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Project Summary

Field Sampling and Selecting On-Site Analytical Methods for Explosives in Soil

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A large number of defense-related sites are contaminated with elevated levels of second-ary explosives. Levels of contamination range from barely detectable to levels above 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 environ-ment and within samples. To improve site characterization, several options exist includ-ing collecting more samples, providing on-site analytical data to help direct the investigation, compositing samples, improving homogenization of samples, and extracting larger samples. On-site analytical methods are essential for more economical and improved charac-terization, and what they may lack in accuracy relative to laboratory methods, is more than offset by the increased number of samples that may be run. While verification using a stan-dard analytical procedure should be part of any quality assurance program, reducing the number of samples analyzed by the more expensive methods may 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 explo-sives 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 explosives-contaminated soils, the use of on-site methods designed to detect only these or similar compounds may 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/cross-reactivity of the method, the skill required, analytical costs per sample, and the need for and availability of support facilities and services. Other factors to be considered are the precision and bias of the on-site analytical method, but it should be remembered that 1) the analytical error is generally small compared to field error and 2) the precision and bias of a method are dependent on the site (compounds present and relative concen-tration) and the specific objectives. Modifi-cations to on-site methods may improve method performance including extracting a larger soil sample to improve the repre-sentativeness of the analytical sample, ensuring that the shaking/extraction phase of all methods lasts at least 3 minutes, and evaluating the rate of extraction for heavy soils by conducting a simple kinetic study. With appropriate use, on-site analytical methods are valuable tools for characterization of soils containing explosive residues and monitoring remediation operations.

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 pro-tect life, health, and property. This publica-tion 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). Specifi-cally, this paper is not intended to serve as a guide for sampling and analysis of unex-ploded 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.

Introduction

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. 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. A number of these facilities have high levels of soil and groundwater contamination, although waste disposal was discontinued 20 to 50 years ago. Because of such extensive contamination, the Environmental Protection Agency's Federal Facilities Forum determined that remedial project managers need guidance about field sampling and on-site analytical methods for detecting and quantifying secondary explosive compounds (Table 1) in soils.

Under ambient environmental conditions, explosives are highly persistent in soils and groundwater, exhibiting a resistance to naturally occurring volatilization, biodegradation, and hydrolysis. 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.

The frequency of occurrence of specific explosives in soils was assessed by Walsh et al. (1993), who compiled data on soils collected from 44 Army ammunition plants, arsenals, and depots and two explosive ordnance disposal sites. Of the 1,155 samples, 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 detected in 66% of the samples and 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 these facilities, 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 to identify the extent of contamination at munitions sites.

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

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

A = Ammonium Picrate/Picric Acid (Thorne and Jenkins 1995).
Cp = Colorimetric field method, primary target analyte(s).
Cs = Colorimetric field method, secondary target analyte(s).
G = Nitroguanidine (Walsh 1989).
Ip = Immunoassay field method, primary target analyte(s).
Is = Immunoassay field method, secondary target analyte(s).
L = Nitrocellulose (Walsh unpublished CRREL method).
N = EPA SW-846, Nitroaromatics and Nitramines by HPLC, Method 8330.
P = PETN and NG (Walsh unpublished CRREL method).
* The performance of a number of field methods have not been assessed utilizing "approved" laboratory methods.

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

Nitroaromatics	% Samples with Analyte Present	Maximum Level (μg/g)
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 of concern from a potential reactivity standpoint and may affect sampling and materials handling processes during remediation.

Reliance on laboratory analyses only for site investigations may result in a large percentage of the samples with nondetectable levels (up to 80%) at a high analytical cost ($250 to 350 per sample). 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 on-site method costs per sample are lower, more samples may be analyzed and the availability of near-real-time results permit redesign of the sampling scheme while in the field. The use of on-site methods also facilitates more effective use of off-site laboratories.

Data Quality Objectives

The Environmental Protection Agency (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. 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 (EPA 1992), identifying candidate waste for treatability studies, identifying the volume of soil to be remediated, determining whether the soil presents a potential detonation hazard (reactive according to Resource Conservation and Recovery Act regulations), and determining whether remediation activities have met the cleanup criteria (typically 10 to 100 ppm).

Unique Sampling Design Considerations for Explosives

Heterogeneity Problems and Solutions - Jenkins et al. (1996) recently collected and analyzed seven soil cores within a radius of 2 ft from nine locations. Results showed extreme variation in concentration in five of the nine locations, and in all cases only a small fraction of the total error was because of analytical error; field sampling error dominated total error. To improve site characterization and reduce sampling error, the major effort should be to increase sampling densities and composite samples. 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.

