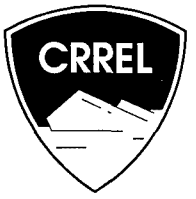
SPECIAL REPORT 96-10



On-Site Analysis for High Concentrations of Explosives in Soil

Extraction Kinetics and Dilution Procedures

Thomas F. Jenkins, Patricia W. Schumacher, Jane G. Mason
and Philip G. Thorne

May 1996

Abstract: Soils containing high concentrations (>10%) of secondary explosives might detonate from shock or flame, resulting in human injuries or equipment damage during remediation activities. In lieu of expensive and time-consuming protocols involving impact tests, friction tests, and shock gap tests, compositional analysis has been recommended as an expedient method to assess the risk of detonation from heavily contaminated soils. A number of methods now available allow determination of TNT and RDX on site. All of these methods specify solvent extraction with either acetone or methanol to transfer the analyte from the soil matrix to a solvent as the first step in the determination. The rate of extraction of TNT and RDX, when present at percent levels in soil, has not been determined. Protocols currently in use specify very short extraction times (one to three minutes) and results could be biased low if extraction kinetics are slow. The objective of this work was to document the rate of extraction of secondary explosives by acetone and methanol and make recommendations for possible modification of current protocols if warranted. Because solvent extracts from highly contaminated soils will have very high concentrations of secondary explosives, compared with the range of concentrations that can be determined using the various on-site methods, large dilutions will be required. Recommendations are made for a field-expedient method making appropriate dilutions.

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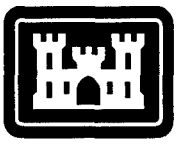

US Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

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PREFACE

This report was prepared by Dr. Thomas F. Jenkins, Patricia W. Schumacher, Jane G. Mason, and Philip G. Thorne, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire. Funding was provided by the U.S. Army Environmental Center (USAEC), Aberdeen Proving Ground, Maryland, Martin H. Stutz, Project Monitor.

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AND PHILIP G. THORNE

INTRODUCTION

Background

For the greater part of this century, the U.S. Army has manufactured explosives and munitions and demilitarized munitions at Army facilities throughout the United States. Disposal of wastes generated in these manufacturing operations has contaminated some Army lands with residues of explosives. For example, the Army utilized unlined evaporation/percolation lagoons for disposal of wastewaters from manufacturing, demilitarization, and load, assemble, and pack operations. After many years of operation, explosives tended to accumulate at the soil surface of these lagoons, sometimes at concentrations in the percent range. Whether sampling for site characterization or conducting remediation activities, these areas of very high explosives concentration are a major concern relative to the potential for detonation.

Several years ago, the U.S. Army Toxic and Hazardous Materials Agency (now the U.S. Army Environmental Center) sponsored a study to document the reactivity (propagation of a detonation) hazard associated with high concentrations of secondary explosives in soil (Kristoff et al. 1987). A series of tests was conducted to define the reactivity of explosives-contaminated soils to flame and shock as a function of explosives composition. The results of this work indicated that soils containing concentrations of TNT (2,4,6-trinitrotoluene) and RDX (1,3,5-hexahydro-1,3,5-trinitrotriazine) below 15% were not reactive to shock stimuli, and soil concentrations below 12% could not be detonated by flame initiation. To provide a margin of safety, the U.S. Army Environmental Center has established a level of 10% as the concentration of secondary explosives in soil at which a detonation would not propagate. Any concentration above 10% would be considered an explosive operation and would require the approval of the Department of Defense Explosive Safety Board. Because of the cost and specialized nature of these reactivity tests, it was recommended that compositional analysis be used to identify potentially reactive soils (those above the 10% criteria). Because of the explosive hazard involved, a simple, rapid method for on-site analysis is useful in order to allow decisions to be made expeditiously or to screen samples prior to shipment to off-site laboratories. Three approaches have been developed for rapid on-site analysis: colorimetric methods, immunoassays, and ion mobility spectrometry (Table 1). All of these methods rely on an initial step involving rapid extraction of the soil with an organic solvent. Acetone or methanol have been the solvents of choice because of the large solubility of these compounds in these polar solvents, and their compatibility with on-site methods of determination. However, the applicability of these solvents to extraction of soil samples with very high concentrations of nitroaromatics and nitramines has not been evaluated.

Table 1. Extraction techniques used with on-site analysis methods.

