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EPA Federal Facilities Forum Issue

FIELD SAMPLING AND SELECTING ON-SITE ANALYTICAL METHODS FOR EXPLOSIVES IN SOIL

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The Federal Facilities Forum is a group of U.S. Environmental Protection Agency (EPA) scientists and engineers, representing EPA regional offices, committed to the identification and resolution of issues affecting the characterization and remediation of federal facility Superfund and Resource Conservation and Recovery Act (RCRA) sites. Current forum members are identified in the text. The forum members identified a need to provide Remedial Project Managers (RPMs) and other federal, state, and private personnel working on hazardous waste sites with a technical issue paper that identifies screening procedures for characterizing soils contaminated with explosive and propellant compounds. Forum members Scott Marquess and Paul Leonard provided technical guidance and direction in the development of this Issue paper and other Forum members provided comments.

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It is imperative that any persons working on sites believed to be contaminated with explosive residues thoroughly familiarize themselves with the physical and toxic properties of the materials potentially present and to take all measures as may be prudent and/or prescribed by law to protect life, health, and property. This publication is not intended to include discussions of the safety issues associated with sites contaminated with explosive residues. Examples of safety issues to be considered include but are not limited to: explosion hazards, toxicity of secondary explosives, and/or personal protective equipment. Information pertaining to these concerns can be found in Roberts and Hartley (1992) and Yinon (1990). Specifically, this paper is not intended to serve as a guide for sampling and analysis of unexploded ordnance, bulk high explosives, or where secondary explosives concentrations in soil exceed 100,000 mg/kg (10%). **These conditions present a potential detonation hazard, and as such, safety procedures and safety precautions should be identified before initiating site characterization activities in these environments.** Finally, this paper does not address primary explosives or initiating compounds, such as lead azide, lead styphnate, or mercury fulminate, which are extremely unstable and present a substantial safety risk at any concentration.

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PURPOSE AND SCOPE

The purpose of this issue paper is to provide guidance to Remedial Project Managers regarding field sampling and on-site analytical methods for detecting and quantifying secondary explosive compounds in soils (Table 1). The paper also includes a brief discussion of EPA Method 8330 (EPA 1995a), the reference analytical method for the determination of 14 explosives and co-contaminants in soil.

This issue paper is divided into the following major sections: (1) background, (2) an overview of sampling and analysis for explosives in soil, (3) data quality objectives, (4) unique sampling design considerations for explosives, (5) a summary of on-site analytical methods, and (6) a summary of the EPA reference analytical method. While some sections may be used independently, joint use of the field sampling and on-site analytical methods sections is recommended to develop a sampling and analytical approach that achieves project objectives.

Many of the explosives listed in Table 1 are not specific target compounds of screening methods, yet they may be detected by one or more screening methods because of their similar chemical structure. Also listed are the explosive and propellant compounds targeted by high performance liquid chromatography (HPLC) methods including EPA SW-846 Method 8330, the standard method required by EPA regions for laboratory confirmation.

BACKGROUND

Evaluating sites potentially contaminated with explosives is necessary to carry out EPA, U.S. Department of Defense, and U.S. Department of Energy policies on site characterization and remediation under the Superfund, RCRA, Installation Restoration, Base Closure, and Formerly Used Defense Site environmental programs. Facilities that may be contaminated with explosives include, for example, active and former manufacturing plants, ordnance works, Army ammunition plants, Naval ordnance plants, Army depots, Naval ammunition depots, Army and Naval proving grounds, burning grounds, artillery impact ranges, explosive ordnance disposal sites, bombing ranges, firing ranges, and ordnance test and evaluation facilities.

Historical disposal practices from manufacturing, spills, ordnance demilitarization, lagoon disposal of explosives-contaminated wastewater, and open burn/ open detonation (OB/OD) of explosive sludges, waste explosives, excess propellants, and unexploded ordnance often result in soils contamination. Common munitions fillers and their associated secondary explosives include Amatol (ammonium nitrate/TNT), Baratol (barium nitrate/TNT) Cyclonite or Hexogen (RDX), Cyclotols (RDX/TNT), Composition A-3 (RDX), Composition B (TNT/RDX), Composition C-4 (RDX), Explosive D or Yellow D (AP/PA), Octogen (HMX), Octols (HMX/TNT), Pentolite (PETN/TNT), Picratol (AP/TNT), tritonal (TNT), tetrytols (tetryl/TNT), and Torpex (RDX/TNT).

Propellant compounds include DNTs and single base (NC), double base (NC/NG), and triple base (NC/NG/NQ) smokeless powders. In addition, NC is frequently spiked with other compounds (e.g., TNT, DNT, DNB) to increase its explosive properties. AP/PA is used primarily in Naval munitions such as mines, depth charges, and medium to large caliber projectiles. Tetryl is used primarily as a boosting charge, and PETN is used in detonation cord.

A number of munitions facilities have high levels of soil and groundwater contamination, although on-site waste disposal was discontinued 20 to 50 years ago. Under ambient environmental conditions, explosives are highly persistent in soils and groundwater, exhibiting a resistance to naturally occurring volatilization, biodegradation, and hydrolysis. Where biodegradation of TNT occurs, 2-AmDNT and 4-AmDNT are the most commonly identified transformation products. Photochemical decomposition of TNT to TNB occurs in the presence of sunlight and water, with TNB being generally resistant to further photodegradation. TNB is subject to biotransformation to 3,5-dinitroaniline, which has been recommended as an additional target analyte in EPA Method 8330. Picrate is a hydrolysis transformation product of tetryl, and is expected in environmental samples contaminated with tetryl. Site investigations indicate that TNT is the least mobile of the explosives and most frequently occurring soil contamination problem. RDX and HMX are the most mobile explosives and present the largest groundwater contamination problem. TNB, DNTs, and tetryl are of intermediate mobility and frequently occur as co-contaminants in soil and groundwater. Metals are co-contaminants at facilities where munitions compounds were handled, particularly at OB/OD sites. Field analytical procedures for metals, such as x-ray fluorescence, may be useful in screening soils for metals in conjunction with explosives at munitions sites.

Table 1. Analytical Methods for Commonly Occurring Explosives, Propellants, and Impurities/Degradation Products.

Acronym	Compound Name	Field Method	Laboratory Method
		Cs	N
TNT	2,4,6-trinitrotoluene	Cp, Ip	N
TNB	1,3,5-trinitrobenzene	Cs, Is	N
DNB	1,3-dinitrobenzene	Cs	N
2,4-DNT	2,4-dinitrotoluene	Cp, Cs	N
2,6-DNT	2,6-dinitrotoluene	Cs, Is	N
Tetryl	Methyl-2,4,6-trinitrophenylnitramine	Cs	N
2AmDNT	2-amino-4,6-dinitrotoluene		N
4AmDNT	4-amino-2,6-dinitrotoluene	Is	N
NT	Nitrotoluene (3 isomers)		N
NB	Nitrobenzene		N
Nitramines		Cs	N
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine	Cp, Ip	N
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	Cs	N
NQ	Nitroguanidine	Cs	G
Nitrate Esters		Cs	
NC	Nitrocellulose	Cs	*L
NG	Nitroglycerin	Cs	*P
PETN	Pentaerythritol tetranitrate	Cs	*P
Ammonium Picrate/Picric Acid			
AP/PA	Ammonium 2,4,6-trinitrophenoxide/2,4,6-trinitrophenol	Cp, Is	A

Cp = Colorimetric field method, primary target analyte(s).
Cs = Colorimetric field method, secondary target analyte(s).
Ip = Immunoassay field method, primary target analyte(s).
Is = Immunoassay field method, secondary target analyte(s).
N = EPA SW-846, Nitroaromatics and Nitramines by HPLC, Method 8330 (EPA 1995a).
P = PETN and NG (Walsh unpublished CRREL method).
G = Nitroguanidine (Walsh 1989).
L = Nitrocellulose (Walsh unpublished CRREL method).
A = Ammonium Picrate/Picric Acid (Thorne and Jenkins 1995a).

*The performance of a number of field methods have not been assessed utilizing "approved" laboratory methods. It is recommended that verification of the performance of any analytical method be an integral part of a sampling/analysis projects quality assurance program.

The frequency of occurrence of specific explosives in soils was assessed by Walsh et al. (1993), who compiled analytical data on soils collected from 44 Army ammunition plants, arsenals, and depots, and two explosive ordnance disposal sites. Of the 1,155 samples analyzed by EPA Method 8330, a total of 319 samples (28%) contained detectable levels of explosives. The frequency of occurrence and the maximum concentrations detected are shown in Table 2. TNT was the most commonly occurring compound in contaminated samples and was detected in 66% of the contaminated samples and in 80% of the samples if the two explosive ordnance disposal sites are excluded. Overall, either TNT or RDX or both were detected in 72% of the samples containing explosive residues, and 94% if the ordnance sites are excluded. Thus, by screening for TNT and RDX at ammunition plants, arsenals, and depots, 94% of the contaminated areas could be identified (80% if only TNT was determined). This demonstrates the feasibility of screening for one or two compounds or classes of compounds to identify the initial extent of contamination at munitions sites. The two ordnance sites were predominantly contaminated with DNTs, probably from improper detonation of waste propellant. The table also shows that NB and NTs were not detected in these samples; however, NTs are found in waste produced from the manufacture of DNT.

Table 2. Occurrence of Analytes Detected in Soil Contaminated with Explosives.

Compound	% Sample with Analyte Present	Maximum Level (μg/g)
Nitroaromatics		
TNT	66	102,000
TNB	34	1790
DNB	17	61
2,4-DNT	45	318
2,6-DNT	7	4.5
2-AmDNT	17	373
4-AmDNT	7	11
Tetryl	9	1260
Nitramines		
RDX	27	13,900
HMX	12	5700
TNT and/or RDX	72	

Derived from Walsh et al. (1993).

OVERVIEW OF SAMPLING AND ANALYSIS FOR EXPLOSIVES IN SOIL

The environmental characteristics of munitions compounds in soil indicate that they are extremely heterogenous in spatial distribution. Concentrations range from nondetectable levels (< 0.5 ppm) to percent levels (> 10,000 ppm) for samples collected within several feet of each other. In addition, the waste disposal practices at these sites, such as OB/OD, exacerbate the problem and may result in conditions ranging from no soil contamination up to solid "chunks" of bulk secondary explosives, such as TNT or RDX. Secondary explosives concentrations above 10% (> 100,000 ppm) in soil are also of concern from a potential reactivity standpoint and may affect sample and materials handling processes during remediation. An explosives hazard safety analysis is needed for materials handling equipment to prevent initiating forces that could propagate a detonation throughout the soil mass.

Reliance on laboratory analyses only for site characterization may result in a large percentage of the samples (up to 80% depending upon the site) with nondetectable levels. The remaining samples may indicate concentrations within a range of four orders of magnitude. Analyzing a small number of samples at an off-site laboratory may result in inadequate site characterization for estimating soil quantities for remediation and may miss potentially reactive material. Laboratory analytical costs vary depending on the turnaround time required. Typical costs for EPA Method 8330 analysis range from $250 to $350 per sample for 30-day turnaround, $500 to $600 for 7-day turnaround, and approximately $1,000 per sample for 3-day turnaround, if it is available.

