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DEVELOPMENT OF FIELD SCREENING METHODS FOR TNT, 2,4-DNT AND RDX IN SOIL

THOMAS F. JENKINS and MARIANNE E. WALSH
U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, U.S.A.

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Summary—Simple field-screening methods are presented for detecting 2,4,6-TNT, 2,4-DNT and RDX in soil. A 20-g portion of soil is extracted by manually shaking with 100 ml of acetone for three minutes. After the soil settles, the supernatant is filtered and divided into three aliquots. Two aliquots are reacted with potassium hydroxide and sodium sulfite to form the red-colored Janowsky complex when 2,4,6-TNT is present or the blue–purple complex when 2,4-DNT is present. The third aliquot of the extract is passed through a strong anion exchange resin to remove nitrate and nitrite. Then the extract is acidified and RDX is reduced with zinc to nitrous acid, which is reacted with a Griess reagent to produce a highly colored azo dye. Concentrations of TNT, 2,4-DNT and RDX are estimated from their absorbances at 540, 570 and 507 nm, respectively. Detection limits are about 1 μg/g for 2,4,6-TNT and RDX and about 2 μg/g for 2,4-DNT. Concentration estimates from field analyses correlate well with laboratory analyses.

One of the most serious environmental problems facing the Army is the presence of soil contaminated with residues of high explosives and propellants at sites where the munitions were formerly manufactured, stored, used or demilitarized. The residues TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) are most commonly encountered in munition-contaminated soils because these explosives were extensively produced and used by the military. A major impurity in production grade TNT[1] is 2,4-DNT (2,4-dinitrotoluene), which is a component of several propellant compositions. These compounds do not rapidly decompose in the environment, and, since they leach through the unsaturated zone in water, they pose an immediate problem to ground water.[2] Thus contaminated soil must be located and treated or isolated. Though laboratory methods for determining munitions residues in soil and water have been developed,[3,4,5] reliable field methods are also desirable. Use of field methods would enable efficient identification of zones of high contamination during initial surveys and the interface between clean soil and contaminated soil during clean-up. These methods can also be used for selection of samples for in-depth laboratory examination. The objective of this work was to develop rapid field methods based on simple color-forming reactions for the detection of 2,4,6-TNT, 2,4-DNT and RDX.

As early as 1891 Janowsky[6] observed that colored reaction products were formed when polynitroaromatic compounds reacted with alkali such as potassium hydroxide. Meisenheimer[7] and Jackson and Earle[8] independently proposed a quinoidal structure to explain this phenomenon. In general, Jackson–Meisenheimer anions for dinitroaromatics are blue to purple in color and those from trinitroaromatics are red.[9]

When sulfite ion is present along with hydroxide, addition of sulphite to the aromatic ring can also occur.[10] This anion is more stable than the anion formed from hydroxide alone,[11] with stabilities extended from about 30 min for the hydroxide[12] complex to at least six hours.[11]

When the base catalyzed reaction takes place in a ketone solution such as acetone (Janowsky reaction), addition of the carbanion can also occur, with resulting production of a Janowsky complex (Fig. 1).[13]

These reactions have been used analytically for a number of applications. Yinon and Zitrin[14] give examples of their use for forensic detection of TNT in post-blast debris. Heller *et al.*[15] used the reaction of strong base with TNT as the basis of a field kit for detection of low levels of TNT in water. The use of this kit was later extended to estimation of TNT in soil extracts.[16] In general, their kit provides a field method to detect the presence of TNT in soil, but is less useful for estimating concentration.[17] These

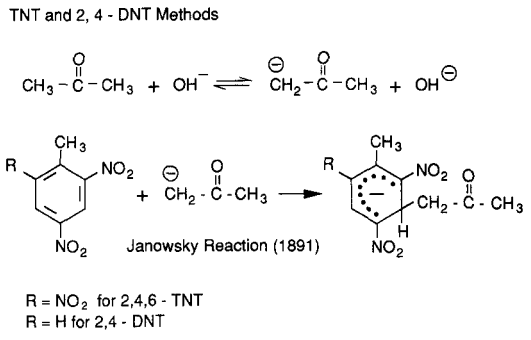

Fig. 1. Reactions used for colorimetric determination of 2,4,6-TNT and 2,4-DNT.

color-forming reactions have not been used to detect 2,4-DNT in soil.