TYPE *Method*	*Solvent*	*Extraction time*	*Soil/solvent*	*Concentration range (μg/g)*
Colorimetric				
EnSys	Acetone	3 min	10 g/50 mL	1 to 30
Erickson	Methanol	1 min	6 g/20 mL	0.3 to 30
Jenkins	Acetone	3 min	20 g/100 mL	1 to 22
Medary	Methanol	1 min	6 g/35 mL	4 to 90
Immunoassay				
EM Science (D TECH)	Acetone	3 min*	4.5g†/9 mL	0.5 to 5.0
Idetek (Quantix)	Acetone	3 min	4.2g/21 mL	0.25 to 100
Millipore (EnviroGard)	Acetone	2 min	2 g/8 mL	1 to 100
Ohmicron	Methanol	1 min	10 g/20 mL	0.07 to 5
Ion mobility spectrometry				
Barringer	Acetone-hexane	3 min	1 g/1 mL	Low ppb

* Shaking several times over three-minute period.
† Actual mass of soil will vary depending on soil density.

Objective

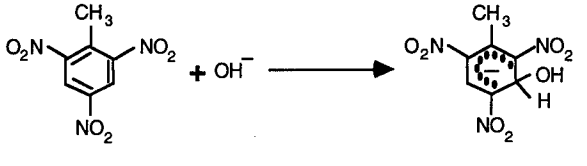
The main objective of our study was to determine the rate of extraction of secondary explosives from highly contaminated soil to ensure that on-site methods currently available can provide sufficiently accurate results for soils contaminated with percent levels of TNT and RDX. Field-contaminated soils from a number of installations were utilized in these assessments. Because the most commonly used on-site methods for explosives in soil specify either acetone or methanol as the extraction solvent, much of the work evaluated extraction using these solvents. Based on these results, recommendations will be made on modifications to established protocols for available on-site methods for determining whether concentrations exceed the 10% safety criterion. Since large dilution factors (about 1 to 10,000) are required to reduce extract concentrations to the range suitable for these tests, a dilution procedure that is simple and sufficiently accurate and precise will be provided.

Overview of on-site methods

Colorimetric TNT methods

The first on-site screening method for TNT in environmental matrices was reported by Heller et al. (1982). This method was initially developed for water analysis and utilized a detection tube containing two sections. The first section contained a basic oxide that converted TNT to its Meisenheimer anion (eq 1), which was retained by the anion exchanger in the second section of the tube.

Equation 1. MEISENHEIMER ANION



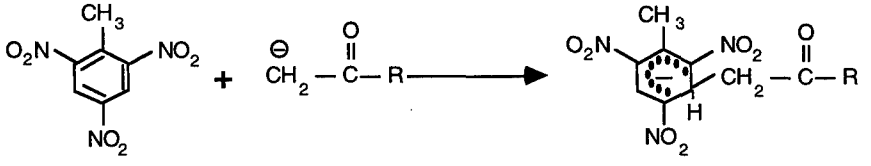
TNT

Since the Meisenheimer anion for TNT is highly colored, detection is achieved visually and quantitation is made by measuring the length of the colored region of the tube. The use of these tubes for detection of TNT in soil was reported by Erickson et al. (1984). Their method specifies extraction of about 6 g of soil with 20 mL of methanol by manually shaking for one minute followed by filtering

through filter paper. The detection tubes used for this method have been available as a special order item from Supelco (Bellefonte, Pennsylvania).

In 1990 we reported a colorimetric-based method for TNT in soil (Jenkins 1990). In this method, 20-g samples of field-moist soils are extracted with 100 mL of acetone by shaking manually for three minutes (Table 1), allowing the soil to settle, and filtering the extract through a 0.5-µm syringe filter. The resulting extract is then reacted with potassium hydroxide and sodium sulfite to form the highly colored (reddish for TNT) Janowsky anion (eq 2),

Equation 2. JANOWSKY ANION



TNT

and the TNT concentration is estimated from absorbance measurements at 540 nm. A similar method was developed by Medary (1992) at about the same time. Medary's method uses a 6-g portion of field-moist soil and 35 mL of methanol, and requires manual shaking for one minute for extraction (Table 1). The extracted TNT is reacted with a 10% aqueous solution of sodium hydroxide. TNT is estimated from the absorbance of the colored Meisenheimer anion produced at 516 nm (eq 1). The method developed by Medary is sometimes referred to as the Corps of Engineers method.

EnSys (Research Triangle Park, North Carolina) commercialized a colorimetric method for TNT in soil using an approach similar to that developed by Jenkins (1990). The EnSys method (RisC) specifies that a 10-g portion of dried soil is extracted with 50 mL of acetone. Extraction is conducted by manually shaking for three minutes, allowing the soil to settle for five minutes, and filtering the extract through a 0.5-µm Millex SR syringe filter. This method has been issued as SW846 Method 8515, "Colorimetric Screening Method for Trinitrotoluene (TNT) in Soil," by the USEPA Office of Solid Waste.