Because of the extremely heterogeneous distribution of explosives in soils, on-site analytical methods are a valuable, cost-effective tool to assess the nature and extent of contamination. Because costs per sample are lower, more samples can be analyzed and the availability of near-real-time results permit redesign of the sampling scheme while in the field. On-site screening also facilitates more effective use of off-site laboratories using more robust analytical methods. Even if only on-site methods are

used to determine the presence or absence of contamination (i.e., all positive samples are sent off-site for laboratory analysis), analytical costs can be reduced considerably. Because on-site methods provide near-real-time feedback, the results of screening can be used to focus additional sampling on areas of known contamination, thus possibly saving additional mobilization and sampling efforts. This approach has been successfully used for a Superfund remedial investigation of an OB/OD site (Craig et al. 1993).

During site remediation, such as Superfund remedial actions, data are needed on a near-real-time basis to assess the progress of cleanup. On-site methods can be used during remediation to guide excavation and materials handling activities and to evaluate the need for treatment on incremental quantities of soil (EPA 1992b). Final attainment of soil cleanup levels should be determined by an approved laboratory method, such as EPA Method 8330. This approach was effectively used at a Superfund remedial action for an explosives washout lagoon (Oresik et al. 1994; Markos et al. 1995).

DATA QUALITY OBJECTIVES

The EPA Data Quality Objectives process is designed to facilitate the planning of environmental data collection activities by specifying the intended use of the data (what decision is to be made), the decision criteria (action level), and the tolerable error rates (EPA 1994; ASTM 1996). Integrated use of on-site and laboratory methods for explosives in soil facilitate achieving such objectives as determining the horizontal and vertical extent of contamination, obtaining data to conduct a risk assessment, identifying candidate wastes for treatability studies, identifying the volume of soil to be remediated, determining whether soil presents a potential detonation hazard (reactive according to RCRA regulations), and determining whether remediation activities have met the cleanup criteria.

Environmental data such as rates of occurrence, average concentrations, and coefficients of variation are typically highly variable for contaminants associated with explosive sites. These differences are a function of fate and transport properties, occurrence in different media, and interactions with other chemicals, in addition to use and disposal practices. Information on frequency of occurrence and coefficient of variation determines the number of samples required to adequately characterize exposure pathways and is essential in designing sampling plans. Low frequencies of occurrence and high coefficients of variation, such as with explosives, mean that more samples will be required to characterize the exposure pathways of interest. Sampling variability typically contributes much more to total error than analytical variability (EPA 1990, 1992a). Under these conditions, the major effort should be to reduce sampling variability by taking more samples using less expensive methods (EPA 1992a).

EPA's Guidance for Data Useability in Risk Assessment (EPA 1992a) indicates that on-site methods can produce legally defensible data if appropriate method quality control is available and if documentation is adequate. Field analyses can be used to decrease cost and turnaround time as long as supplemental data are available from an analytical method capable of quantifying multiple explosive analytes (e.g., Method 8330) (EPA 1992a). Significant quality assurance oversight of field analysis is recommended to enable the data to be widely used. The accuracy (correctness of the concentration value and a combination of both systematic error [bias] and random error [precision]) of on-site measurements may not be as high in the field as in fixed laboratories, but the quicker turnaround and the possibility of analyzing a larger number of samples more than compensates for this factor. Remedial project managers, in consultation with chemists and quality assurance personnel, should set accuracy levels for each method and proficiency standards for the on-site analyst.

On-site methods may be useful for analysis of waste treatment residues, such as incineration ash, compost, and bioslurry reactor sludges. However, on-site methods should be evaluated against laboratory methods on a site and matrix-specific basis because of the possibility of matrix interference. Treatability studies are used to evaluate the potential of different treatment technologies to degrade target and intermediate compounds and to evaluate whether cleanup levels may be achieved for site remediation. Treatability study waste for explosives-contaminated soils should be of higher than average concentration to evaluate the effects of heterogeneous concentrations and for potential toxicity effects for processes such as bioremediation.

During remediation of soils contaminated with explosives, monitoring the rate of degradation and determining when treatment criteria have been met are necessary so that residues below cleanup levels can be disposed of and additional soil treated. Soils contaminated with explosives are currently being treated by incineration, composting, and

solidification/stabilization (Noland et al. 1984; Turkeltaub et al. 1989; EPA 1993; Craig and Sisk 1994; Miller and Anderson 1995; Channell et al. 1996). Other biological treatment systems that have been evaluated for treating explosives-contaminated soils include anaerobic bioslurry, aerobic bioslurry, white rot fungus, and land farming (Craig et al. 1995; Sundquist et al. 1995).

UNIQUE SAMPLING DESIGN CONSIDERATIONS FOR EXPLOSIVES

Heterogeneity Problems and Solutions

The heterogeneous distribution of explosives in soil is often alluded to but seldom quantified. The problem is probably considerably greater for explosive residues in soil than most other organic waste. From available Superfund site data, the median coefficient of variation (CV) (standard deviation divided by the mean) for volatiles, extractables, pesticides/polychlorinated biphenyls (PCBs), and tentatively identified compounds in soils ranges from 0.21 to 54% for individual contaminants (EPA 1992b). Data from 10 munitions sites show the median CV for TNT was 284%, and the TNT CV ranged from 127% to 335% for individual sites. Comparable data for RDX are median CV of 137% with a range of 129% to 203%, and the median CVs for 2,4-DNT and AP/PA were 414% and 184% respectively. If the natural variability of the chemicals of potential concern is large (e.g., CV > 30%), the major planning effort should be to collect more environmental samples (EPA 1992b).

Jenkins et al. (1996a, 1996b) recently conducted a study to quantify the short range sampling variability and analytical error of soils contaminated with explosives. Nine locations, three at each of three different facilities, were sampled. At each location, seven core samples were collected from a circle with a radius of 61 cm: one from the center and six equally spaced around the circumference. The individual samples and a composite sample of the seven samples were analyzed in duplicate, on-site, using the EnSys RIS^{c} colorimetric soil test kit for TNT (on-site method) and later by Method 8330 at an off-site laboratory. Results showed extreme variation in concentration in five of the nine locations, with the remaining four locations showing more modest variability. For sites with modest variability, only a small fraction of the total error was because of analytical error, i.e., field sampling error dominated total error. For the locations showing extreme short-range heterogeneity, sampling error overwhelmed analytical error. Contaminant distributions were very site specific, dependant on a number of variables such as waste disposal history, the physical and chemical properties of the specific explosive, and the soil type. The conclusion was that to improve the quality of site characterization data, the major effort should be placed on the use of higher sampling densities and composite sampling strategies to reduce sampling error.

There are several practical approaches to reducing overall error during characterization of soils contaminated with explosives, including increasing the number of samples or sampling density, collecting composite samples, using a stratified sampling design, and reducing within sample heterogeneity. Because explosives have very low volatility, loss of analytes during field preparation of composite samples is not a major concern.

Increasing the Number of Samples - One simple way to improve spatial resolution during characterization is by collecting more samples using a finer sampling grid such as a 5-m grid spacing instead of a 10-m spacing. Though desirable, this approach has been rejected in the past because of the higher sampling and analytical laboratory costs. When inexpensive on-site analytical methods are used, this approach becomes feasible. The slightly lower accuracy associated with on-site methods is more than compensated for by the greater number of samples that can be analyzed and the resultant reduction in total error.

Collection of Composite Samples - The collection of composite samples is another very effective means of reducing sampling error. Samples are always taken to make inferences to a larger volume of material, and a set of composite samples from a heterogeneous population provides a more precise estimate of the mean than a comparable number of discrete samples. This occurs because compositing is a "physical process of averaging" (adequate mixing and subsampling of the composite sample are essential to most compositing strategies). Averages of samples have greater precision than the individual samples. Decisions based on a set of composite samples will, for practical purposes, always provide greater statistical confidence than for a comparable set of individual samples. In the study discussed above by Jenkins et al. (1996a, 1996b), the composite samples were much more representative of each plot than the individual samples that made up the composites. Using a composite sampling strategy, usually allows the total number of samples

analyzed to be reduced which reduces costs while improving characterization. Compositing should be used only when analytical costs are significant. An American Society for Testing and Materials (ASTM) guide was developed on composite sampling and field subsampling (Gagner and Crockett, 1996), (ASTM, 1997).

Stratified Sampling Designs - Stratified sampling may also be effective in reducing field and subsampling errors. Using historical data and site knowledge or results from preliminary on-site methods, it may be possible to identify areas in which contaminant concentrations are expected to be moderately heterogeneous (pond bottom) or extremely heterogeneous (open detonation sites). Different compositing and sampling strategies may be used to characterize different areas that may result in a more efficient characterization.

Another means of stratification is based on particle size. Because explosive residues often exist in a wide range of particle sizes (crystals to chunks), it is possible to sieve samples into various size fractions that may reduce heterogeneity. If large chunks of explosive are present, it may be practical to coarse-sieve a relatively large sample (many kilograms), medium-sieve a portion of those fines, and subsample the fines from medium screening as well. This would yield three samples of different particle size and presumes that heterogeneity increases with coarseness. Each fraction would be analyzed separately but not necessarily by the same method (visual screening of the coarser fractions for chunks of explosive may be possible) and then could be summed to yield the concentration on a weight or area basis. In addition, aqueous disposal of explosive wastewaters such as washout lagoons or spill sites often results in preferential sorption to fine-grained materials, such as fines or clays, particularly for nitroaromatics.

Reducing Within Sample Heterogeneity - The heterogeneity of explosives in soils is frequently observed during the use of on-site analytical methods in which duplicate subsamples are analyzed and differ by more than an order of magnitude. Grant et al. (1993) conducted a holding time study using field-contaminated soils that were air-dried, ground with a mortar and pestle, sieved, subsampled in triplicate, and analyzed using Method 8330. Even with such sample preparation, the results failed to yield satisfactory precision [the relative standard deviations (RSDs) often exceeded 25% compared with RSDs below 3% at two other sites]. Subsampling in the field is much more challenging because complete sample processing is not feasible. However, most screening procedures specify relatively small samples, typically a few grams.

To reduce within-sample heterogeneity, two methods can be employed: either homogenization and extraction or analysis of a larger sample. Unless directed otherwise, an analyst should assume that information representative of the entire contents of the sample container is desired. Therefore, the subsample extracted or directly analyzed should be representative of the container. The smaller the volume of that subsample removed for analysis and extraction, the more homogeneous the entire samples should be before subsampling (e.g., a representative 0.5-g subsample is more difficult to obtain than a 20-g subsample from a 250-g sample). Collecting representative 2-g subsamples from 300 g of soil is difficult and can require considerable sample processing such as drying, grinding, and riffle splitting. Even in the laboratory, as discussed above, obtaining representative subsamples is difficult. An ASTM guide is being developed to help in this regard (Gagner and Crockett 1996). While sample-mixing procedures such as sieving to disaggregate particles, mixing in plastic bags, etc., can and should be used to prepare a sample, extracting a larger sample is perhaps the easiest method of improving representativeness. For this reason, 20 g of soil is extracted for the Cold Regions Research and Engineering Laboratory (CRREL) method, and the same approach may easily be used to improve results with most of the on-site methods shown in Table 3. The major disadvantage of extracting the larger sample is the larger volume of waste solvent and solvent-contaminated soil that needs disposal.