Colorimetric chemical methods have also been developed for RDX for forensic applications.[14] These procedures generally rely on sequential reactions where RDX is first converted to nitrous acid with the Franchimont reaction (Fig. 2). The nitrous acid is used to nitrosate an aniline derivative such as sulfanilic acid and the resulting diazo cation couples to a naphthylamine to form a highly colored azo dye (Griess Reaction). Several pairs of reagents may be used to produce azo dyes.[18] A reagent containing procaine and *N,N*-dimethyl–naphthylamine was initially used for the procedure described in this paper. This choice was based on the work of Wyant,[19] who tested several reagents and found this combination to be best in terms of detection capability and shelf life. However, this liquid reagent was cumbersome to work with in the field since it is sensitive to sunlight. Also, we were concerned about the possible cancer risk associated with *N,N*-dimethylnaphthylamine. Subsequently, we found

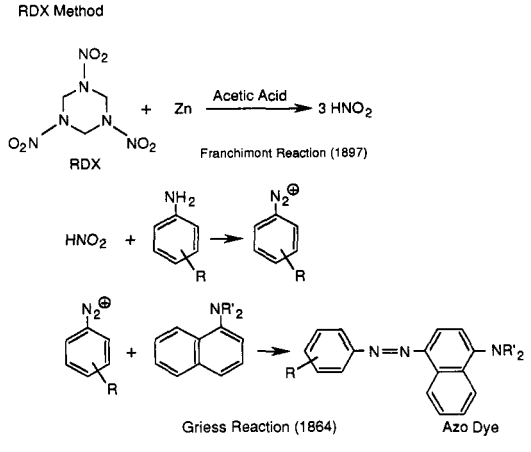

Fig. 2. Reactions used for colorimetric determination of RDX.

that a Hach NitriVer3 powder pillow, which is specifically designed for the determination of nitrite in the field, and distilled water can be substituted for the liquid Griess reagent. The powder pillow contains sodium sulfanilate, 4,5-dihydroxy-2,7-naphthalene–disulfonic acid disodium salt, potassium phosphate monobasic, potassium pyrosulfate and *trans*-1,2-diaminocyclohexanetetra acetic acid trisodium salt. The authors are not aware of a field method for RDX in soil based on the reaction sequence shown in Fig. 1.

Procedure

For these soil methods[20–22] about 20 g of wet soil is shaken with 100 ml of acetone to extract the munition residues, and the extract is filtered with a disposable syringe filter. The methods then depend on the production of colored reaction products (Fig. 3) when three aliquots of these extracts are subjected to two simple reaction sequences. For TNT and 2,4-DNT, portions of the extract are reacted with a strong base and sodium sulfite (Fig. 1). The main difference between the two procedures is the contact time with the reactants before filtration; 3 min for TNT and 30 min for 2,4-DNT. For extracts containing only TNT, a reddish colored Janowsky complex is produced. For those containing only 2,4-DNT (or 2,4- and 2,6-DNT), a bluish–purple complex is produced. If 2,4-DNT is present as a minor component and TNT is present at much higher concentration, DNT will not be detectable with this procedure. The DNT procedure is, however, capable of detecting the presence of DNT in soils contaminated with several types of single-based propellants in which 2,4-DNT is a major component. Several other polynitroaromatics also produce colored complexes and hence are potential interferences.[9] For RDX another portion of the extract is passed through a disposable anion exchange cartridge to remove any nitrate or nitrite. Then the extract is acidified and reacted with powdered zinc. This converts RDX to nitrous acid, which is detected by adding a Hach NitriVer3 powder pillow (Fig. 3) and distilled water. The development of a pink color is indicative of the presence of RDX or one of several other military explosives which are potential interferences (HMX, nitroglycerine, PETN or nitrocellulose).