One simple way to improve spatial resolution is by collecting more samples on a finer sampling grid such as a 5-m instead of a 10-m spacing. This approach has been rejected in the past because of the higher costs but when inexpensive on-site analytical methods are used, this approach becomes feasible.

Samples are always taken to apply inferences from the samples to a larger volume of material, and a set of composite samples 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." Decisions based on a set of composite samples provides greater statistical confidence than a comparable set of individual samples (Gagner and Crockett 1996). In Jenkins' study, composite samples were much more representative of each plot than the individual samples that made up the composites. Using a composite sampling, it is possible to reduce costs and the total number of samples collected while improving characterization.

Stratified sampling also may be effective in reducing field and subsampling errors. Using historical data and site knowledge or results from an exploratory study, 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, which may reduce heterogeneity.

Within-sample heterogeneity is frequently observed with on-site analyses when duplicate subsamples are analyzed and the results differ by an order of magnitude. To reduce within-sample heterogeneity and obtain a representative analytical sample, two methods may be employed: either homogenization and extraction or analysis of a larger sample. The smaller the volume of the subsample removed for extraction and analysis, the more homogeneous the entire sample should be before subsampling. This may require sample drying, grinding, and riffle splitting (Gagner and Crockett 1996).

While sample-mixing procedures such as sieving to disaggregate particles, mixing in plastic bags, etc., should be used to prepare a sample. Extracting a larger sample is perhaps the easiest method of improving representativeness. Jenkins recommends extraction of 20 g of soil, and the same approach may be used easily to improve the results with most on-site analytical methods.

Sample Holding Times and Preservation Procedures - Based on spiking clean soils with explosives in acetonitrile, Maskarinec et al. (1991) 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 et al. (1993, 1995) 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). Soils spiked with nitroaromatics should be frozen as soon as possible because some results showed significant TNT and TNB degradation within 2 hours. However, both compounds and 2,4-DNT may be adequately preserved for 8 weeks or longer by freezing. The results for field-contaminated soils did not show the rapid degradation of TNT, and TNB 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. Explosives in air-dried soils

are stable at room temperature if kept in the dark. Acetonitrile extracts of soil samples are expected to be stable for at least 6 months under refrigeration. Acetone extracts are also thought to be stable if stored in the dark under refrigeration.

Explosion Hazards and Shipping Limitations - EPA regions and the U.S. Army Environmental Center consider soils containing more than 10% secondary explosives (i.e., TNT, RDX, HMX, DNT, TNB, and DNB) by weight to be susceptible to initiation and propagation (EPA 1993). If on-site analyses indicate that soil samples contain less than 10% total secondary explosives by weight, they may be shipped to off-site laboratories as environmental samples. Samples with more than 10% explosives must be shipped to a explosives-capable laboratory for analysis, and they 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). For sampling at sites with unknown or greater than 10% by weight of secondary explosives contamination, special sampling procedures must be followed (AEC 1994).

Summary of On-site Analytical Methods For Explosives in Soil

Ideally, on-site 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 on-site methods may not be ideal (not capable of providing compound specific concentrations of multiple compounds simultaneously), they have proven very valuable during the characterization and remediation of numerous sites. Currently available on-site analytical methods that have been evaluated against standard analytical methods and demonstrated in the field include colorimetric and immunoassay methods (Table 1). Each method has relative advantages and disadvantages; therefore, one method may not be optimal for all applications. To assist in the selection of one or more on-site methods for various users needs, Table 3 was developed comparing the available colorimetric and immunoassay on-site analytical methods for detecting explosives in soil. The selection criteria presented include method type, analytes determined, detection limit and range, sample preparation and extraction procedure, analytical production rate, interferences and cross-reactivities, recommended quality assurance/quality control, suggested storage conditions and shelf life, skill required, availability of training, cost per sample, and, among others, additional method selection considerations. The comparable table in the complete issue paper also includes references to comparisons with Method 8330 and other references.