Enzyme immunoassay (EIA) methods for TNT

Keuchel et al. (1992a, b) and Keuchel and Neissner (1994) were the first to report the development of a competitive enzyme immunoassay (EIA) method to detect TNT in water. The immunoassay used polystyrene microtiter plates coated with antibodies. Enzyme-analyte conjugate was synthesized from 2,4,6-trinitrobenzene sulfonic acid conjugated to the enzyme horseradish peroxidase.

A commercially available enzyme immunoassay for TNT in water and soil was issued in 1993 by EM Science (Gibbstown, New Jersey) as D TECH Environmental Detection Systems (Hutter et al. 1993, Teaney et al. 1995). This assay makes use of a competitive reaction between enzyme-labeled TNT and free TNT for binding sites on antibody-coated latex particles. The particles are trapped on a membrane, washed clean of unbound enzyme conjugate, and treated with a substrate to induce a color change inversely proportional to the amount of free TNT in the sample. Homogenized, field-moist soils are collected in a calibrated 3-mL syringe, transferred to a plastic bottle, and extracted with 6.5 mL of acetone. Extraction is conducted by manually shaking several times over a three-minute period, allowing the soil to settle for one minute, and pipetting off a 1.0-mL aliquot of the supernatant. Results are quantitated with a hand-held, dual-beam reflectometer that measures the difference between the sample and the reference control.

Three other commercial enzyme immunoassay methods are currently available for TNT. The EnviroGard TNT kit (Millipore ImmunoSystems, Scarborough, Maine) is intended to be a laboratory assay for semi-quantitative analysis of TNT in both soil and water. Field-moist soil samples are

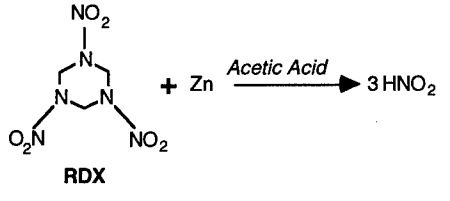
extracted with acetone, and the diluted acetone extracts are incubated with TNT-enzyme conjugate in microtiter wells coated with antibody. Upon completion of the incubation, the unbound analytes are rinsed away, substrate is added, and the developed color is measured with an ELISA plate-reading spectrophotometer at 450 nm. The extraction step specifies a 2-g portion of soil and 8 mL of acetone and two minutes of mechanical shaking.

Enzyme immunoassay methods for TNT are also available from Ohmicron (RaPID Assay, Newtown, Pennsylvania) and Idetek (Quantix, Sunnyvale, California). The Ohmicron method is a magnetic particle-based method run in test tubes; it specifies extraction of a 10-g portion of undried soil with 20 mL of methanol in a special extraction container by manually shaking for one minute followed by a five-minute settling time prior to filtration with a filter cap. The Idetek method, which is functionally very similar to the EnviroGard method described above (Table 1), specifies that a volumetric portion of soil (corresponding to about 4.2 g of soil) is added to a soil extraction bottle with 21 mL of acetone; the sample is shaken manually for three minutes and is used without filtration.

Field methods for RDX

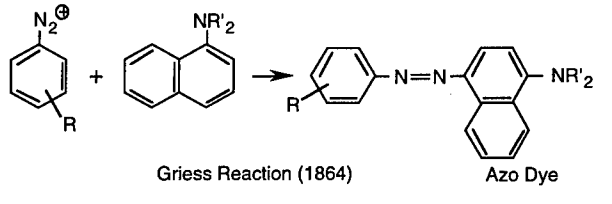
Considerably less attention has been devoted to field screening for RDX than for TNT. RDX does not respond to either the TNT colorimetric or EIA-based screening methods and is one of the compounds most often found at munitions-contaminated sites in the U.S. (Walsh et al. 1993). Forensic chemists have used colorimetric-based tests for RDX for many years to identify RDX in post-blast residues (Yinon and Zitrin 1981), and in 1991 we reported the development of a colorimetric field screening method for RDX in soil (Walsh and Jenkins 1991) utilizing a similar approach. This method was based on two classical chemical reactions that have been known since the nineteenth century. Using the Franchimont reaction (eq 3),

Equation 3. FRANCHIMONT REACTION (1897)



RDX, in the acetone extract described above, is reacted with zinc under acidic conditions to produce nitrous acid, and the nitrous acid is converted to an azo dye using the Griess reaction (eq 4). The reddish-colored product can be detected visually and quantified using absorbance measurements at 507 or 510 nm.

Equation 4. GRIESS REACTION (1864)



This method utilizes the same acetone extract described above for the TNT test (Jenkins 1990) and thus allows a single soil extract to be screened for both TNT and RDX. A similar colorimetric approach has been commercialized by EnSys.