The effectiveness of proper mixing in the field is illustrated in the recent report by Jenkins et al. (1996a, 1996b). Duplicate laboratory analyses of the same samples, including drying, grinding, mixing, and careful subsampling resulted in an RSD of 11%. Because this field-mixing procedure was so effective in homogenizing the sample, the sampling and subsampling procedure is presented here (Jenkins et al. 1996a). Soil cores (0 to 15 cm in length and 5.6 cm in diameter) were collected into plastic resealable bags, and vegetation was removed. The sample of dry soil, a mixture of sand and gravel, was placed into 23-cm aluminum pie pans, the soil was broken up using gloved hands, and large rocks were

Table 3. Comparative Data for Selecting On-Site Analytical Methods for Explosives in Soil[a].

Method/ Kit	Criteria						
	Method Type Analytes and EPA Method No.	**Detection Range and Range Factor**	**Type of Results**	**Samples per Batch**	**Soil Sample Size**	**Sample Preparation & Extraction**	**Analysis Time - Production Rate (one person)**
CRREL	Colorimetric TNT, RDX, 2,4-DNT, Ammonium Picrate /Picric Acid	TNT: 1 to 22 mg/kg (22 X) RDX: 1 to 20 mg/kg (20 X) 2,4-DNT: 2 to 20 mg/kg (10X) AP/PA: 1.3 to 69 mg/kg (53 X)	TNT, RDX: Quantitative 2,4-DNT: Semiquantitative AP/PA: Quantitative	TNT: Batch or single RDX: 6 to 7/batch or single 2,4-DNT & AP/PA: Single or batched	20 g	3 min shaking in 100 mL acetone; settling; filtration.	30 minute extract 6/samples; TNT: 5 minutes/sample; RDX: 30 minutes/6 RDX samples; 25 samples/day for TNT + RDX DNT: 30 minutes/6 samples AP/PA: 15 minutes/sample
EnSys RISC®	Colorimetric TNT: Method 8515 draft RDX: Method 8510 proposed	TNT: 1 to 30 mg/kg (30 X) RDX: 1 to 30 mg/kg (30 X)	Quantitative	Single	10 g	Dry < 10% moisture (optional); 3 min shaking in 50 mL acetone; 5 min settling; filtration.	TNT: 30 to 35 minutes/10 samples in lab; estimated 40 to 45 minutes in field. RDX: 60 minutes/6 samples. Optional drying time not included.
USACE	Colorimetric TNT	6 to 100 mg/kg (17 X)	Quantitative	Single or batched	6 g	1 min shaking in 35 mL methanol; settling; filtration as needed.	10 to 20 samples/day depending on soil characteristics
D TECH™	Immunoassay - ELISA TNT: Method 4050 draft RDX: Method 4051 draft	TNT: 0.5 to 5.0 mg/kg (10 X) RDX: 0.5 to 6.0 mg/kg (12 X)	Semiquantitative (concentration range)	4 (single or batch)	3 mL (~4.5 g)	3 min shaking in 6.5 mL acetone; settle 1 to 10 min.	30 minutes for 1 to 4 samples for TNT or RDX.
Idetek Quantix™	Immunoassay - ELISA Antigen-Antibody TNT	TNT: 0.25 to 100 mg/kg (400 X)	Quantitative	20 to 40 (batch only)	~4.2 g	3 min shaking in 21 mL acetone; settle several minutes.	2.5 to 3.5 hours for 20 to 40 samples. Idetek estimates - 2 hours for up to 40 TNT samples.
EnviroGard™	Immunoassay - ELISA TNT: Plate kit TNT: Soil (tube) kit	Plate kit: 1 to 100 mg/kg (100 X) Tube kit: 0.2 to 15 mg/kg (75 X)	Plate: Quantitative Tube: Semiquantitative (concentration range)	Plate: batch of 8 Tube: batch of 14	2 g	Air dry soil, 2 min shaking in 8 mL acetone; filter.	Plate: 90 minutes for 8 samples Tube: 30 minutes for 14 samples Drying time not included.
Ohmicron RaPID Assay®	Immunoassay - ELISA Magnetic particle/tube kit TNT: Method 4050 proposed	TNT: 0.07 to 5 mg/kg (71 X)	Quantitative	5 to 51 (batch only)	10 g	1 min shaking in 20 mL methanol; settle 5 min; filter	1 hour for 20 extractions; 45 minutes for analysis (51 samples)

[a] Expanded and modified from EPA 1995b

Table 3. Comparative Data for Selecting On-Site Analytical Methods for Explosives in Soil[a] (continued).

Method/ Kit	Criteria			
	Interferences and Cross-reactivities > 1% based on IC50 (see text)	**Recommended QA/QC**	**Storage Conditions and Shelf Life of Kit or Reagents**	**Skill Level**
CRREL	TNT = TNT + TNB + DNB + DNTs + tetryl; - detection limits (ppm); TNB 0.5; DNB < 0.5; 2,4-DNT 0.5; 2,6-DNT 2.1; tetryl 0.9 RDX = RDX + HMX + PETN+ NQ + NC + NG - detection limits (ppm); HMX 2.4; PETN 1; NQ 10; NC 42; NG 9 Soil moisture > 10%, and humics interfere with TNT and RDX; nitrate and nitrite interfere with RDX. 2,4-DNT = 2,4-DNT + 2,6-DNT + TNT + TNB + tetryl; high copper, moisture and humics interfere. AP/PA = relatively free of humic and nitroaromatic interferences.	Blank and calibration standards analyzed daily before and after sample analyses. Blank and spiked soil run daily.	Store at room temperature.	Medium
EnSys RISC®	TNT = TNT + TNB + DNB + DNTs + tetryl; - detection limits (ppm); TNB 0.5; DNB < 0.5; 2,4-DNT 0.5; 2,6-DNT 2.1; tetryl 0.9 RDX = RDX + HMX + PETN + NQ + NC + NG - detection limits (ppm); HMX 2.4; PETN 1; NQ 10; NC 42; NG 9 Soil moisture > 10%, and humics interfere with TNT and RDX; nitrate and nitrite interfere with RDX.	Method and soil blanks and a control sample daily, one duplicate/20 samples. Some positive field results (1:10) should be confirmed.	Store at room temperature. Shelf life: TNT = 2 to 24 months at 27°C RDX = 2 to 12 months at 27°C	TNT: Low RDX: Medium
USACE	TNB interferes by raising minimum detection limit.	Blank soil sample, and calibration standard prepared from clean site soil.	Store at room temperature	Medium
D TECH™	Cross reactivity: TNT: tetryl = 35%; TNB = 23%; 2AmDNT = 11%; 2,4-DNT = 4%; AP/PA unknown but ~100% at lower limit of detection RDX: HMX = 3%	Samples testing positive should be confirmed using standard methods.	Store at room temperature or refrigerate; do not freeze or exceed 37°C for prolonged period. Shelf life 9 months at room temperature	Low
Idetek Quantix™	Cross reactivity: TNB = 47%; tetryl = 6.5%; 2,4-DNT = 2%; 4AmDNT = 2%	Duplicate extractions 1 in 10 replicate 2 sample wells/extract	Refrigerate 2 to 8°C, do not freeze or exceed 37°C. Shelf life 9 to 12 months. Avoid direct light.	Medium-high, initial training recommended
EnviroGard™	Cross reactivity: Plate: 4-AmDNT = 41%; 2,6-DNT = 41%; TNB = 7%; 2,4-DNT = 2% Tube: 2,6-DNT = 20%; 4AmDNT = 17%; TNB = 3%; 2,4-DNT = 2%	Plate: Samples run in duplicate.	Store 4 to 8°C; do not freeze or exceed 37°C. Do not expose substrate to direct sunlight. Shelf life: Plate 3 to 14 months. Tube 3 to 6 months.	Plate: Medium-high Tube: Medium
Ohmicron RaPID Assay®	Cross reactivity: TNB = 65%; 2,4-Dinitroaniline = 6%; tetryl = 5%; 2,4-DNT = 4%; 2AmDNT = 3%; DNB = 2%	Duplicate standard curves; positive control sample supplied. Positive results requiring action may need confirmation by another method.	Refrigerate reagents 2 to 8°C. Do not freeze. Shelf life 3 to 12 months.	Medium-high, initial training recommended

[a] Expanded and modified from EPA 1995b

Table 3. Comparative Data for Selecting On-Site Analytical Methods for Explosives in Soil[a] (continued).

Method/ Kit	Criteria					
	Training Availability	Costs (not including labor)	Comparisons to Method 8330 References	Other References	Developer Information	Additional Considerations
CRREL	Free video for TNT and RDX, see text for address. None available for 2,4-DNT, AP/PA.	$15/sample plus $1,500 for Hach spectrometer.	Brouillard et al. 1993; EPA 1993, 1995a (Method 8515), 1995b; Jenkins 1990; Jenkins and Walsh 1992; Markos et al. 1995; Lang et al. 1990; Walsh and Jenkins 1991; Jenkins et al. 1996a; Jenkins and Walsh 1991, 1992; Thorne and Jenkins 1995a	Jenkins et al. 1995; Thorne and Jenkins 1995b	Dr. Thomas F. Jenkins CRREL 72 Lyme Road Hanover, NH 03755-1290 (603) 646-4385	Large work area (2 large desks); requires the most setup time; possible TNB interference, no electricity or refrigeration required; deionized water required; must assemble materials; glassware must be rinsed between analyses; larger volume of acetone waste, color indicative of compounds.
EnSys RISC®	Training available. Applicable video on CRREL method available, address in text.	$21/sample for TNT, $25/sample for RDX plus $160/day or $430/wk for lab station. Lab station cost = $1,950	EPA 1995a (Method 8515); EPA 1995b; IT 1995; Jenkins et al. 1996a, 1996b; Markos et al. 1995; Myers et al. 1994.		Strategic Diagnostics, Inc. 375 Pheasant Run Newtown, PA 18940 (800) 544-8881	Large work area (desk size) power supply required to charge Hach spectrometer; possible TNB interference; color indication of other compounds; requires acetone and deionized water; cuvettes must be rinsed between analyses. Nitrate and nitrate interferences with RDX kit can be corrected using alumin-a-cartridges from EnSys.
USACE	None available.	$4/sample or $5/sample if filtered plus $1,500 for Hach spectrometer	IT 1995; Medary 1992		Dr. Richard Medary U.S. Army Corps of Eng. 601 E. 12th Street Kansas City, MO 64106 (816) 426-7882	Large work area (2 large desks); requires the most setup time; possible TNB interference; no electricity or refrigeration required; must assemble materials; glassware must be rinsed between analyses.
D TECH™	2 to 4 hours free on-site training.	$30/sample for TNT or RDX plus $300 for DTECHTOR (optional)	EPA 1995a (Methods 4050 and 4051); EPA 1995b; Haas and Simmons 1995; Markos et al. 1995; Myers et al. 1994; Teaney and Hudak 1994	Teaney et al. 1993. Calif. EPA 1996a and 1996b	Strategic Diagnostics, Inc. 375 Pheasant Run Newtown, PA 18940 (800) 544-8881	Small working area; few setup requirements; no electricity or refrigeration required; temperature dependent development time (effect can be reduced by changing DTECHTOR setting); significant amount of packing; relatively narrow range; no check on test; easy to transport or carry; kits can be customized. Out-or range reruns require use of another kit.
Idetek Quantix™	1 day free on-site training.	$21/sample for TNT plus $5,880 for lab station or $500/month rental.	EPA 1995b; Haas and Simmons 1995; Markos et al. 1995		Idetek, Inc. 1245 Reamwood Ave. Sunnyvale, CA 94089 (800) 433-8351	Large work area (desk); requires setup time, electricity, refrigeration and deionized water; requires careful washing of microwells; replicate run for each sample, average of the two is the result; less temperature dependent. Out of range reruns require use of another kit.
Enviro-Gard™	Free training available.	Plate: $17/sample plus $4129 for equip. & small supplies. Tube: $20/sample plus $2409 for equip. & small supplies.	Haas and Simmons 1995	Calif. EPA 1996c	Strategic Diagnostics, Inc. 375 Pheasant Run Newtown, PA 18940 (800) 544-8881	Large work area (desk size); requires setup time, refrigeration and power; acetone not supplied. Out-of-range reruns require use of another kit.
Ohmicron RaPID Assayer®	4 hours free on-site training.	$13 to $20/sample plus $5,500 for equip. (purchase) or $800 for first month, $400 each additional month (rental).	EPA 1995b; Haas and Simmons 1995; Markos et al. 1995; Rubio et al. 1996	Calif. EPA 1996d	Strategic Diagnostics, Inc. 375 Pheasant Run Newtown, PA 18940 (800) 544-8881	Large work area (desk); requires setup time, electricity and refrigeration; less temperature dependent; low detection limit; all reagents supplied; reagents and kit need refrigeration. Out-of-range reruns require use of another kit.