The intensities of the colors produced by these reactions can be measured with a battery-operated spectrophotometer. The absorbances at 540 nm for TNT and 507 nm for RDX are

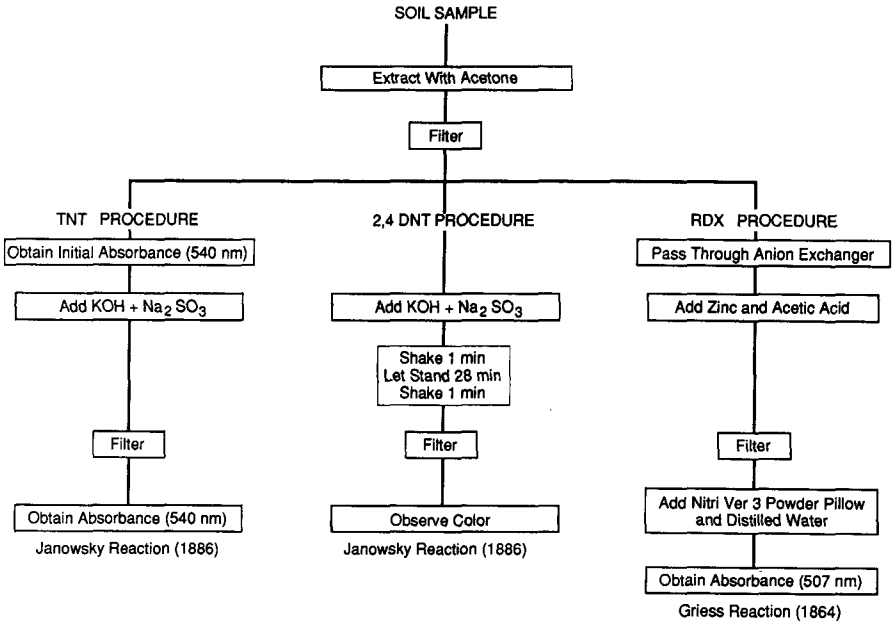

Fig. 3. Flow diagram for colorimetric field methods for 2,4,6-TNT, 2,4-DNT and RDX.

linearly related to concentration. Daily calibration is obtained with a single standard at 2 mg/l. Detection limits are about 1 μg/g for both TNT and RDX.[20,21] The linear range extends to 50 μg/g for TNT and 20 μg/g for RDX, respectively, for undiluted extracts. The absorbance for the 2,4-DNT complex (570 nm) is dependent on the water content of the extract, thus the method is only semiquantitative. The detection limit was 2 μg/g for a standard soil over a moisture content range of 10–50% (wet weight basis).[22]

EXPERIMENTAL

Analytical standards

Analytical standards for TNT and RDX were prepared from Standard Analytical Reference Material (SARM) obtained from the US Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, Maryland. Test solutions of 2,4-DNT were prepared from reagent grade 2,4-DNT (Eastman Organic Chemicals). Standard materials were dried to constant weight in a vacuum desiccator in the dark and standard solutions were prepared in HPLC grade acetone.

Soils

Soils used for laboratory extraction studies included field-contaminated and uncontaminated soils from a number of present and former military installations in ten different states. Interference tests utilized a humus-rich commercial potting soil obtained locally and uncontaminated soils obtained from a variety of military installations.

Soil extraction

Munition residues were extracted by manually shaking a 20-g soil subsample for 3 min with 100 ml of acetone and filtering the extracts with Millex-SR disposable syringe filters.

Generation of the Janowsky complexes for TNT and 2,4-DNT tests

For the TNT test, a pellet of potassium hydroxide and about 0.2 g of sodium sulfite were added to 25 ml of acetone soil extracts. Samples were manually shaken for 3 min, then filtered through a Millex-SR filter unit into a cuvette. The absorbance was measured at 540 nm. Unless the extracts contain a large amount of water, the solid reactants do not completely dissolve.

A similar procedure is used for the 2,4-DNT test except that two pellets of potassium hydroxide and about 0.75 g of sodium sulfite were added, the samples were shaken for one minute, allowed to stand for 28 min, and then shaken again for one minute prior to filtration. Absorbance was read at 570 nm.