A commercial EIA-based test for RDX has also been developed by Strategic Diagnostics (Newark, Delaware) and is available from EM Science as the D TECH RDX Test. This method uses the same

Table 2. Extraction techniques used with on-site analysis methods for RDX.

Method	*Type*	*Solvent*	*Extraction time*	*Soil/solvent*
Barringer	IMS*	Acetone	3 min	
EM Science (D TECH)	Immunoassay	Acetone	3 min†	3 mL**/15 mL
EnSys	Colorimetric	Acetone	3 min	10 g/50 mL
Walsh & Jenkins	Colorimetric	Acetone	3 min	20 g/100 mL

* Ion Mobility Spectrometry.
† Shaking several times over three-minute period.
** Actual mass of soil will vary depending on soil density.

extract as their TNT test and hence a single extract can be tested for both TNT and RDX. Soil extraction methods for these RDX tests are summarized in Table 2.

Ion mobility spectrometry

Ion mobility spectrometry (IMS) has been used extensively for the detection of explosives associated with potential terrorist activities. Recently there has been interest in the use of this technology for rapid on-site analysis of explosives in soil. Rodacy and Leslie (1993) presented an initial investigation of the use of IMS for this purpose.

Avolio et al. (1995), from Barringer Instruments Inc. (New Providence, New Jersey), have also described the use of IMS for rapid on-site analysis of TNT, DNT, and RDX. The best results were obtained when acetone extracts were deposited on a PTFE filter and thermally desorbed into the IMS. A 1-g soil sample is extracted with a 1-mL portion of acetone by shaking for three minutes. A 1-mL portion of hexane is added and an aliquot of the acetone-hexane extract is used for thermal desorption (Avolio, pers. comm.*). An advantage of the IMS approach is that it provides an estimate of TNT and RDX in a single analysis.

EXPERIMENTAL

Chemicals and reagents

All standards for TNT, DNT, and RDX were prepared from Standard Analytical Reference Materials (SARMS) obtained from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland. Stock standards of TNT, DNT, and RDX in acetone were prepared using HPLC-grade acetone. Working standards in the field were prepared using hardware-store-grade acetone.

All acetone used for soil extraction and glassware cleaning was hardware grade obtained locally. Methanol used for soil extraction was HPLC grade. Acetonitrile and methanol used in the laboratory for preparation of HPLC eluents and extract dilution were Baker, EM, or Mallinckrodt HPLC grade. Water used for preparation of HPLC eluents, and for addition to extracts to ensure that an adequate water content was present for the color-forming reaction, was reagent-grade water prepared from a Millipore Milli-Q Type 1 reagent-grade water system.

RP-HPLC analyses

Reversed phase HPLC analysis was conducted as described in EPA SW846 Method 8330. Primary analysis was conducted on a Supelco LC-18 column eluted with 1:1 methanol/water at 1.5 mL/min. Absorbance was recorded at 254 nm on a Spectra Physics Model 8490 variable-wavelength detector, and peaks were recorded on a Hewlett Packard 3396 Digital Integrator in the peak height mode. Selected samples were subjected to second-column confirmation on a Supelco LC-CN column using either 35:65 methanol/water or 23:12:65 acetonitrile/methanol/water, depending on the specific analytes detected in the primary analysis (Jenkins and Golden 1993).

* J. Avolio, Applications Chemist, Barringer Instruments, Inc., New Providence, New Jersey.

Because the extracts had very high concentrations of TNT, DNT, or RDX, they were diluted by introduction of microliter volumes of the acetone or methanol extracts into a measured volume of 1:1 methanol/water. Dilutions ranged from 1:100 to 1:10,000.

Field-contaminated soils

Several high-concentration field-contaminated soils from a number of installations were utilized for this study. Initial experiments used archived soil samples that had been air dried, ground, and thoroughly homogenized. These samples were rewetted with water prior to extraction to simulate field conditions. To do so, about 4 mL of water was added to each 20-g sample of soil, mixed, and allowed to stand for 30 minutes before adding the extracting solvent. Archived samples from Weldon Springs Army Ammunition Plant (AAP), Nebraska Ordnance Works, Iowa AAP, Volunteer AAP, and Hawthorne AAP were used in this portion of the study.

Kinetic extraction tests were also conducted with undried soils from Volunteer AAP. These field-moist samples were processed by removing large stones and thoroughly mixing prior to removing a 20-g subsample for extraction.