[a] Expanded and modified from EPA 1995b

removed (sieving may work well too). A second pie pan was used to cover the sample, which was then shaken and swirled vigorously to disperse and homogenize the soil. The sample was then coned and quartered, and 5 g subsamples were removed from each quarter and composited to form the 20-g sample for analysis. Splits of the same sample were obtained by remixing the soil and repeating the coning and quartering.

Wilson (1992) studied sample preparation procedures for homogenizing compost prior to analysis for explosives. Wilson (1992) method involves macerating air-dried compost using a No. 4 Wiley mill followed by sample splitting using a Jones-type riffle splitter. The improved method decreased the RSD from more than 200% to 3% for TNT analyses.

Sample Holding Times and Preservation Procedures

The EPA-specified holding time for nitroaromatic compounds in soil is 7 days until extraction and extracts must be analyzed within the following 40 days (EPA 1995a). The specified sample preservation procedure is cooling to 4°C. This criterion was based on professional judgment rather than experimental data.

Two significant holding time studies have been conducted on explosives (Maskarinec et al. 1991; Grant et al. 1993, 1995). Based on spiking clean soils with explosives in acetonitrile, Maskarinec recommended the following holding times and conditions: TNT—immediate freezing and 233 days at -20°C; DNT—107 days at 4°C; RDX—107 days at 4°C; and HMX—52 days at 4°C. Grant spiked soils with explosives dissolved in water to eliminate any acetonitrile effects and also used a field-contaminated soil. The results on spiked soils showed that RDX and HMX are stable for at least 8 weeks when refrigerated (2°C) or frozen (-15°C) but that significant degradation of TNT and TNB degradation can occur within 2 hours without preservation. Freezing provides adequate preservation of spiked 2,4-DNT for 8 weeks or longer. The results on field-contaminated soils did not show the rapid degradation of TNT and TNB that was observed in the spiked soils, and refrigeration appeared satisfactory. Presumably, the explosives still present in the field soil after many years of exposure are less biologically available than in the spiked soils.

Another study (Bauer et al. 1990) has shown that explosives in spiked, air-dried soils are stable for a 62-day period under refrigeration. Data from the Grant et al. (1993) study indicate that air drying of field-contaminated soils may not result in significant losses of explosive contaminants. Explosives in air-dried soils are stable at room temperature if they are kept in the dark.

Acetonitrile extracts of soil samples are expected to be stable for at least 6 months under refrigeration. Acetone extracts also are thought to be stable if the extracts are stored in the dark under refrigeration (acetone enhances photodegradation of explosives).

Explosion Hazards and Shipping Limitations

The Department of Defense Explosive Safety Board approved the two-test protocol (Zero Gap and Deflagration to Detonation Transition tests) in March 1988 for determining the explosive reactivity of explosive-contaminated soil. Tests on TNT and RDX in sands with varied water content showed that soils with 12% or more explosive are susceptible to initiation by flame, and soils containing more than 15% explosives are subject to initiation by shock (EPA 1993). Explosives exist as particles in soil ranging in size from crystals to chunks, which can detonate if initiated. However, if the concentration of explosives is less than 12%, the reaction will not propagate. The water content of the soil has minimal effects on reactivity. The test results apply to total weight percent of secondary explosives such as TNT, RDX, HMX, DNT, TNB, and DNB. The tests do not apply to primary or initiating explosives such as lead azide, lead styphnate, and mercury fulminate. As a conservative limit, the EPA Regions and the U.S. Army Environmental Center consider soils containing more than 10% secondary explosives, on a dry weight basis, to be susceptible to initiation and propagation (EPA 1993). If chemical analyses indicate that a sample is below 10% explosives by dry weight, that sample is considered to be nonreactive. In most cases, this eliminates the requirement to conduct the expensive two-test reactivity protocol.

In sampling to determine whether an explosion hazard exists, a biased sampling approach must be adopted (Sisk 1992). Soils suspected of having high concentrations of explosives should be grab-sampled and analyzed to determine whether the level of explosives exceeds 10%. Samples to be shipped for off-site analysis must be subsampled

and analyzed on-site. Explosive residues are usually concentrated in the top 5 to 10 cm of soil; therefore, deep samples must not be collected, blended, and analyzed to determine reactivity. Vertical compositing of surficial soils with high levels of explosives with deeper, relatively clean material provides a false indication of reactivity. Soils containing explosive residues over the 10% level can, using proper precautions, be blended with cleaner material to reduce the reactivity hazard and permit shipment to an off-site laboratory. The dilution factor must be provided with the sample. If analytical results indicate that explosives are present at a concentration of 10% or greater, the samples must be shipped to an explosives-capable laboratory for analysis. The samples must be packaged and shipped in accordance with applicable Department of Transportation and EPA regulations for reactive hazardous waste and Class A explosives (AEC 1994).

In addition to the above information, the Army Environmental Center requires certain minimum safety precautions, as summarized below, for field sampling work at sites with unknown or greater than 10% by weight of secondary explosives contamination (AEC 1994). An extensive records search and historical documentation review must be conducted regarding the contaminated area to identify the specific explosives present, determine how the area became contaminated, estimate the extent of contamination, and determine the period of use. Personnel responsible for taking, packaging, shipping, and analyzing samples must be knowledgeable and experienced in working with explosives. Soil samples must be taken using nonsparking tools, and wetting the sampling area with water may be necessary. If plastic equipment is used, it must be conductive and grounded. Sample containers must be chemically compatible with the specific explosive, and screw tops are prohibited. Samples are to be field screened for explosives if possible. Sufficient soil samples must be collected to characterize the site in a three-dimensional basis in terms of percent secondary explosives contamination with particular attention paid to identifying hot spots, chunks of explosives, layers of explosives, discolorations of the soil, etc.

In screening samples for reactivity, it should be remembered that most screening procedures test for only one analyte or class of analyte. Without other supporting knowledge, concluding that a soil is not reactive based upon just one analysis could be dangerous. For assessing reactivity when multiple compounds are present at high levels, the CRREL

and EnSys RISc colorimetric methods for TNT and RDX are more appropriate than immunoassay test kits because colorimetric tests detect a broader range of explosive analytes. Some conservatism in evaluating potential reactivity using colorimetric methods is appropriate. For example, Jenkins et al. (1996c) recommended using a limit of 7% explosives for conservatively estimating the lower limit of potential reactivity. High levels of explosives in soils may result in a low bias for on-site methods because of low extraction efficiencies. Colorimetric tests of chemical composition are used only to estimate potential reactivity. There are no on-site methods available to actually determine explosive reactivity. Explosive reactivity is a determination made from validated laboratory analyses.

PROCEDURES FOR STATISTICALLY COMPARING ON-SITE AND REFERENCE ANALYTICAL METHODS

When on-site methods are used, their performance needs to be evaluated and this is commonly done by analyzing splits of some soil samples by both the on-site method and a reference method (commonly Method 8330). The performance of the on-site method is then statistically compared to the reference method using a variety of methods, depending upon the objective and the characteristics of the data. In most cases, measures of precision and bias are determined. Precision refers to the agreement among a set of replicate measurements and is commonly reported as the RSD (standard deviation divided by the mean and expressed as a percent), the coefficient of variation (standard deviation divided by the mean), or the relative percent difference. Bias refers to systematic deviation from the true value.

The following discussion of statistical methods applies to comparisons of analytical results based on paired sample data, e.g., soil samples are analyzed by both an on-site method and a reference method, or soil extracts are analyzed by two different on-site methods. Care must be taken in interpreting the result. For example, if subsamples of a jar of soil (splits) are analyzed by an on-site and reference method, the differences detected may be caused by subsampling error (sample was not homogeneous and the splits actually contained different concentrations of explosives), extraction efficiency (shaking with acetone versus ultrasonication with acetonitrile) rather than the analytical methods which may also produce different results. However, if a group of acetone extracts are analyzed by two different on-site methods, the subsampling and extraction errors are minimized and any significant differences should be from the analytical methods.

Precision and Bias Tests for Measurements of Relatively Homogenous Material - When multiple splits of well-homogenized soil samples are analyzed using different analytical methods, statistical procedures described in Grubbs (1973), Blackwood and Bradley (1991), and Christensen and Blackwood (1993) may be used compare the precision and bias of the methods. Grubbs (1973) describes a statistical approach appropriate for comparing the precision of two methods that takes into account the high correlation between the measurements from each method. An advantage of Grubbs' approach is that it provides unbiased estimates of each method's precision by partitioning the variance of the measurement results into its component parts (e.g., variance caused by subsampling and by the analytical method). Blackwood and Bradley (1991) extend Grubbs' approach to a simultaneous test for equal precision and bias of two methods. Christensen and Blackwood (1993) provide similar tests for evaluating more than two methods.

For comparisons involving bias alone, t-tests or analysis of variance may be performed. For comparing two methods, paired t-tests are appropriate for assessing relative bias (assuming normality of the data, otherwise data transformations to achieve normality must be applied, or nonparametric tests used). A paired t-test can be used to test whether the concentration as determined by an on-site method is significantly different from Method 8330 or any other reference method. For comparing multiple methods, a randomized complete block analysis of variance can be used, where the methods are the treatments and each set of split samples constitutes a block.

These tests are best applied when the concentrations of explosives are all of approximately the same magnitude. As the variability in the sample concentration increases, the capability of these tests for detecting differences in precision or bias decreases. The variability in the

true quantities in the samples is of concern, and high variability in sample results caused by poor precision rather than variability in the true concentration is well handled by these methods.

Precision and Bias Tests for Measurements over Large Value Ranges - When the concentrations of explosives cover a large range of values, regression methods for assessing precision and accuracy become appropriate. Regression analysis is useful because it allows characterization of nonconstant precision and bias effects and because the analysis used to obtain prediction intervals for new measurements (e.g., the results of an on-site method can be used to predict the concentration if the samples were analyzed by a reference method).

In a regression analysis, the less precise on-site method is generally treated as the dependent variable and the more precise reference analytical method (e.g., SW-846 Method 8330) as the independent variable. To the extent that the relationship is linear and the slope differs from a value of 1.0, there is an indication of a constant relative bias in the on-site method (i.e., the two methods differ by a fixed percentage). Bias should be expected if on-site methods based on wet-weight contaminant levels are compared to laboratory methods based on the dry weight of soil samples. Similarly, an intercept value significantly different from zero indicates a constant absolute bias (i.e., the two methods differ by a fixed absolute quantity). There, may of course be both fixed and relative bias components present.