Production of an azo dye from RDX

Acetone soil extracts were passed through an Alumina-A strong anion exchange cartridge

Table 1. Absorbance maxima and molar absorptivities for colored products from TNT, 2,4-DNT and RDX field screening tests

Analyte	Absorbance maxima (λ_{max})	Concentration of standard, *mg/l.*	Molar absorptivity $\times 10^{-4}$, *l. mole*$^{-1}$. *cm*$^{-1}$	Color
2,4,6-TNT	462	2.1	2.7	Red
	540		1.77	
2,4-DNT	570	2.9	1.12	Blue→purple
RDX	507	4.0	1.67	Pink

(Supelco, Inc) at 5 ml/min to remove any nitrate and nitrite which could be present. A 5-ml aliquot was acidified with 0.5 ml of glacial acetic acid and reacted with 0.3 g of zinc dust in the barrel of a syringe fitted with a disposable filter unit. This solution was rapidly filtered into a vial containing 20 ml of distilled water. The contents of a Hach NitriVer3 powder pillow were added. The sample is shaken briefly and allowed to stand for 10–15 min. Absorbance is read at 507 nm.

Spectrophotometers

Spectrophotometers were used to measure absorbance at various wavelengths in the visible region of the spectrum. A Coleman Junior II (Model 6/20) (bandpass 20 nm) was used for laboratory tests and either a Hach DR/2 or DR/2000 (bandpass 12 nm) was used in the field. Path length for the cuvettes was either 19 or 25 mm.

RESULTS AND DISCUSSION

Absorbance spectra and molar absorptivities

The visible absorbance spectra of the colored products produced from standards of TNT, 2,4-DNT and RDX (Figs 1 and 2) were obtained from 400–700 nm.[20–22] The absorbance maxima and molar absorptivities are given in Table 1.

The color-forming reactions used for these field screening methods are not specific for TNT, 2,4-DNT and RDX. Other polynitroaromatics such as 1,3-dinitrobenzene (DNB) and 1,3,5-trinitrobenzene (TNB) and polynitrophenols such as picric acid also give colored anions when reacted with strong base. During site clean-up activities, however, the ability to detect these other compounds as well as TNT and 2,4-DNT would be quite useful. Similarly, the same azo dye produced from the RDX test is also produced when other nitramines such as HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and tetryl (2,4,6-trinitrophenylnitramine) or nitrate esters such as NG (nitroglycerine), PETN (pentaerythritol tetranitrate) and NC (nitrocellulose) are treated under similar conditions. Table 2 lists munition-related compounds detected by these screening procedures.

Effects of variable concentrations of water in acetone extracts

In the field, soil extracts will be obtained by manually shaking 20 g of soil with 100 ml of

Table 2. Colors and λ_{max} obtained for acetone solutions of munition related compounds treated with (a) KOH and sodium sulfite or (b) zinc and acetic acid followed by Griess reagent

	KOH and Na_2SO_3		Zinc and acetic acid, Griess reagent	
Compound	Color observed	λ_{max} (400–600 nm)	Color observed	λ_{max} (400–600 nm)
1,3-Dinitrobenzene	Purple[7,17]	570	None	—
2,4-Dinitrotoluene	Blue[7,17]	570	None	—
2,6-Dinitrotoluene	Pinkish-purple[17]	550	None	—
1,3,5-Trinitrobenzene	Red[7,17]	460, 560	None	—
Tetryl	Orange[17]	460, 550	Pink	507
2-Amino-DNT	Pale yellow[17]	400	None	—
4-Amino-DNT	None[17]	—	None	—
Nitroglycerine	None[17]	—	Pink	507
PETN	None[17]	—	Pink	507
RDX	None[17]	—	Pink	507
HMX	None[17]	—	Pink	507
Picric Acid	Reddish-orange[7]	420	None	—
2,4-Dinitrophenol	Yellowish-orange[7]	430	None	—
TNT	Red[7,17]	462, 540	None	—

acetone. Since the soil will be moist in most cases, water will be a component of the soil extracts. In addition to a small amount of dilution, the presence of water may affect the kinetics of these reactions. To investigate this effect, standard solutions of TNT, 2,4-DNT and RDX were prepared with water added to simulate the extracts that would be obtained from soils with moisture contents ranging from 0–100% (wet weight basis). For all three analytes, little or no color formed when no water was present (Fig. 4). Over the range of moisture contents (10–75%) that should include the large majority of surface soils from potentially contaminated sites, absorbance varied little for the TNT and RDX solutions. However, absorbance for the 2,4-DNT standard significantly declined for water contents greater than 10%. Based on this variability, determinations for 2,4-DNT will be semi-quantitative while the corresponding procedures for TNT and RDX may be used quantitatively.