Protocol for kinetic extraction studies

A 20-g portion of field-moist soil was placed in a 125-mL (4 oz) polypropylene bottle containing five stainless steel balls. A 100-mL aliquot of either acetone or methanol was added and the bottle was capped and vigorously shaken for three minutes on a mechanical shaker. After the shaking period, the soil was allowed to settle for about five minutes; a 2-mL aliquot was then removed and passed through a 0.5-μm Millex SR filter unit into a labeled autosampler vial. The Nalgene bottle was then recapped and shaken for additional time increments. After each shaking time increment, soils were allowed to settle and samples of the supernatant were collected and processed as above. When all the kinetic samples were collected, portions of the filtered extracts were diluted into 1:1 methanol/water and analyzed by RP-HPLC as described above.

Colorimetric field-screening analysis

Colorimetric analysis of the acetone extracts was conducted using the EnSys reagent. A reference standard of TNT in acetone (containing 3% water) was prepared with a concentration of 3 mg/L. This standard was analyzed with each set of samples and was used to establish the response factor (RF-TNT) for estimating TNT concentration for the sample extracts. The filtered sample extracts were diluted with acetone (containing 3% water) using a microliter syringe. A 25-mL portion of the diluted extract was placed in a spectrophotometer cuvette and the initial absorbance (ABS-initial) obtained at 540 nm on a Hach DR/2000 battery-operated spectrophotometer. The cuvette was then removed from the spectrophotometer and one drop of the EnSys developer solution (referred to as the EnSys reagent) was added. The contents of the vial were mixed thoroughly and allowed to stand for one minute. The absorbance at 540 nm was then obtained (ABS-final) as described above. Dilutions were made to obtain final absorbances below 1.0 A.U. after addition of the EnSys reagent. The TNT concentration in the sample was calculated as follows:

$$\text{TNT } (\mu g/g) = \{[\,(\text{ABS-final}) - 2 \times (\text{ABS-initial})] \,/\, \text{RF-TNT}\} \times 5.$$

A response factor of 0.177 A.U./mg/L was obtained from calibration. The factor of 5 is used to convert concentration in mg/L to concentration on a μg/g basis. Results were then corrected for the specific dilution used.

Results on moist samples from Volunteer AAP were obtained as described above except that the soil extraction step was modified. A short kinetic study conducted at Volunteer revealed that extractions needed to be extended to get stable concentrations. Samples were shaken for three minutes, allowed to stand for 30 minutes, and shaken for an additional three minutes. After allowing the soil to settle, an aliquot was filtered, diluted using microliter syringes as described above, and analyzed using the EnSys method.

RESULTS AND DISCUSSION

Kinetic extraction tests

Initial extraction rate studies were conducted with archived soil samples from a variety of installations. These samples had been air dried and stored for several years at room temperature. Soils were moistened by adding water prior to adding extraction solvent to simulate the field-moist conditions that would be present when samples are subjected to on-site analysis. Results of RP-HPLC analyses of these acetone and methanol extracts are presented in Tables 3a–3c.

Table 3. High concentration extraction rate study for archived soils.

a. TNT.

	*TNT concentration (μg/g)**													
	Hawthorne AAP (#12)		*Hawthorne AAP (#14)*		*Weldon Springs AAP (#29)*		*Nebraska Ordnance Works (#39)*		*Iowa AAP (SS-8-005)*		*Iowa AAP (SS-8-001)*		*Volunteer AAP (SE-5369)*	
Extr. time	*A†*	*M†*	*A*	*M*	*A*	*M*	*A*	*M*	*A*	*M*	*A*	*M*	*A*	*M*
3 min	921	1020	9170	10400	4360	4380	25500	28100	2240	15900	9880	6450	110000	94900
10 min	1000	1080	9470	10700	4490	4430	27200	28700	2500	15900	9780	6650	117000	95400
30 min	1040	1100	9830	10800	4640	4440	26700	27400	2590	15600	9970	6750	127000	97000
60 min	1060	1140	9870	10700	4650	4490	26700	28600	2780	16100	10100	6850	130000	101000
18 hr	1130	1360	9970	11000	4610	4600	26800	28600	2770	15900	10300	6850	130000	101000
Ratio: 3 min/ 18 hr	0.82	0.75	0.92	0.95	0.95	0.95	0.95	0.98	0.81	1.00	0.96	0.94	0.85	0.94

* Estimated by RP-HPLC.
†A = Acetone extraction, M = Methanol extraction.

b. RDX.

