soil types are present on the site, either horizontally or vertically, and only a few soils need long extraction times, the samples might be split into two groups and the appropriate extraction time used for each. It is recommended that this extraction time determination be made at a fixed laboratory during the initial investigation of the site, however, it may also be conducted in the field.

Select soil samples expected to contain target analytes from several locations on the site if soil composition varies. Also select several samples at different depths if soil composition appears to change.

11.2.3.1 Determine the extraction time by weighing out one 20-g sample from each sampling location chosen and perform the extraction procedure outlined in Sec. 11.2.4, except shake each sample for a total of 30 min.

11.2.3.2 Remove a 5.0-mL aliquot from each sample after 3 min of shaking, again after 10 min, and finally again at the end of 30 min.

11.2.3.3 Follow the remainder of the procedure to determine the concentration of RDX or HMX in each aliquot. Choose the shortest extraction time that produces acceptable extraction.

11.2.4 Extraction of soil samples

Place a 20-g sample of soil into a 125-mL polypropylene bottle and add 100 mL of acetone with 3% added water (Sec. 7.3.7), using a graduated cylinder. Cap the bottles and shake for 3 min (or whatever time was determined to be necessary in Sec. 11.2.3). Allow the soil to settle for 5 min. The extracts are ready for analysis of RDX or HMX.

11.2.5 Sample analysis

11.2.5.1 Attach a 0.45-µm filter to a 10-mL syringe and attach an anion exchange resin tube to the tip of the filter. Pour 5 mL of acetone into the syringe. Force the acetone through the filter at about 1 mL/min to condition the resin.

11.2.5.2 Shake the 10-mL syringe dry and reuse for the next step.

11.2.5.3 Nitrate-nitrite cleanup

Transfer a 10-mL aliquot of soil extract to the 10-mL syringe with the filter and resin tube attached. Discard the first few mL and collect 5.0 mL in a 10-mL graduated cylinder. Filter the remaining extract in the syringe into a small vial to retain for dilutions, in case the intensity of the color exceeds the calibration curve.

11.2.5.4 Add 0.5 mL glacial acetic acid to the 5.0-mL aliquot and mix.

11.2.5.5 Add 20 mL of deionized water to a 40-mL vial. Tear open a NitriVer 3 powder pillow and add the contents to the 20 mL of water. Shake the contents of the vial until completely dissolved then allow to set for at least 5 min, but no longer than 10 min, before adding the extract from Sec. 11.2.5.6.

11.2.5.6 Add 0.2 g of zinc dust into the barrel of a 10-mL syringe equipped with a filter unit. Tap the syringe so that all zinc dust is at the bottom of the syringe. Make sure the filter is securely attached, then add the extract from Sec. 11.2.5.4. Fit the plunger to the barrel of the syringe, invert the syringe once. After 10 sec, filter the solution into the 20 mL of deionized water containing the contents of the NitriVer 3 powder pillow prepared in 11.2.5.5.

NOTE: The reaction of the acidified extract with the zinc dust is the most crucial step in obtaining consistent and correct results. This step should be done as quickly and consistently as possible (taking at most 15 sec). Longer contact between the solution and the zinc will result in a decrease in color development. The reaction is also somewhat temperature dependent and should be performed at an ambient temperature between 65 °F to 80 °F (18 EC to 27 EC).

11.2.5.7 Shake the vial to mix and let it stand for 15 - 30 min. A pink-to-rose colored solution is indicative of the presence of RDX or HMX. After color development, transfer the solutions into clean 30-mL syringes with filters attached.

11.2.5.8 Filter the extract into a 25-mL cuvette and measure the absorbance at 507 nm. Establish the zero absorbance setting using a filtered mixture of 5 mL of acetone and 20 mL of deionized water containing the contents of a NitriVer 3 powder pillow mixed in a 40-mL vial. Filter the blank solution into a 25-mL reference cuvette. Record the absorbance.

NOTE: Some samples may display a milky or cloudy appearance even after being filtered into the sample cuvette. These samples should be refiltered and the cuvette cleaned. If the extract is still cloudy, read and record the absorbance but make note of the cloudiness and indicate that this is a false positive. If a pink color is also present, this should be taken as a positive reaction for RDX. However, the associated result should be noted as biased high because of cloudiness in the extract. Allow bubbles to dissipate before reading the absorbance.

11.2.5.9 Between samples, clean the cuvettes with deionized water and acetone (in that order), using a stopper and shaking vigorously.