Reagent contact time

Experiments were conducted to determine if reagent contact time had an effect on measured absorbance. Contact time with potassium hydroxide and sodium sulfite was varied from 1 to 18 min for TNT and from 1.5 to 60 min for 2,4-DNT, after which solutions were filtered and absorbances measured. All experiments were conducted at laboratory temperature ($22 \pm 2°$).

Maximum absorbance for TNT was obtained after 3 min of continuous shaking.[20] Exposure to the reagents for periods longer than 8 min resulted in reduced absorbance at 540 nm. Thus a 3-min reaction time was selected.

For 2,4-DNT solutions, the time at which maximum absorbance was obtained depended on the water content of the solutions. In general, the absorbance obtained after 30 min of intermittent shaking was at least 90% of the maximum.[22] An additional experiment was performed to compare various shaking protocols. We found that if the solution was shaken initially for one minute, allowed to stand for 28 min, then shaken again for one minute just prior to filtration, the absorbance obtained was not significantly different from protocols that required more shaking.[22]

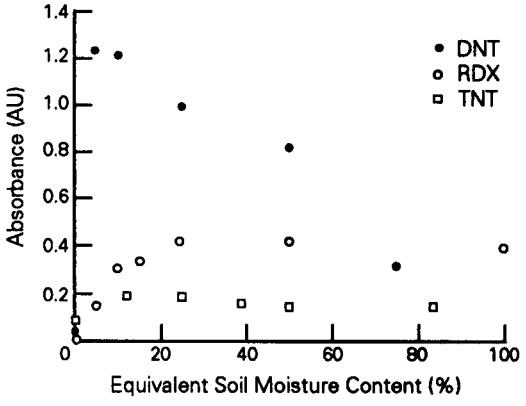

Fig. 4. Dependence of measured absorbance on water content of soil extracts.

Development of the azo dye from RDX is a two-step procedure. First, the RDX is reacted with zinc dust and acetic acid to produce nitrous acid. The nitrous acid then reacts with a Griess color reagent to produce the azo dye. The length of time the RDX is allowed to react with the zinc dust and acetic acid was found to be critical.[21] Reaction kinetics are fast when water is present in the acetone extract.[21] Contact times exceeding 30 sec resulted in less nitrous acid production, presumably because the nitrous acid was further reduced. Once the nitrous acid is produced, the solution must be filtered to remove the zinc dust. Because of the fast kinetics, this filtration is conveniently performed by reducing the RDX in the barrel of a syringe fitted with a disposable filter unit. Once the filtered solution is added to the color developing solution, full color development takes about 15 min.

For all three tests, the colors of the final solutions were stable for at least one hour.[20–22]

Potential interferences (other than munitions-related compounds)

Experiments with a variety of blank soils indicated that the color of acetone extracts will vary from colorless to yellow depending on the amount of humic matter present. Background absorbances for the yellow extracts is greatest over the range 400–500 nm,[20] and for this reason TNT determinations are made at 540 nm rather than at 462 nm, despite the lower molar absorptivity at 540 nm (Table 1). After soil extracts are reacted with potassium hydroxide and sodium sulfite for 3 min, the absorbance at 540 nm approximately doubles; thus an initial absorbance measurement must be made on aliquots of acetone extracts subjected to the TNT screening procedure and the DNT procedure as well, if used quantitatively. The initial absorbance is doubled and subtracted from the final absorbance to estimate TNT concentration.

As will be discussed later, heavy metal cations such as copper were found to interfere with 2,4-DNT determinations. These cations could form complexes with either the unreacted DNT[23] or the Janowsky complexes (Fig. 5).