	*RDX concentration (μg/g)**							
	Hawthorne AAP (#12)		*Hawthorne AAP (#14)*		*Iowa AAP (SS-8-005)*		*Iowa AAP (SS-8-001)*	
Extr. time	*Acetone*	*Methanol*	*Acetone*	*Methanol*	*Acetone*	*Methanol*	*Acetone*	*Methanol*
3 min	318	307	7670	6240	927	1990	3200	846
10 min	336	300	7820	6550	1160	2620	3150	957
30 min	340	306	8100	6660	1210	2880	3210	954
60 min	334	310	8110	6680	1430	2960	3240	972
18 hr	343	340	8170	7070	1400	2970	3290	1000
Ratio: 3 min/18 hr	0.93	0.90	0.94	0.88	0.66	0.67	0.97	0.85

* Estimated by RP-HPLC.

c. 2,4-DNT

	*2,4-DNT concentration (μg/g)**			
	Volunteer AAP (SE-5538)		*Volunteer AAP (SE-5369)*	
Extraction time	*Acetone*	*Methanol*	*Acetone*	*Methanol*
3 min	130000	101000	31800	24300
10 min	94500	85600	37400	24700
30 min	144000	90200	43600	25900
60 min	158000	94800	45400	27000
18 hr	150000	92800	45500	27900
Ratio: 3 min/18 hr	0.87	1.09	0.70	0.87

* Estimated by RP-HPLC.

Table 3a presents kinetic results for TNT from seven archived soil samples from five installations. Extracted concentrations generally increase with extraction time for both acetone and methanol, indicating that extraction is not complete in three minutes; however, the additional increase is generally small. The concentration obtained for the three-minute extraction time was always at least 75% of the value obtained after shaking for 18 hours for both solvents. Thus for these high concentration samples, the extraction rate is relatively fast for both acetone and methanol compared to that observed for air-dried, lower concentration field-contaminated soils using acetonitrile and ultrasonic extraction (Jenkins et al. 1989).

Similar kinetic results were obtained for the extraction of RDX from these archived soils (Table 3b). For one soil (Iowa SS-8-005), only 66–67% of the RDX extractable at 18 hours was extracted in the first three minutes. For the other three soils, at least 85% of the concentration found after 18 hours of extraction was attained after only three minutes of shaking for both methanol and acetone. Comparison of the extraction efficiencies of acetone versus methanol cannot be made because extractions were performed on separate subsamples and the analytes were heterogeneously distributed between subsamples. This heterogeneity is evident in both samples from Iowa AAP (Table 3a).

2,4-DNT is a propellant rather than a secondary explosive and its sensitivity to shock and flame in soil was not evaluated by Kristoff et al. (1987). Nevertheless, an on-site method for 2,4-DNT in soil is available (Jenkins and Walsh 1991) and two samples of soil contaminated with high levels of 2,4-DNT were available. Therefore, we decided to determine the extraction rate for this compound when present at high concentrations in soil. Kinetic extraction results for 2,4-DNT in archived soils are presented in Table 3c. Here again, the rate of extraction was rapid with extracted concentrations after only three minutes of shaking, at least 70% of that attained after 18 hours with either acetone or methanol.

Additional kinetic extraction studies were conducted with four field-moist soil samples from Volunteer AAP that contained high levels of TNT (Table 4). The rate of extraction for these samples was quite rapid. At least 88% of the TNT concentration obtained after 18 hours of shaking was attained after only a three-minute extraction time using either acetone or methanol. Concentrations extracted after the three-minute acetone or methanol extraction were at least 70% of the values obtained using the standard laboratory extraction procedure of 18 hours of ultrasonic extraction

Table 4. Extraction rate data for TNT from field-moist soils.

	TNT concentration (µg/g)							
	Volunteer AAP (7R-1)		*Volunteer AAP (7R-4)*		*Volunteer AAP (7R-6)*		*Volunteer AAP (8-3)*	
Time	*Acetone*	*Methanol*	*Acetone*	*Methanol*	*Acetone*	*Methanol*	*Acetone*	*Methanol*
3 min	85300	84000	88800	83500	101000	102000	24600	26700
10 min	88400	85000	91300	82500	97500	102000	28700	26700
30 min	90900	85000	94300	83000	118000	101000	27100	26400
60 min	87700	85500	94800	82500	101000	102000	26900	26300
18 hrs	85800	85500	96300	85500	102000	104000	28000	27000
Ratio:								
3 min/18 hr	0.99	0.98	0.92	0.98	0.99	0.98	0.88	0.99
Method	109000		119000		100000		21300	
8330*	(ACN)		(ACN)		(ACN)		(ACN)	
Ratio:								
3 min/8330	0.78	0.77	0.75	0.70	1.01	1.02	1.15	1.25
EnSys†	82000		76200		78200		23200	
Ratio:								
EnSys/8330	0.75		0.64		0.78		1.09	

* Method 8330 results from acetonitrile ultrasonic extraction for 18 hr followed by RP-HPLC determination.

† EnSys results determined in the field prior to laboratory sample homogenization using acetone extraction and colorimetric determination.

using acetonitrile (Table 4). Also, concentrations obtained in the field using acetone extraction and the EnSys colorimetric method ranged from 64% to 109% of the value obtained after subsequent laboratory homogenization and determination by SW846 Method 8330. These field determinations utilized a three-minute shaking period with acetone followed by a 24-minute rest period and another three-minute period of shaking.