11.2.5.10 Periodically verify that the instrument is reading zero using the reference cuvette.

11.2.5.11 If the absorbance exceeds 0.7 absorbance units, the original acetone extract (Sec. 11.2.5.3) should be diluted with acetone and reacted with acetic acid and zinc dust. When dilutions are made, add about 3 mL of deionized water per each 100 mL of total volume, to ensure that the reaction proceeds at a rapid rate. Develop the color with 5.0 mL of the diluted extract, starting at Sec. 11.2.5.4. Transfer to a 25-mL cuvette and measure the absorbance at 507 nm. Record the absorbance.

11.3 Calculations

11.3.1 If using the commercial testing product, calculate the concentration of RDX and HMX in the sample by following the manufacturer's instructions.

11.3.2 If using the generic procedure, calculate the concentration of RDX and HMX in the sample using the equation below:

$$\text{Soil concentration (mg/kg)} = \frac{(A_s - A_b) \times DF}{CF_d}$$

where:

A_s = Absorbance of sample
A_b = Absorbance of the instrument blank
DF = Dilution factor, use a value of 1 unless the calibration curve is exceeded and a dilution is needed.
CF_d = Daily single-point calibration factor determined at the beginning of each day

11.3.3 Whichever procedure is used, note in the data report whether the data are calculated on a dry- or wet-weight basis, depending on whether the soil samples were dried prior to extraction or extracted as received.

11.3.4 The analyst should keep in mind that the results may reflect a mixture of nitramines and/or organonitrate esters (see Sec. 4.0). Because of the possibility that compounds in addition to the target analytes are reacting to form the color, it is recommended that at least 5% of the samples from sites with no historical data be analyzed by HPLC to confirm the explosives that are present.

11.3.5 When the concentration of a sample exceeds an absorbance of 0.7, the sample extract should be diluted and reanalyzed. Another aliquot of the extract is diluted with solvent and taken through the reaction steps and the absorbance read and recorded.

12.0 DATA ANALYSIS AND CALCULATIONS

See Sec. 11.3 for information on data analysis and calculations.

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. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 In the case of this method (which may be used in either the field or the laboratory), any test kits used must be able to meet the performance specifications for the intended application. However, required performance criteria for a particular testing product may be included in the manufacturer's instructions.

13.3 Tables 2 and 3 compare performance data of a trained operator versus four untrained operators performing the RDX analysis using the commercial testing product. In each case, the data represent replicate analysis of a blank and also of a soil sample spiked with 10 mg/kg of RDX. The mean recoveries for both the trained and untrained operators are almost identical. However, the precision data for the trained operator are tighter, which would be expected. The data demonstrate that the method is quite rugged and the analysis may be performed by personnel with very limited experience. These data are taken from Reference 3 and are provided for guidance purposes only.

13.4 The generic procedure described in Sec. 11.2 was applied to a series of soil samples whose RDX concentrations were also determined by HPLC (Method 8330). The soil samples were taken from a site contaminated with RDX. These results are provided in Table 4. A high degree of correlation was observed between the HPLC method and the on-site method. These data are taken from Reference 1 and are provided for guidance purposes only.

13.5 Table 5 compares HPLC data using Method 8330 with data from the two screening procedures (the commercial testing product and the generic procedure) described in this method. The soil samples were taken from a site contaminated with a mixture of RDX and HMX. The data were randomly selected from a database representing 149 samples, and are taken from Reference 5. The results for both the commercial testing product and the generic procedure were compared to the HPLC results using a percent difference (%D) calculation that assumes that the HPLC results are the "true value." Because both screening procedures respond to both RDX and HMX, the %D was calculated using the sum of the HPLC results for these two compounds. The negative %D values indicate that the screening method results were lower than the HPLC results. In addition, because the HMX response in the screening procedures is about one-third that of the RDX response, the %D values for the screening procedures were also calculated using the sum of the HPLC RDX result and one-third of the HPLC HMX result as the true value. These data are provided for guidance purposes only.

13.6 Table 6 provides a comparison of HMX soil data generated by utilizing the commercial testing product versus HPLC analysis of either the same acetone extract or a separate acetonitrile extract prepared as outlined in Method 8330. Based on a short extraction kinetic study with the initial samples collected, a 30-min extraction on a vortex mixer was needed rather than the short 3-min shake procedure described in the commercial testing product. The acetone extract was diluted 1:5 with reagent water prior to HPLC analysis utilizing an LC-CN column. A reversed-phase C-18 column was used for HPLC analysis by Method 8330. The soil samples were collected one week following firing at an anti-tank weapon firing range which has been routinely used for the past 20 years. The anti-tank missiles contained octol, which is a mixture of 70% HMX and 30% TNT. These data are taken from Reference 6 and 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 operations. 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.