When uncertainty is associated with the concentration of an explosive as measured by the reference method, standard least squares regression analysis can produce misleading results. Standard least squares regression assumes that the independent variable values are known exactly as in standard reference material. When the on-site method results contain appreciable error compared to the reference method, regression and variability estimates are biased. This is known as an errors-in-variables problem.

Because of the errors-in-variables problem, the slope coefficient in the regression of the on-site data on the reference data will generally be biased low. Hence a standard regression test to determine whether the slope is significantly different from 1 can reject the null hypothesis even when there is in fact no difference in the true bias of the two methods. A similar argument applies to tests of the intercept value being equal to zero.

To perform a proper errors-in-variables regression requires consideration of the measurement errors in both variables. The appropriate methods are outlined in Mandel (1984). These methods require estimating the ratio of the random error variance for the on-site method to that of the reference analytical method. With split sample data, suitable estimates of these ratios may generally be obtained by using variance estimates from Grubbs' test or the related tests mentioned above.

If the variance ratio is not constant over the range under study, more complicated models than those analyzed in Mandel (1984) must be employed. Alternatively, transformations of the data might stabilize the variance ratio. Note that it is the variance ratio, not the individual variances, that must remain constant. The ratio of variances for two methods with nonconstant absolute variances but constant relative variances will still have a constant variance ratio.

Two other caveats about the use of regression techniques also are appropriate. First, standard regression methods produce bias regression parameters estimation and may produce misleading uncertainty intervals. Similarly, the interpretation of R-squared values also is affected. Second, performing regressions on data sets in which samples with concentrations below the detection limit (for one or both methods) have been eliminated may also result in biased regression estimates, no matter which regression analysis method is used.

Comparison to Regulatory Thresholds, Action Limits, etc. - When the purpose of sampling is to make a decision based on comparison of results to a specific value such as an action level for cleanup, on-site and reference analytical method results may be compared simply on the basis of how well the two methods agree regarding the decision. The appropriate statistical tests are based on the binomial distribution and include tests of equality of proportions and chi-square tests comparing the sensitivity and specificity (or false positive and false negative rates) of the on-site method relative to the

reference analytical method. Note that any measure of consistency between the two methods is affected by how close the true values in the samples are to the action level. The closer the true values are to the action level, the less the two methods will agree, even if they are of equal accuracy. For example, if the action level is 30 μg/g and most samples have levels of above 1000 μg/g, the agreement between the on-site method and reference should be very good. If, however, the concentration in most samples is 5 to 100 μg/g , the two methods will be much more likely to disagree. This must be kept in mind when interpreting results, especially when comparing across different studies that may have collected samples at considerably different analyte levels.

SUMMARY OF ON-SITE ANALYTICAL METHODS FOR EXPLOSIVES IN SOIL

There is considerable interest in field methods for rapidly and economically determining the presence and concentration of secondary explosives in soil. Such procedures allow much greater flexibility in mapping the extent of contamination, redesigning a sampling plan based on near-real-time data, accruing more detailed characterization for a fixed cost, and guiding continuous remedial efforts. Ideally, screening methods provide high-quality data on a near-real-time basis at low cost and of sufficient quality to meet all intended uses including risk assessments and final site clearances without the need for more rigorous procedures. While the currently available screening procedures may not be ideal (not capable of providing compound specific concentrations of multiple compounds simultaneously), they have proved to be very valuable during the characterization and remediation of numerous sites. Currently, available field methods that have been evaluated against standard analytical methods and demonstrated in the field include colorimetric and immunoassay methods (Table 4). Each method has relative advantages and disadvantages, so that one method may not be optimal for all applications. To assist in the selection of one or more screening methods for various users needs, Table 3 (modified and expanded from EPA 1995b) provides information on on-site test kits for detecting explosives in soil. Selection criteria are discussed in the following sections.

Table 4. Available On-Site Analytical Methods for Explosives in Soil.

Analyte(s)	Type Test	Developer/Test Kit
A. Nitroaromatics	Colorimetric	CRREL[1], Ensys RISC®
1. TNT	Colorimetric	CRREL, Ensys RISC®
	Colorimetric	USACE[2]
	Immunoassay	D TECH™
		Idetek Quantix™
		Ohmicron RaPID Assay®
		EnviroGard™
2. TNB	Colorimetric	CRREL, EnSys RISC®
	Immunoassay	Ohmicron RaPID Assay®
3. DNT	Colorimetric	CRREL, EnSys RISC®
4. Tetryl	Colorimetric	CRREL
B. Nitramines	Colorimetric	CRREL, EnSys RISC®
1. RDX	Colorimetric	CRREL, EnSys RISC®
	Immunoassay	D TECH™
2. HMX	Colorimetric	CRREL, EnSsy RISC®
3. NQ	Colorimetric	CRREL
C. Nitrate Esters	Colorimetric	CRREL
1. NC	Colorimetric	CRREL
2. NG	Colorimetric	CRREL
3. PETN	Colorimetric	CRREL
D. AP/PA	Colorimetric	CRREL

[1]U.S. Army Cold Regions Research and Engineering Laboratory.
[2]U.S. Army Corps of Engineers, Kansas City District.

The two types of currently available on-site methods, colorimetric and immunoassay, are fundamentally quite different. Both methods start with extracting a 2- to 20-g soil sample with 6.5 to 100 mL acetone or methanol for a period of 1 to 3 minutes followed by settling and possibly filtration. The basic procedure in the CRREL and EnSys RISC colorimetric methods for TNT is to add a strong base (KOH) to the acetone extract, which produces the red-colored Janowsky anion. Absorbance is then measured at 540 nanometers (nm) using a spectrophotometer. The TNT concentration is calculated by comparing results to a control sample. The RDX test involves a couple of more steps.

The various immunoassay methods differ considerably in their steps with the D TECH method for TNT being the simplest. In the D TECH kit, antibodies specific for TNT and closely related compounds are linked to solid particles. The TNT molecules in the soil extract are captured by the solid particles and collected on the membrane of a

cup assembly. A color-developing solution is added to the cup assembly and the presence (or absence) of TNT is determined by comparing the solution in the assembly cup to a color card or by using the simple field test meter. The color is inversely proportional to the concentration of TNT.

Method Type, Analytes, and EPA Method Number

The first criteria column in Table 3 lists the type of soil screening method, the analytes it detects, and the EPA SW-846 draft or proposed method number. A commercially available colorimetric kit, EnSys RIS^{c}, is used to determine TNT and RDX in soil. EnSys RIS^{c} is the commercial version of the CRREL method for TNT and RDX. In addition to the CRREL method the U.S. Army Corps of Engineers (USACE) developed a colorimetric method for TNT. The EnSys RIS^{c} and CRREL colorimetric methods can also be used to determine nitroaromatics (TNB, DNB, DNTs, tetryl), nitramines (HMX, and NQ), nitrate esters (NC, NG, and PETN), and AP/PA.

Two companies, Idetek Inc. and Strategic Diagnostics Inc. manufacture commercial enzyme linked immunosorbent assay (ELISA) kits to detect TNT in soil. Idetek, Inc. produces the Quantix kit (both a plate and tube method are available), and Strategic Diagnostics, Inc., offers D TECH, Enviro-Gard, and Ohmicron RaPID Assay. D TECH kits are also available for RDX. Other explosives compounds can sometimes be detected using immunoassay kits because their cross reactivity (see Interferences and Cross Reactivity section). The EnviroGard TNT immunoassay kit was formerly produced by Millipore Corp.

Detection Limits and Range

The lower detection limits of most methods are near or below 1 part per million (ppm). The detection range of a test kit can be important, and a broad range is generally more desirable. The importance of the range depends on the range of concentrations expected in samples, the ability to estimate the approximate concentration from the sample extract, the amount of effort required to dilute and rerun a sample and the sampling and analytical objective. Some test kits have a range factor (upper limit of range ÷ lower limit) of just one order of magnitude (10X), while other methods span two or more orders of magnitude (100 to 400X). Because explosives concentrations in soil may range five orders of magnitude (100,000X), reanalyzing many out-of-range samples may be necessary. The D TECH immunoassay methods require an additional test kit to run each sample dilution. Other immunoassay methods can run dilutions in the same analytical run, but one must prepare the dilutions without knowing whether they are needed. The CRREL, USACE, and EnSys RIS^{c} colorimetric procedures for RDX provide sufficient reagent to allow running several dilutions at no additional cost. For the EnSys RIS^{c} TNT kit, the color developed can simply be diluted and reread in the spectrophotometer. The procedures that the test methods use for samples requiring dilution should be evaluated as part of the site-specific data quality objectives.

The detection range of a kit becomes much less relevant when the objective is to determine whether a soil is above or below a single action limit; the same dilution can be used for all samples. In some cases, changing the range of a kit may be desirable to facilitate decision-making. If a method has a range 1 to 10 ppm and the contamination level of concern is 30 ppm, diluting all samples (using acetone or methanol or as directed by the instructions) by a factor of five would change the test kit range to 5 to 50 ppm and permit decisions to be made without additional dilutions.

Cleanup levels for explosives in soil vary considerably depending upon the site conditions, compound present and their relative concentration, threats to groundwater, results of risk assessments, remedial technology, etc. (EPA 1993). Based on a review of data from many sites, Craig et al. (1995) suggested preliminary remediation goals of 30 ppm for TNT, 50 ppm for RDX, and 5 ppm for 2,4-DNT and 2,6-DNT.

Type of Results

The type of results provided by the various screening methods are quantitative or semiquantitative. The CRREL (TNT, RDX, and AP/PA), EnSys RIS^{c}, USACE, Idetek Quantix, Ohmicron RaPID Assay, and EnviroGard (Plate) kits are quantitative methods, providing a numerical value. The CRREL 2,4-DNT method is considered

semiquantitative and provides a somewhat less accurate numerical value. The D TECH and EnviroGard (Tube) test kits are semiquantitative (concentration range), and indicate that the level of an analyte is within one of several ranges. For example, the D TECH TNT soil kit, without dilution, indicates a concentration within one of the following ranges: < 0.5, 0.5 to 1.5, 1.5 to 2.5, 2.5 to 4.5, 4.5 to 6.0, and > 6.0 ppm.

Samples per Batch

Several of the available test kits are designed to run batches of samples or single samples or both. Using a test kit designed for analyzing a large batch to analyze one or two samples may not be very cost-effective or efficient. In most cases, samples may easily be batched for extraction and processed simultaneously.

Sample Size

The size of the soil sample extracted contributes to the representativeness of a sample. Explosive residues in soil are quite heterogeneously distributed (Jenkins et al. 1996a, 1996b), and as the subsample size actually extracted decreases, heterogeneity increases. While sample preparation procedures such as drying, mixing, sieving, and splitting can reduce within sample heterogeneity, such procedures can be time-consuming. Based on work by Jenkins et al. (1996b), field compositing and homogenization greatly improve sample representativeness. The commercial test kits use 2 to 10 g of soil, while the CRREL methods extract 20 g of soil to improve the representativeness of the results. For some test kits, it is possible to extract a larger sample using solvent and glassware not provided in the kit, and then using the required volume of extract for the analytical steps. The smaller the sample size, the more important is the mixing of the sample before subsampling.