These kinetic extraction experiments indicate that a short three-minute extraction of TNT and RDX from highly contaminated soils is incomplete, whether using acetone or methanol. For the soils we tested, however, extract concentrations after a three-minute extraction were at least 70% of those attained after 18 hours of shaking. The rate of extraction into acetone and methanol appear to be comparable.

It is possible that the rate of extraction of TNT and RDX from other highly contaminated soils could be slower, resulting in a smaller percentage extracted after the short three-minute extraction. However, contaminants present at these high (%) concentrations far exceed the amount required to form a mono-layer on soil surfaces, and so most of the contaminant must be present in crystalline form. Differences in the rate of extraction of crystalline material from soil to soil should be small since it is controlled by the rate of dissolution of the crystalline material. It appears that a value of 70% can be used to represent the percentage of TNT or RDX that would be extracted from a high-concentration sample in a short three-minute extraction. Therefore, field analyses that result in concentrations above 7% should be considered potentially explosive.

Extract dilution study

Because all of the current on-site methods for TNT and RDX in soil were developed to detect low levels (low µg/g) in soil, all these methods, when used for high concentration samples, require that the extracts be diluted substantially before they can be analyzed by colorimetric, immunoassy, or IMS methods. For the EnSys colorimetric method, for example (Table 1), the concentration of TNT in acetone extract from a soil containing 10% TNT is 20,000 mg/L. The linear range for the EnSys method extends from about 0.2 to 10 mg/L, so a dilution of at least 1:2000 is necessary to allow accurate determination. Similar dilutions are necessary for the other colorimetric and immunoassay methods and are probably required for the IMS method as well, although this is yet to be determined. In the laboratory, dilutions of this magnitude are generally conducted using volumetric pipets and serial dilution techniques. In the field, however, this approach is cumbersome and produces a significant amount of solvent waste that requires costly disposal. A simple one-step approach is possible using glass syringes that can deliver microliter quantities of extract. The following experiments were conducted to assess whether the precision and accuracy of this approach is acceptable for this application.

Three experiments were conducted to assess the precision of the syringe dilution. Acetone soil extracts from three field-contaminated soils from Volunteer AAP were used. Five replicate dilutions for each extract were made using 10-µL glass microliter syringes (Hamilton #701, Reno, Nevada). For one sample, a 1:2000 dilution was made by diluting 10.0 µL of the filtered acetone extract into 20.0 mL of 1:1 methanol/water. In another, a 1:10,000 dilution was made by diluting 2.0 µL of the acetone extract to 20.0 mL of 1:1 methanol/water. For the third, a 4.0-µL aliquot was diluted with 20.0 mL of 1:1 methanol/water (1:5000). The methanol/water diluent was selected because analyte concentrations for the diluted samples were determined using RP-HPLC.

The analyte concentrations obtained in the 1:5000 syringe dilution study were compared with a 1:5000 dilution obtained using a two-step serial dilution with glass volumetric pipets and volumetric flasks to assess the accuracy of the syringe dilution approach. This was a two-step dilution: 5.00 mL of extract diluted to 100.0 mL with acetone followed by a 1.00 mL dilution to 250.0 mL with methanol/water. The diluted extracts were determined using RP-HPLC.

Results of the syringe dilution tests are presented in Table 5. For Volunteer sample #1, a 2.0-µL volume of filtered extract was diluted to 20 mL and the precision, as measured by the relative stan-

Table 5. Syringe dilution study—precision and accuracy.

Replicate	Volunteer AAP (#1*) TNT concentration (mg/L)	Volunteer AAP (#2†) TNT concentration (mg/L)	Volunteer AAP (#3**) TNT concentration (mg/L)	Volunteer AAP (#3**) DNT concentration (mg/L)
1	19700	5700	13000	6230
2	20200	5760	13100	6270
3	19800	5700	12400	5980
4	20200	5700	13300	6430
5	20000	5800	13200	6390
Mean	20000	5730	13000	6260
Std Dev	241	46	354	177
RSD	2.41%	0.80%	2.72%	2.83%
			106%	106%
			Concentration relative to that obtained by serial dilution.	

* 1:10000 = 2 µL to 20 mL.
† 1: 2000 = 10 µL to 20 mL.
** 1: 5000 = 4 µL to 20 mL.

dard deviation (RSD), was 2.41%. For Volunteer sample #2, a 10.0-µL sample of filtered extract was diluted to 20 mL and the calculated RSD was 0.80%. For Volunteer #3, a 4-µL sample was diluted to 20 mL and the RSD was 2.72% for TNT and 2.83% for 2,4-DNT. In all cases, the random error introduced using syringe dilution is minor compared with that due to short-range heterogeneity in soil (Jenkins et al. 1996). Likewise, the concentration estimates for TNT and 2,4-DNT were 106% of estimates using serial dilution, indicating that no significant bias would be introduced using this approach.