14.3 This procedure generally conforms with EPA's pollution prevention initiatives, in that it may be used to minimize the number of sample aliquots collected at a site and shipped to a laboratory, thereby reducing the need to dispose of sample materials following laboratory analysis.

14.4 Analysis for RDX and HMX using the colorimetric screening procedures conforms with EPA's pollution prevention goals. The method uses only 50 mL of acetone per sample when performed by the kit procedure or 100 mL per sample when performed by the generic procedure.

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.

Field waste management procedures must also be consistent with Federal, State and local regulations.

16.0 REFERENCES

1. M. E. Walsh and T. F. Jenkins, "Development of a Field Screening Method for RDX in Soil," US Army Cold Regions Research and Engineering Laboratory, Special Report 91-7, Hanover, New Hampshire 03755, 1991.

2. T. F. Jenkins, M. E. Walsh, P. W. Schumacher and P. G. Thorne, "Development of Colorimetric Field Screening Methods for Munitions Compounds in Soil," *Society of Photo-Optical Instrumentation Engineers*, 2504, 324 - 333, 1995.

3. RDX Soil Test System Users Guide, EnSys, Inc., 1996.

4. S. P. Arrowood, P. P. McDonald and J. P. Mapes, "RDX Soil Test Kit Validation Results," EnSys, Inc., March, 1993.

5. "Onsite Analytical Technologies Umatilla Army Depot," USEPA Project No. 71370, Prepared by Black and Veatch Special Projects Corporation for USEPA Region 10, Draft May, 1997.

6. T. F. Jenkins, M. E. Walsh, P. G. Thorne, S. Thiboutot, G. Ampleman, T. A. Ranney and C. L. Grant, "Assessment of Sampling Error Associated with Collection and Analysis of Soil Samples at a Firing Range Contaminated with HMX," US Army Cold Regions Research and Engineering Laboratory, Special Report 97-22, Hanover, New Hampshire 03755, September, 1997.

17.0 TABLES, DIAGRAMS, FLOW CHARTS AND VALIDATION DATA

The following pages contain the tables referenced by this method.

TABLE 1

EXAMPLE PREPARATION OF CALIBRATION SOLUTIONS
FOR THE GENERIC PROCEDURE

Solution	Vol. of Working Std. (mL)	Vol. of Acetone Added (mL)	Vol. of Distilled Water Added (mL)	RDX Conc. In Soln.[1] (mg/L)	RDX Soil Conc.[2] (mg/kg)	HMX Conc. In Soln.[1] (mg/L)	HMX Soil Conc.[2] (mg/kg)
A	0	100	3	0	0	0	0
B	0.5	99.5	3	0.2	1	0.6	3
C	1	99	3	0.4	2	1.2	6
D	2	98	3	0.8	4	2.4	12
E	5	95	3	2	10	6	30
F	10	90	3	4	20	12	60

[1] All field soils will contain water of an unknown quantity, and all calculations will ignore this small volume contribution.

[2] This concentration is the comparable soil RDX or HMX concentration if 20 g of soil is extracted with 100 mL of acetone. The concentration is based on the wet weight of soil.

These data are provided for guidance purposes only.

TABLE 2

EXAMPLE RDX SOIL TEST VALIDATION DATA GENERATED BY TRAINED OPERATORS USING THE COMMERCIAL TESTING PRODUCT

Mean Optical Density of the Blank	Mean Optical Density of a Sample Containing 10 ppm of RDX	%RSD at 10 ppm RDX
0.028	0.226	4.0

Data are taken from Reference 3.
These data are provided for guidance purposes only.

TABLE 3

EXAMPLE RDX SOIL TEST VALIDATION DATA GENERATED BY UNTRAINED OPERATORS USING THE COMMERCIAL TESTING PRODUCT

Operator No.	Mean Optical Density of the Blank	Mean Optical Density of a Sample Containing 10 ppm of RDX	%RSD at 10 ppm RDX
1	0.024	0.208	5.9%
2	0.025	0.242	8.5%
3	0.028	0.208	3.4%
4	0.029	0.234	14.9%
Mean ± 2SD	0.026 ± 0.004	0.224 ± 0.025	11.2%
Range	0.018 - 0.034	0.174 - 0.274	

Data are taken from Reference 3.