Sample Preparation and Extraction

Soil extractions procedures for most of the screening methods are similar, shaking 2 to 20 g of soil in 6.5 to 100 mL of solvent (acetone or methanol) for 1 to 3 minutes. This may be followed by settling or filtration or both. One test kit (EnviroGard) specifies air drying and for the EnSys RISC colorimetric test kits, drying to less than 10% moisture is optional. For the CRREL methods, samples must contain 2 to 3% water by weight, therefore, water must be added to the extract for very dry soils or incomplete color development will occur, resulting in a false negative.

The solvent extraction times of 1 to 3 minutes used in on-site methods result in incomplete extraction of explosives compared with the 18-hour ultrasonic bath extraction step used in EPA Method 8330. The percent of explosives extracted is sample-specific but is generally higher for high concentration samples, higher for sandy soils, lower for clayey soils, and lower if 1-minute extractions are used relative to 3-minute extractions. For most soils, a 3-minute extraction time is adequate; ratios of 3-minute versus 18-hour extractions of TNT and RDX using acetone or methanol range from 66 to 109% as reported by Jenkins et al. (1996c). Jenkins recommends at least a 3-minute solvent extraction procedure for explosives. When pinpointing concentrations, a short kinetic study should be conducted of the specific soils encountered at a site (Jenkins et al. 1996c). The kinetic study would involve analyzing an aliquot of extract after 3 minutes of shaking, and again after 10, 30, and 60 minutes of standing followed by another 3 minutes of shaking. If the concentration of explosives increased significantly with the longer extraction time, a longer extraction period is needed. Jenkins et al. (1996a) found that 30-minute extraction times worked well for clay soils at the Volunteer Army Ammunition Plant, Chattanooga, Tennessee. Where multiple analytes are of interest in each sample, a common extract may be used for both the colorimetric and immunoassay test methods.

Analysis Time

The analysis time or throughput for the colorimetric and immunoassay procedures ranges from 3 to 11 minutes per sample for batch runs. The EnviroGard kits specify air drying of samples (which would add considerable time), and drying is optional with the EnSys RISC colorimetric kits. Cragin et al. (1985) investigated various procedures for drying soils contaminated with explosives including air, oven, desiccator, and microwave drying. Air and desiccator drying appear to result in only minor losses of explosives. Oven drying of highly contaminated soil (15% TNT) at 105°C for an unspecified period resulted in a 25% loss of

TNT; however, oven drying of less-contaminated samples, for only 1 hour, resulted in little loss of TNT and 30 minutes of drying was estimated to be sufficient for analytical purposes. Microwave drying was not recommended because of spotty heating and drying. In addition, microwave drying should not be used because it may present a safety hazard and such drying degrades thermally unstable explosives in the soil. The effective production rate depends on the number of reruns required because a sample is out of the detection range.

Interferences and Cross-Reactivity

One of the major differences among the field methods is interference for colorimetric methods and cross-reactivity for immunoassay methods. The colorimetric methods for TNT and RDX are broadly class sensitive; that is, they are able to detect the presence of the target analyte but also respond to many other similar compounds (nitroaromatics and nitramines/nitrate esters, respectively). For colorimetric methods, interference is defined as the positive response of the method to secondary target analytes or co-contaminants similar to the primary target analyte. Immunoassay methods are relatively specific for the primary target analytes that they are designed to detect. For immunoassay methods, cross-reactivity is defined as the positive response of the method to secondary target analytes or co-contaminants similar to the primary target analyte. The cross-reactive secondary target analytes for TNT are mainly other nitroaromatics. The cross-reactivity to these compounds varies considerably among the four TNT immunoassay test kits. The immunoassay test kit for RDX is quite specific with only 3% cross-reactivity for HMX.

Depending upon the sampling objectives, broad sensitivity or specificity can be an advantage or disadvantage. If the objective is to determine whether any explosive residues are present in soil, broad sensitivity is an advantage. For the CRREL and the EnSys RISC colorimetric methods for TNT, the color development of the extracts can give the operator an indication of what type of compounds are present in soil, for example, TNT and TNB turn red, DNB turns purple, 2,4-DNT turns blue, 2,6-DNT turns pink and tetryl turns orange. For the CRREL method and the EnSys RISC RDX kit, RDX turns pink as well as HMX, nitroglycerine, PETN, and nitrocellulose. An orange color indicates that both TNT and RDX are present. Another advantage of the broad response of some colorimetric methods is they may be used to detect compounds other than the primary target analyte. For example, the colorimetric RDX methods may be used to screen for HMX when RDX levels are relatively low, and for NQ, NC, NG, and PETN in the absence of RDX and HMX. The USACE colorimetric procedure is more specific to TNT than the CRREL and EnSys RISC colorimetric methods, but has not been as thoroughly evaluated. If a secondary target analyte is present at only low concentrations in a sample, the effect on the analytical result is minimal. If the objective is to determine the concentration of TNT or RDX when relatively high levels of other nitroaromatics and nitramines are present, immunoassay or the USACE methods may be appropriate.

Extremes of temperature, pH and soil water content can interfere with on-site analytical methods. According to the California Military Environmental Coordination Committee, the following physical conditions are generally not recommended for both colorimetric and immunoassay methods, temperatures outside the 4 to 32° C range, pH levels less then 3 or greater than 11, and water content greater than 30% (CMECC 1996). Specific product literature should be consulted for more information.

Colorimetric Methods - For TNT methods, the primary target analyte is TNT, and the secondary target analytes are other nitroaromatics such as TNB, DNB, 2,4-DNT, 2,6-DNT, and tetryl. For RDX methods, the primary target analyte is RDX, and the secondary target analytes are nitramines (HMX and NQ), and nitrate esters (NC, NG, and PETN). If the primary target analyte is the only compound present in soil, the colorimetric methods measure the concentration of that compound. If multiple analytes are present in soil, the field methods measure the primary target analyte plus the secondary target analytes, nitroaromatics for the TNT test kit, and nitramines plus nitrate esters for the RDX test kits. In addition, the response of colorimetric methods to the secondary target analytes is equivalent to that of the primary target analyte, and remain constant throughout the concentration range of the methods, although the observed colors may be different.

If multiple analytes are present in soil, colorimetric field results can be compared directly with EPA Method 8330 results. For example, if a soil sample (as analyzed by Method 8330) contains 100 ppm each of TNT, TNB, RDX, HMX, and tetryl, the CRREL and the EnSys RISC colorimetric methods for TNT would measure ~300 ppm (100 TNT + 100 TNB + 100 tetryl), and the RDX test kit would measure ~200 ppm (100 RDX + 100 HMX). If the sample did not contain tetryl, the TNT test kit would measure ~200 ppm (100 TNT + 100 TNB), and the RDX test kit would still measure ~200 ppm (100 RDX + 100 HMX).

Immunoassay Methods - For TNT kits, the primary target analyte is TNT, and the secondary target analytes are nitroaromatics TNB, DNTs, Am-DNTs, and tetryl. For RDX kit, the primary target analyte is RDX, and there is but little cross-reactivity with HMX (3%). If the primary target analyte is the only compound present in soil, the immunoassay methods measure the concentration of that compound.

If multiple analytes are present in soil, the immunoassay kits measure the primary target analyte plus some percentage of the cross-reactive secondary target analytes. The response of immunoassay kits to the secondary target analytes is not equivalent to that of the primary target analyte. Additionally the response does not remain constant throughout the concentration range of the kits. In addition, different immunoassay kits have different cross-reactivities to secondary target analytes based on the antibodies used to develop each method. Cross-reactivities for immunoassay kits are usually reported at the 50% response level (IC_{50}), typically the midpoint of the concentration range of the kits. Table 5 shows the reported cross-reactivities at IC_{50} for the immunoassay kits. A complete cross-reactivity curve for the entire concentration range should be obtained from the manufacturers for the immunoassay kits being considered. Where multiple analytes exist in soil samples, immunoassay results may not directly compare with EPA Method 8330 results. For example, an immunoassay kit may have cross-reactivities of 23% for TNB and 35% for tetryl for the TNT test kit, and 3% HMX cross-reactivity for the RDX test kit. The following simple example illustrates cross-reactivity but in practice, it is not practical to calculate contaminant concentrations in this manner because of synergistic effects and because cross-reactivity is nonlinear. Using the same sample as the colorimetric example above, if a soil sample (as analyzed by Method 8330) contains 100 ppm each

Table 5. On-Site Analytical Methods for Explosives in Soil, Percent Interference[a] or Cross-Reactivity[b].

Test Method	Nitroaromatics								Nitramines		Other
	TNT	TNB	DNB	2,4-DNT	2,6-DNT	2AmDNT	4AmDNT	Tetryl	RDX	HMX	PETN
TNT											
CRREL	100	100	100	100	100	NC	NC	100	NC	NC	
EnSys RISC®	100	100	100	100	100	NC	NC	100	NC	NC	
USACE	100		NC	NC							
D TECH	100	23		4		11	<1	35	<1	<1	
Idetek Quantix	100	47	1	2		0.5	2	6.5	<1	<1	
EnviroGard: plate tube	100 100	7 3		2 2	41 20	<1 1	41 17	<1 0.3	<1	<1	
Ohmicron RaPID Assay	100	65	2	4	<1	3	1	5	<1	<1	
RDX											
CRREL	NC	NC	NC	NC	NC	NC	NC	NC	100	100	100
EnSys RISC®	NC	NC	NC	NC	NC	NC	NC	NC	100	100	100
D TECH	<1	<1	<1	<1	<1	<1	<1	<1	100	3	<1

[a] Interference for colorimetric methods.
[b] Cross-reactivity for immunoassay methods at 50% response (IC_{50}).
Blank cell = no data.

NC = No color development.

of TNT, TNB, RDX, HMX, and tetryl, the TNT field immunoassay kit would measure ~158 ppm (100 TNT + 23 TNB + 35 tetryl), and the RDX field method would measure ~103 ppm (100 RDX + 3 HMX). If the same sample did not contain tetryl, the TNT test kit would measure ~123 ppm (100 TNT + 23 TNB), and the RDX test kit would still measure ~103 ppm.

Matrix Interferences - Both colorimetric and immunoassay methods may be subject to positive matrix interference from humic substances in soils, which results in yellow extracts. For colorimetric methods, interference may be significant for samples containing less than 10 ppm of the target analyte. Through careful visual analysis prior to colorimetric analysis, these interferences can be observed. Many of the immunoassay methods use a reverse coloration process, and humic matrix interference results in less color development, hence on-site method results are biased high as compared to laboratory results. Nitrate and nitrite, common plant nutrients in soil, are potential interferents with the CRREL and EnSys RIS[c] colorimetric procedures for RDX. An extra processing step may be used to remove these interferents in soils that are rich in organic matter or that may have been recently fertilized.

The performance of field explosives analytical methods on other solid-phase environmental treatment matrices such as incineration ash, biotreatment residues such as compost or sludges from slurry phase bioreactors, cement-based solidification or stabilization material, or granular activated carbon from groundwater treatment systems have not been extensively evaluated and will most likely be subject to matrix interferences or low extraction efficiencies. The performance of field methods on these matrices should be evaluated against laboratory methods on a site-specific basis.