Interferences/Cross-Reactivity - A major difference among the field methods is with interferences for colorimetric methods and cross-reactivity for immunoassay methods. The colorimetric methods for TNT and RDX are broadly class sensitive, that is, they respond to many other similar compounds (nitroaromatics and nitramines/nitrate esters, respectively). Immunoassay methods are relatively specific for the primary target analytes. The cross-reactive secondary target analytes for TNT are mainly other nitroaromatics, but this varies considerably among the four TNT immunoassay test kits. Depending upon the sampling objectives, broad sensitivity or specificity may be an advantage or a disadvantage. If the objective is to determine whether any explosive residues are present in soil, broad sensitivity is an advantage. For the Cold Regions Research and Engineering Laboratory (CRREL) and EnSys RIS[c] colorimetric methods, the color development of the extracts may give the operator an indication of what types of compounds are present in soil. An advantage 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.

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. For TNT methods, the primary target analyte is TNT, and the secondary target analytes are other polynitroaromatics 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, 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 similar to that of the primary target analyte, and remain constant through-out the concentration range of the methods.

For immunoassay methods, cross-reactivity is defined as the positive response of a method to secondary target analytes or co-contaminants similar to the primary target analyte. For TNT methods, the prim-ary target analyte is TNT, and the secondary target analytes are nitroaromatics TNB, DNTs, Am-DNTs, and tetryl. For RDX methods, the primary target analyte is RDX, and cross-reactivity is slight, 3% with HMX. 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 methods measure the primary target analyte plus some percen-tage of the cross-reactive secondary target.

Both colorimetric and immunoassay methods may be subject to positive matrix interference from humic substances in soils. For colorimetric methods, this typically occurs below 10 ppm, and is indicated by yellow extracts. These interferences may be reduced by careful visual analysis prior to colorimetric analysis. 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 fertilized recently.

Comparisons to Laboratory Method, SW-846 Method 8330 - Precision and bias of the on-site 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, percent false positive and false negative results, and analysis of variance and paired t-tests. It also should be remembered that analytical accuracy is generally quite small compared to total error (field error is the major contributor).

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 RISE®	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 RISE®	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 Assay®	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

Three studies have evaluated multiple methods under slightly different field conditions. Readers should consult the original studies for more details; however, some summary conclusions from the three cited studies follow. An EPA study (EPA 1995) compared the CRREL, EnSys RIS^c (colorimetric), D TECH, Idetek Quantix, and Ohmicron RaPID Assay methods for TNT. The study concluded that overall "no single method significantly out-performed other methods" and accuracies for all the on-site methods were comparable. However, CRREL, EnSys RIS^c, and Ohmicron RaPID Assay 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 CRREL, EnSys RIS^c, and D TECH methods for RDX in soil and con-cluded that they were slightly less accurate than the corresponding TNT methods.

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. For quantitative analyses, several of the assays had “significant positive bias” compared with high performance liquid chromatography (HPLC) results below 1 ppm; 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 RIS^c and D TECH methods for TNT in soil versus EPA Method 8330. "EnSys demonstrated a good one-to-one linear correlation with RP [reverse phase]-HPLC that may 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 (as opposed to single value) and because "one-to-one linear correlation with RP-HPLC was poorer." The study concluded that the EnSys RIS^c 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 in which all samples above a certain range will be sent forward to a laboratory for confirmation by the standard method.”

Emerging Methods and Other Literature Reviewed - Other on-site procedures are being used but limited information is available on them. Emerging procedures include an antibody-based continuous-flow immunosensor for TNT and RDX and a fiber optic biosensor for TNT that are being evaluated by the Navy for use in soil, the U.S. Army is developing a cone penetrometer for *in situ* detection of explosives, ion mobility spectrometry is being evaluated by several organizations, a modified Method 8330 has been used in a mobile trailer, thermal desorption followed by gas chromatography/mass spectrometry analysis has been reported, and 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.

Summary

The heterogeneity of explosives in soils poses significant problems for site characterization. Several options exist including collecting more samples, providing on-site analytical data to help direct the investigation, compositing samples, improving homogenization of samples, and extracting larger samples. On-site analytical methods are essential for more economical and improved characterization. What the on-site methods lack in terms of precision and accuracy in simultaneously identifying specific multiple compounds, they more than make up for in the increased number of samples that can be run.

Modifications to on-site methods may be able to improve method performance. In most cases, a larger soil sample may be extracted to improve the representativeness of the analytical sample. Also, with heavy soils or soils with high organic matter content, it may be useful to conduct a short-term kinetic study to determine whether a 3-minute extraction period is adequate. It is recommended that the shaking/extraction phase of all methods last at least 3 minutes. In all cases, it is recommended that a portion of the on-site analytical results is confirmed using a standard laboratory method.

Notice

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