Based on these results, we believe that extracts to be analyzed to determine whether soils are heavily contaminated with secondary explosives can be successfully diluted using a 10-µL syringe

Table 6. Recommended modifications of methods for commercial kits for high-level determination of explosives.

TYPE Method	Concentration of TNT in extraction solvent for soil sample containing 10% TNT	Solvent diluent recommended	Additional extract dilution required for linear range of test	Resulting concentration and estimated detector response
Colorimetric				
EnSys	20 g/L	Acetone	1:10000	2 mg/L A ≈ 0.35*
Erickson	30 g/L	Methanol	1:10000	3 mg/L Stain length ≈ 28 mm
Jenkins	20 g/L	Acetone	1:10000	2 mg/L A ≈ 0.377
Medary	17.1 g/L	Methanol	1:2500	6.8 mg/L A ≈ 0.28**
Immunoassay				
EM Science (D TECH)	64.6 g/mL	50 µL/15 mL Acetone (1/300)	50 µL/15 mL Bottle B (1/300)	0.71 µg/g ≈ 50 on DTechtor
Idetek (Quantix)	25 g/mL	100 µL/4 mL Acetone (1/40)	100 µL/10 mL MQ (1/100) Diluent tube	5 µg/g ≈ 50% B/Bo†
Millipore (EnviroGard)	25 g/mL	100 µL/25 mL Acetone (1/250)	100 µL/10 mL MQ (1/100) user supplied	4 µg/g ≈ 40% B/Bo
Ohmicron	50 g/mL	100 µL/25 mL MeOH (1/250) Diluent tube	100 µL/25 mL Buffer (1/250)	1.6 µg/g ≈ 40% B/Bo

* Absorbance.
** Estimated for 25-mL cuvette.
† Absorbance of test vs. absorbance of control.

to deliver quantities in the 2.0- to 10.0-µL range. Recommendations for dilution procedures for specific on-site methods are presented in Table 6.

RECOMMENDATIONS

1. Current on-site methods for TNT and RDX in soil rely on a short (one- to three-minute) extraction of soil with either acetone or methanol, prior to determination. Kinetic extraction studies on highly contaminated soils indicate that extraction of TNT and RDX is incomplete when a three-minute extraction period is used with either acetone or methanol. In general, however, a concentration of at least 70% of that attained after an 18-hour extraction is achieved after three minutes of manual extraction. To account for this incomplete extraction, concentrations determined using this short extraction and on-site analysis, at or above 7%, should be considered potentially reactive. We also recommend that protocols that now specify a one- or two-minute extraction period be changed to require a minimum of three minutes of shaking with the extracting solvent. When it is necessary to pinpoint concentrations, a kinetic extraction study as detailed in this report can be carried out on the sample.

2. Current on-site methods for TNT and RDX in soil were developed for detecting low (µg/g) concentrations. For this reason, extracts from highly contaminated soils must be diluted by as much as 1 to 10,000 in order to obtain concentrations in the linear range of the tests. These dilutions can be made using a one-step procedure utilizing glass microliter syringes. The resulting precision and accuracy is adequate for this application.

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13. ABSTRACT (*Maximum 200 words*)

Soils containing high concentrations (>10%) of secondary explosives might detonate from shock or flame, resulting in human injuries or equipment damage during remediation activities. In lieu of expensive and time-consuming protocols involving impact tests, friction tests, and shock gap tests, compositional analysis has been recommended as an expedient method to assess the risk of detonation from heavily contaminated soils. A number of methods now available allow determination of TNT and RDX on site. All of these methods specify solvent extraction with either acetone or methanol to transfer the analyte from the soil matrix to a solvent as the first step in the determination. The rate of extraction of TNT and RDX, when present at percent levels in soil, has not been determined. Protocols currently in use specify very short extraction times (one to three minutes) and results could be biased low if extraction kinetics are slow. The objective of this work was to document the rate of extraction of secondary explosives by acetone and methanol and make recommendations for possible modification of current protocols if warranted. Because solvent extracts from highly contaminated soils will have very high concentrations of secondary explosives, compared with the range of concentrations that can be determined using the various on-site methods, large dilutions will be required. Recommendations are made for a field-expedient method making appropriate dilutions.

14. SUBJECT TERMS

Dilutions	Extraction kinetics	RDX	TNT
DNT	High concentrations	Reactive	
Explosives	On-site analysis	Soils	

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