Recommended Quality Assurance/Quality Control

The recommended quality assurance/quality control (QA/QC) procedures vary considerably with the screening procedure. Some test methods do not specify QA/QC procedures and leave to the investigator the determination of the numbers of blanks, duplicates, replicates, and standards that are run. During field application of these methods, it is common to send at least 10 to 20% of the positive samples to an off-site laboratory for analysis by EPA Method 8330, and a smaller fraction of the nondetect samples also may be verified. In some cases, field methods are used to identify samples containing explosive residues. Samples containing explosives are sent for on-site analysis. In any case, the QC samples recommended by the method developer should be used.

While ensuring that field methods perform as intended is essential, requiring laboratory type QC requirements may be inappropriate for on-site analytical methods. Because site characterization efforts may be cost constrained, excess QC samples reduce the number of field samples that can be analyzed. Since sampling error (variability) is typically much greater than analytical error (Jenkins et al. 1996a, 1996b), especially for explosive residues, overall error is more effectively reduced by increasing the number of field as opposed to the number of QC samples. Good sample preparation procedures and correlation of the field methods with the laboratory HPLC method over the concentration range of interest should be the primary performance criteria. Documentation of procedures and results must be emphasized.

During the initial evaluation of on-site and off-site analytical methods, it may be desirable to analyze a variety of QC samples to determine sources of error. The methods can then be modified to minimize error as efficiently as practical. This may involve collection and analysis of composite versus grab samples, duplicates, replicates, splits of samples, splits of extracts, etc. For more complete information on the types and uses of various QC

samples, see A Rational for the Assessment of Errors in the Sampling of Soils (EPA 1990).

Storage Conditions and Shelf Life

Storage conditions and shelf life of immunoassay kits are more critical than colorimetric methods. The reagents for some immunoassay kits should be refrigerated but not frozen or exposed to high temperatures. Their shelf life can vary from 3 months to more than 1 year. Colorimetric reagents can be stored at room temperature. The EnSys RIS^{c} colorimetric kits have shelf lives of at least 2 months and up to 1 or 2 years. Before ordering test kits, it is important to know when they will be used to ensure that they will be used before the expiration date.

Skill Level

The skill level necessary or required to run these tests varies from low to moderate, requiring a few hours to a day of training. The manufacturers of the kits generally provide on-site training. A free training video tape on the CRREL TNT and RDX procedures (which also is useful for the EnSys RIS^{c} colorimetric kits) is available by submitting a written request to Commander U.S. Army Environmental Center, Attn: SFIM-AEC-ETT/Martin H. Stutz, Aberdeen Proving Ground, MD 21010. Training video tapes are also available from some kit suppliers.

Cost

As shown in Table 3, routine sample costs vary by method. The per-sample cost is affected by consumable items and instrument costs to run the method. In figuring costs per sample, it is important to include the costs of reruns for out-of-range analyses. With the EnSys RIS^{c} colorimetric TNT kit, the color-developed extract may be simply diluted and reread with the spectrometer. With all other methods, the original soil extract needs to be reanalyzed, which in the case of immunoassay procedures requires the use of another kit. Colorimetric methods typically have sufficient extra reagents to rerun samples with no increase in cost. It should be noted that the per-sample costs do not include labor hours.

Comparisons to Laboratory Method, SW-846 Method 8330

The objectives of the study or investigation, the site-specific contaminants of concern, the concentration ranges encountered or expected, and their relative concentration ratios affects the selection of a particular on-site method. The accuracy of an on-site method is another selection criteria but care must be used in interpreting accuracy results from comparisons between reference analytical methods and on-site methods.

Colorimetric methods actually measure groups of compounds (i.e., nitroaromatics or nitramines) and immunoassay methods are more compound specific. Therefore the reported accuracy of a method may depend on the mix of explosives in the soil and the reference method data used for the comparison (i.e., data on specific compounds, or total nitroaromatics or nitramines).

The precision and bias of the screening methods are most appropriately assessed by comparison to established laboratory methods such as EPA Method 8330. Methods of comparison that have been used include relative percent difference (RPD), linear regression, correlation, coefficient of determination (R^2), percent false positive and false negative results, analysis of variance, and paired t-tests. It should also be remembered that the contribution of analytical error is generally quite small compared to total error (field error is the major contributor).

Three studies have been conducted comparing the performance of two or more on-site methods with Method 8330. The procedures used in the studies for making the comparisons are given here and a summary of the results of each study follows. EPA (1995b) calculated RPDs (the difference between the field and reference method concentration divided by the mean value and expressed as a percent), established a comparison criterion of ± 50% for RPDs, and determined the frequency with which various methods met that criteria within various sample concentration ranges. EPA (1995b) also calculated regression lines and the R^2. Haas and

Simmons (1995) compared on-site methods using the percentage of false positives and false negatives for determining whether samples were above or below two proposed remediation criteria for TNT in soil, 48 and 64 mg/kg. They also plotted regression data and reported calculated R^2 values. Myers et al. (1994) calculated regression lines with 99% confidence intervals.

While no study has compared all the field methods under the same conditions, the three studies evaluated multiple methods under slightly different field conditions (EPA 1995b; Haas and Simmons 1995, Myers et al. 1994). Summary data from these studies are provided in Table 6. The table includes the intercept and slope of regression lines for TNT and RDX data for two concentration ranges, from the detection limit to 100 mg/kg and from 100 to 1000 mg/kg. Also included are the correlation coefficient (r) and the mean RPD (absolute value of RPDs). The ideal regression line would have a slope of 1 and go through the origin (intercept of 0). The correlation coefficient shows the degree of association between the on-site method and Method 8330 and can range between -1 and +1. For a perfect positive correlation r = 1. The mean RPD closest to 0 shows the greatest agreement with the reference laboratory method. The RPDs presented are for TNT or RDX. The accuracy of colorimetric methods should improve when compared to total nitroaromatics or nitramines because the methods detect numerous related explosives. As the level of nitroaromatics other than TNT increases, the accuracy of the CRREL and EnSys RIS[c] methods should appear to decrease. But when compared to total nitroaromatics, the accuracy should increase. Thus, to attempt to identify the preferred screening method, it is important to determine specifically what analytical information is desired from a screening procedure and the relative concentration of the explosives at a site. Readers should consult the original studies for more details; however, some summary conclusions from the three cited studies follow.

The EPA (1995b) study compared the CRREL, EnSys RIS[c], D TECH, Idetek Quantix, and Ohmicron RaPID Assay methods for TNT. The study concluded that "no single method significantly out-performed other methods" and accuracies for all the on-site methods were comparable. CRREL, EnSys RIS[c], and Ohmicron were more accurate in the greater-than-30-mg/kg TNT ranges, and D TECH was more accurate in the less-than-30-mg/kg range. The same study compared the CRREL, EnSys RIS[c], and D TECH methods for RDX in soil and concluded that they were slightly less accurate than the corresponding TNT methods.

Table 6. Comparison of On-Site Analytical Methods for TNT and RDX to EPA Method 8330.

	MDL < TNT ≤ 100 mg/kg					
Method	**Regression Intercept**	**Regression Slope**	**Correlation Coefficient (r)**	**Mean RPD (absol. value)**	**Number Samples**	**Reference**
CRREL	10	0.84	0.74**	72	86	EPA 1995b
EnSys RIS[c]®	19	0.81	0.45**	90	123	EPA 1995b
D TECH	2.9	0.79	0.76**	63	103	EPA 1995b
Idetek Quantix	13	0.62	0.46**	84	124	EPA 1995b
Ohmicron RaPID Assay	16	1.2	0.51**	97	115	EPA 1995b
D TECH[a]	-17	6.7	0.81**	110	37	Haas & Simmons 1995
one outlier deleted[a]	3.7	2.4	0.91**		36	
EnviroGard plate[a]	13	1.3	0.79**	122	36	Haas & Simmons 1995
EnviroGard tube[a]	6.3	0.99	0.90**	95	21	Haas & Simmons 1995
Idetek Quantix[a]	36	2.1	0.39*	131	37	Haas & Simmons 1995
Ohmicron RaPID Assay[a]	18	1.8	0.83**	127	37	Haas & Simmons 1995

EnSys RIS[c a]	3.8	0.72	0.91**	56	12	Myers et al. 1994
D TECH[a]	5.4	0.94	0.30	88	10/11	Myers et al. 1994
100 < TNT < 1000 mg/kg						
CRREL	-25	1.4	0.67**	33	15	EPA 1995b
EnSys RIS[c]®	50	1.1	0.59**	57	21	EPA 1995b
D TECH	-250	2.2	0.59*	60	17	EPA 1995b
Idetek Quantix	210	0.09	0.30	65	22	EPA 1995b
Ohmicron RaPID Assay	680	0.50	0.12	51	16	EPA 1995b
MDL < RDX ≤ 100 mg/kg						
CRREL	-1.2	0.56	0.89**	74	64	EPA 1995b
EnSys RIS[c]®	6.4	0.57	0.50**	61	114	EPA 1995b
D TECH	2.7	0.20	0.49**	103	94	EPA 1995b
D TECH[a]	-0.35	0.77	0.95**	66	27	Haas & Simmons 1995
100 < RDX < 1000 mg/kg						
EnSys RIS[c]®	-9.9	0.68	0.50**	83	32	EPA 1995b
D TECH	21	0.15	0.49*	127	25	EPA 1995b

[a] Statistics calculated from cited reference.
* Statistically significant at the 95% probability level.
** Statistically significant at the 99% probability level.

Haas and Simmons (1995) evaluated immunoassay kits for TNT (D TECH, EnviroGard Tube and Plate, Idetek Quantix, and Ohmicron RaPID Assay). They concluded that for semiquantitative screening, all kits have the potential to accurately screen soil samples for contamination at risk-based levels (EPA 1993). The study found that compared with HPLC analysis below 1 ppm several of the assays had significant bias. Measurements near the detection limit "are often problematic" and above 1 ppm, the correlation between the immunoassay kits and HPLC was "generally good."

Myers et al. (1994) evaluated and compared the EnSys RISC and D TECH methods for TNT in soil versus EPA Method 8330. The study found that "EnSys demonstrated a good one-to-one linear correlation with RP-HPLC that can be attributed to the procedure for extraction, i.e., a large sample size of dried homogenized soil." For the D TECH kit, comparison was more difficult because of the concentration range type data and because "one-to-one linear correlation with RP-HPLC was poorer." Both methods were susceptible to interferences: "Although both methods showed strong tendencies to cross react with other nitroaromatics, sometimes resulting in false positives, in a sampling of 99 soils, neither method produced a false negative." The study concluded that the EnSys RISC kit was well suited for analyses requiring good quantitative agreement with the standard laboratory method and that the D TECH kit was "better suited for quick, on-site screening in situations where all samples above a certain range will be sent forward to a laboratory for confirmation by the standard method."

Additional Considerations

Other important factors in the selection of an on-site method are the size and type of working area required, the temperature of the working area, the need for electricity and refrigeration, the amount of waste produced, the need to transport solvents, the degree of portability, etc. Immunoassay methods are more sensitive than colorimetric methods to freezing and elevated temperatures, and the ambient temperature affects the speed at which color development takes place on some immunoassay methods. Most tests are best run out of the weather, in a van, field trailer, or nearby building.

Emerging Methods and Other Literature Reviewed

Several other screening procedures exist that have not been included in Table 3 because of the limited information available on published methods or commercial availability.