The mean of the standard signals for the untrained operators is equivalent to 9.3 ppm, with a range of 7.1 to 11.6 ppm. The RSD of all the data from the four operators is 11.6%.
These data are provided for guidance purposes only.

TABLE 4

EXAMPLE COMPARISON OF CONCENTRATION ESTIMATES FOR RDX USING ON-SITE AND FIXED LABORATORY METHODS

Sample No.	Generic Colorimetric Method (mg/kg)	HPLC Method (mg/kg)
1	0.08	0.07
2	1.4	2.27
3	3.53	4.16
4	4.86	5.3
5	4.89	7.61
6	202	273
7	17.9	17.2
8	53.6	48.7
9	755	577
10	1680	1880
11	7730	5930

Data are taken from Reference1 and calculated on a wet weight basis.

The acetone extract generated by the generic on-site method was diluted 1:3 v/v with water and analyzed using an LC-CN column eluted with 1:1 v/v methanol-water. The HPLC procedure employed Method 8330, using the LC-CN column as the primary column because the acetone extraction solvent interferes with RDX when using the recommended C-18 primary column.

These data are provided for guidance purposes only.

TABLE 5

EXAMPLE COMPARISON OF TWO ON-SITE METHODS FOR RDX AND RELATED COMPOUNDS VERSUS METHOD 8330 (HPLC) USING SELECTED DATA FROM A STUDY AT THE UMATILLA ARMY DEPOT, HERMISTON, OREGON

	HPLC Result (mg/kg)			Commercial Testing Product			Generic Procedure		
Sample ID	RDX	HMX	RDX + HMX	Result (mg/kg)	%D	Adjusted %D	Result (mg/kg)	%D	Adjusted %D
G28-L1	0.79	0.59	1.38	0.5	-63.8	-49.3	1.2	-13	21.6
G27-L2	3.5	3.0	6.5	3.0	-53.8	-33.3	5.5	-15	22.2
G20-L5	8.1	0.5	8.6	6 .0	-30.2	-27.4	1.2	-86	-85.5
G21-L4	14	0.5	14.5	10	-31.0	-29.4	7.8	-46	-44.9
G12-L1	24	7.1	31.1	8.0	-74.3	-69.7	10.4	-67	-60.6
G6A-2X	37	5.8	42.8	26	-39.3	-33.2	14.1	-67	-63.8
G15-L	52	5.2	57.2	51	-10.8	-5.1	32.3	-44	-39.9
G2-L1	70	16	86	33	-61.6	-56.2	37.7	-56	-50.0
G16-L3	77	1.2	78.2	94	20.2	21.4	55.8	-29	-27.9
G11-L3	130	3.3	133.3	73	-45.2	-44.3	33.2	-75	-74.7

The data are taken from Reference 5, and were randomly selected from a database representing 149 samples, and are shown in order of increasing concentration of RDX, based on the HPLC results. These data are provided for guidance purposes only.

The results for both the commercial testing product and the generic procedure were compared to the HPLC results using a percent difference (%D) calculation that assumes that the HPLC results are the "true value." Because both screening procedures respond to both RDX and HMX, the %D was calculated using the sum of the HPLC results for these two compounds. The negative %D values indicate that the screening method results were lower than the HPLC results, while positive %D values indicate that the screening results were higher than he HPLC results.

Because the HMX response in the screening procedures is about one-third that of the RDX response, the adjusted %D values were calculated using the sum of the HPLC RDX result and one-third of the HPLC HMX result. The adjusted %D values are generally smaller than the corresponding %D.

TABLE 6

EXAMPLE COMPARISON OF HMX DATA FROM THE COMMERCIAL TESTING PRODUCT AND HPLC ANALYSIS OF SOIL SAMPLES TAKEN FROM AN ANTI-TANK WEAPON FIRING RANGE

Sample No.	Commercial Testing Product Results	HPLC Results of the Testing Product Extract	Results of a Duplicate Sample Analyzed by Method 8330
1	100	111	170
2	16	15.7	11.8
3	183	190	285
4	111	142	135
5	321	328	300
6	324	325	405
7	54	75.2	82
mean	158	169	198

Data are taken from Reference 6. These data are provided for guidance purposes only.

All results are in mg/kg (wet weight) and represent the mean concentration of two sample aliquots.

The commercial testing product method was modified by utilizing a 30-min vortex extraction instead of the standard 3-min shake extraction

The HPLC analysis was performed on the same acetone extract as used for the colorimetric analysis.

The Method 8330 analyses involved the extraction of a second aliquot of each sample using acetonitrile, followed by HPLC analysis on an LC-CN column.