The Naval Research Laboratory Center for Bio/Molecular Science and Engineering has conducted developmental research on an antibody-based continuous-flow immunosensor for TNT and RDX and a fiber optic biosensor for TNT in water (Whelan et al. 1993; Shriver-Lake et al. 1995). Both methods have been evaluated as quantitative methods for explosives in groundwater at two sites (Craig et al. 1996). These methods reportedly tolerate a certain percentage of acetone, and are currently being evaluated for quantifying soil extracts containing explosives. Research of and instrument development for these methods are continuing.

The U.S. Army has been sponsoring the development of a cone penetrometer capable of detecting explosives *in situ* in soil, at levels determined to be 0.5 ppm in laboratory tests (Adams et al. 1995). Field tests have been conducted in which a probe is hydraulically pushed to depth by a 20-ton truck, samples are pyrolized *in situ*, and a sensor selective to nitrogen oxide is used to detect explosives. Research on this method is continuing.

A very simple spot test (colorimetric) kit can be assembled to detect elevated levels of TNT and RDX (>100 ppm) on filter paper swipes of surfaces and soil. Samples can be analyzed in 1 to 2 minutes at very low cost using the highly portable kit. This nonquantitative test kit was developed at Los Alamos National Laboratory and has been used to screen soil to ensure that explosive contamination does not exceed the 10% levels prior to shipping to an analytical laboratory for analysis (Baits 1991; Haywood et al. 1995; McRea et al. 1995).

A semiquantitative method for identifying explosives using thermal desorption followed by ion mobility spectroscopy has been developed for security applications (Rodacy and Leslie 1992). The ion mobile spectroscopy method has been tested on small quantities of soil samples and is currently being evaluated for soil extracts (Atkinson, Crockett and Jenkins 1997). Research on this method is continuing.

The use of a mobile laboratory screening method for detecting high explosives has been described (Swanson et al. 1996). Ten-gram soil samples are extracted with 10 mL of acetone by shaking for 1 hour, and the extract is filtered. Analysis is by high performance liquid chromatography using a photo-array detector, which takes about 15 minutes per sample and quantifies TNT, HMX, RDX, TNB, tetryl, 1,3-DNB, 2-AmDNT + 4-AmDNT, 2,4-DNT + 2,6-DNT, and all three NTs at detection limits of about 1 ppm.

A thermal desorption/Fourier transform infrared spectroscopy screening technique was under investigation by Argonne National Laboratory for the U.S. Army Environmental Center. The estimated detection limit was about 80 ppm without further modifications to the procedure (Clapper-Gowdy et al. 1992; Clapper et al. 1995), and no further research is being conducted.

Fast determination (100 samples/10 h/person) of explosives in soil (TNT, DNT, and NT) using thermal desorption followed by gas chromatography/mass spectrometry analysis has been reported. While no technical report on screening explosives in soil is available, the approach has been described in the literature for use with other contaminants (McDonald et al. 1994; Abraham, Liu, and Robbat 1993).

Work is under way within CRREL to investigate the use of a simple thin-layer chromatographic method for use as a confirmation test following colorimetric-based procedures. This method can be applied to extracts that test positive for TNT or RDX to discriminate among the several analytes that may be present. Work is also under way using x-ray fluorescence for screening for metals containing primary explosives.

SUMMARY OF THE EPA REFERENCE METHOD FOR EXPLOSIVE COMPOUNDS, METHOD 8330

Properties of Secondary Explosives

TNT and RDX have been the two secondary explosives used to the greatest extent by the U.S. military over the past 70 years. With their manufacturing impurities and environmental transformation products, the two compounds account for a large part of the explosives contamination at active and former U.S. military installations. While all of these explosive compounds can all be classified as semivolatile organic chemicals, their physical and chemical properties require different analytical approaches than normally used for other semivolatiles.

Table 7 presents some of the important physical and chemical properties for TNT and RDX, and some of their commonly encountered manufacturing impurities and environmental transformation products. The unique properties that differentiate these chemicals from other semivolatiles such as PCBs and polynuclear aromatic hydrocarbons (PNAs) are their thermal lability and polarity. Many of these compounds thermally degrade or explode at temperatures below 300°C. Thus, methods based on gas chromatography are not recommended for routine use. In addition, log K_{ow} values range from 0.06 to 2.01 compared with values of 4 to 5 for PCBs and PNAs, indicating that these compounds are quite polar and that normal nonpolar extraction solvents used for other semivolatile organics may not elute successfully. For most routine analyses, environmental soil samples are extracted with polar solvents. The sample extracts are analyzed using reversed-phase high performance liquid chromatography (RP-HPLC), often using SW-846 Method 8330 (EPA 1995a).

Soil Extraction

Extraction of TNT and RDX from soils has been studied in terms of process kinetics and recovery using methanol and acetonitrile with several extraction techniques including Soxhlet, shaking, and ultrasonication (Jenkins and Grant 1987). Acetone, while an excellent solvent for these compounds, was not included in this study because extracts were to be analyzed using RP-HPLC-UV, and acetone absorbs in the ultraviolet region used for detection of the contaminants of interest.

Overall, methanol and acetonitrile were found to be equally good for extraction of TNT, but acetonitrile was clearly superior for RDX. Equilibration of the soil with solvent using ultrasonication or a Soxhlet extractor appears to provide equivalent results; however, a subsequent

Table 7. Physical and Chemical Properties of Predominant Nitroaromatics and Nitramines.

Compound	Molecular Weight	Melting Pt. (°C)	Boiling Pt. (°C)	Water Solubility (mg/L at 20°)	Vapor Pressure (torr at 20°)	log K_{ow}
TNT	227	80.1 - 81.6	240 (explodes)	130	$1.1x10^{-6}$	1.86
TNB	213	122.5	315	385	$2.2x10^{-4}$	1.18
2,4-DNT	182	69.5 - 70.5	300 (decomposes)	270	$1.4x10^{-4}$	2.01
Tetryl	287	129.5	(decomposes)	80	$5.7x10^{-9}$	1.65
RDX	222	204.1	(decomposes)	42	$4.1x10^{-9}$	0.86
HMX	296	286	(decomposes)	5 at 25°	$3.3x10^{-14}$	0.061

investigation indicated that tetryl, another secondary explosive often determined in conjunction with TNT and RDX, is unstable at the temperatures required for Soxhlet extraction (Jenkins and Walsh 1994). That, combined with the ability to extract many samples simultaneously using the sonic bath approach, makes ultrasonication the preferred technique.

Results of extraction studies indicate that even when acetonitrile is used with ultrasonic extraction, the extraction is kinetically slow for weathered field-contaminated soils (Jenkins and Grant 1987; Jenkins et al. 1989). For that reason, SW-846 Method 8330 (EPA 1995a) requires acetonitrile extraction in an ultrasonic bath for 18 hours.

RP-HPLC Determination

Generally, detection of the analyte within the proper retention time window on two columns with different retention orders is required for confirmation of the presence of these explosives. Method 8330 specifies primary analysis on an LC-18 (octadecylsilane) column with confirmation on a cyanopropylsilane (LC-CN) column (Jenkins et al. 1989).

Walsh, Chalk, and Merritt (1973) were the first to report on the use of RP-HPLC for the analysis of nitroaromatics in munitions waste. Most subsequent HPLC methods for these compounds rely on ultraviolet detection because of its sensitivity and ruggedness. Initially, determination was specified at 254 nm because of the availability of fixed wavelength detectors based on the mercury vapor lamps and a significant absorbance of all target analytes at this wavelength. Current instruments are generally equipped with either variable wavelength detectors or diode array detectors, and wavelengths of maximum absorption can be selected to optimize detection. However, 254 nm is still often used because of the low incidence of interference at this wavelength.

Method Specifications and Validation

Based on the research described above, SW-846 Method 8330 (EPA 1995a) specifies the following:

1. Soil samples are air-dried and ground in a mortar and pestle for homogenization.

2. A 2-g subsample is placed in an amber vial, 10 mL of acetonitrile is added, and the vial is placed in a temperature-controlled ultrasonic bath for 18 hours.

3. The vial is removed from the bath and the soil is allowed to settle, a 5-mL aliquot is removed and diluted with 5 mL of aqueous $CaCl_2$ to assist in flocculation, and the diluted extract is filtered through a 0.45-μm membrane.

4. A 100-μL portion is injected into an HPLC equipped with a primary analytical column (LC-18) and is eluted with methanol/water (1:1) at 1.5 mL/min; retention times for the 14 target analytes range from 2.44 to 14.23 minutes.

5. If target analytes are detected, their presence is confirmed on a confirmation column (LC-CN).

6. The estimated quantitation limits in soil for most analytes is about 0.25 mg/kg, with RDX and HMX being somewhat higher at 1.0 and 2.2, respectively. No limits are provided for the Am-DNTs.

This procedure was subjected to a ruggedness test (Jenkins et al. 1989) and a full-scale collaborative test (Bauer, Koza , and Jenkins 1990) was conducted under the auspices of the Association of Official Analytical Chemists (AOAC). In addition to acceptance by the EPA Office of Solid Waste as SW-846 Method 8330 (EPA 1995a), this procedure also has been adopted as Standard Method 991.09 by the AOAC (AOAC 1990) and as ASTM Method D5143-90 (ASTM 1990). In addition, the procedure has been used successfully by a large number of commercial laboratories for several years.

SUMMARY

A large number of defense-related sites are contaminated with elevated levels of secondary explosives. Levels of contamination range from barely detectable to levels over 10% that need special handling because of the detonation potential. Characterization of explosives-contaminated sites is particularly difficult because of the very heterogeneous distribution of contamination in the environment and within samples. To improve site characterization, several options exist including collecting more samples, providing on-site analytical data to help direct the investigation, sample compositing, improving homogenization of samples, and extracting larger samples. On-site analytical methods are essential to more economical and improved characterization. What they lack in precision and accuracy when used to simultaneously identify specific multiple compounds, the on-site methods more than make up for in the increased number of samples that can be analyzed. While verification using a standard analytical method such as EPA Method 8330 should be part of any quality assurance program, reducing the number of samples analyzed by more expensive methodology can result in significantly reduced costs. Often 70 to 90% of the soil samples analyzed during an explosives site investigation do not contain detectable levels of contamination.

Two basic types of on-site analytical methods are in wide use for explosives in soil: colorimetric and immunoassay. Colorimetric methods generally detect broad classes of compounds such as nitroaromatics or nitramines, while immunoassay methods are more compound specific. Because TNT or RDX is usually present in explosive-contaminated soils, the use of procedures designed to detect only these or similar compounds can be very effective.

Selection of an on-site analytical method involves evaluation of many factors including the specific objectives of the study, compounds of interest and other explosives present at the site, the number of samples to be run, the sample analysis rate, interferences or cross reactivity of the method, the skill required, analytical costs per sample, and the need for and availability of support facilities or services or both. Another factor that may be considered is the precision and accuracy of the on-site analytical method, but it should be remembered that analytical error is generally small compared to field error and that the precision and accuracy of a method is dependent on the site (compounds present and relative concentration) and the specific objectives (the question being asked).

Modifications to on-site methods may be able to improve method performance. In most cases, a larger soil sample can be extracted to improve the representativeness of the analytical sample. Also, with heavy soils or soils with high organic matter content, conducting a short-term kinetic study may be useful to determine whether a 3-minute extraction period is adequate. The shaking and extraction phase of all on-site methods should last at least 3 minutes. In all cases, a portion of the on-site analytical results should be confirmed by using a standard laboratory method. With appropriate use, on-site analytical methods are a valuable tool for characterization of soils at hazardous waste sites and monitoring soil remediation operations.

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NOTICE

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