For the RDX test, background absorbance from humic material is not a problem. Once the acetone extract is acidified and mixed with the color-forming reagent, the humic material precipitates and may be removed by filtration. Experiments with a wide variety of blank soils showed that background was negligible in all cases.[21]

Since the RDX test measures nitrous acid concentration, soil samples containing nitrite or nitrate would give a false positive if the nitrite and nitrate are not removed prior to reaction of RDX with zinc. This is accomplished by passing the extract through a disposable 3-ml strong anion exchanger (Supelco Alumina A). Experiments indicate that over 98% of the nitrate in a 9.8-mg/l. test solution was removed with this procedure.[21]

Extraction efficiency of field procedure

For a field method to provide accurate estimates of analyte concentration in the soil, the extraction step must be rapid. Previous extraction studies indicated that long extraction times were required when acetonitrile or methanol were used as the extraction solvent for nitroaromatics and nitramines.[24]

In order to determine how rapidly acetone will extract TNT, 2,4-DNT and RDX from soil,

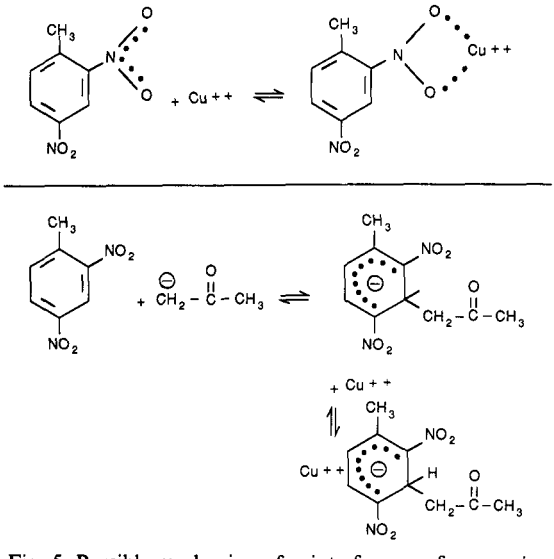

Fig. 5. Possible mechanisms for interference of copper ion with the 2,4-DNT method.

field-contaminated soil samples from 14 different sites were extracted with acetone, with 3 min of manual shaking. An aliquot of the extract was removed and the remaining soil/acetone slurries placed in an ultrasonic bath for 18 hr. Both sets of extracts (3 min and 18 hr) were analyzed by RP–HPLC as described elsewhere.[3,20] The results are presented in Table 3. The average recovery after 3 min of manual shaking with acetone for TNT was 96% and for RDX was 98% of that obtained with the more exhaustive procedure, indicating that acetone is an excellent extraction solvent with respect to its extraction kinetics for these two analytes over a wide concentration range.[20,21] The average recovery for 2,4-DNT was only 80.5%, with one low recovery (40.1%) for the soil with highest 2,4-DNT concentration.[22] Overall, the extraction efficiencies for all three analytes are sufficient for a field screening method.

Comparison of analyte concentration estimates

The field screening procedures were first tested in the laboratory with previously air-dried field-contaminated soils. Prior to extraction, the soils were wetted to simulate the moisture that would normally be present under field conditions. Estimates of analyte concentrations obtained by the colorimetric field procedure were correlated against those obtained by the standard RP–HPLC method. The colorimetric results for TNT were correlated with both the TNT estimate by HPLC and the sum of TNT and TNB. The best correlation was found with the sum of TNT plus TNB and resulted in a slope of 1.15 and an R^2 of 0.985 (Fig. 6). A paired t-test indicated that the concentration estimates for TNT from the colorimetric method and the sum of TNT and TNB by the HPLC procedure were not different at any level of significance.[20] Thus it appears that the colorimetric results are best represented as the sum of TNT plus TNB. The slope of 1.15 indicates that, in general, the colorimetric procedure gives a slightly greater estimate for TNT than can be accounted for by TNT and TNB (Fig. 6). One interpretation of these results is that other TNT degradation products such as trinitrobenzoic acid, trinitrobenzyl alcohol, and trinitrobenzaldehyde,[25] which are not identifiable by RP–HPLC analysis of the extracts, also form colored Janowsky complexes, thereby producing positive interference.

While we do not believe that the 2,4-DNT procedure can be used quantitatively in the field

Table 3. Comparison of extraction efficiency of field procedure and standard laboratory procedure

Sample origin		Analyte	Concentration, μg/g Field procedure*	Lab procedure†	Recovery, % by field procedure‡
Nebraska Ordnance Plant	A	TNT	0.065	0.071	91.5
	B	TNT	340	349	97.4
	C	TNT	63.5	67.9	93.5
	D	TNT	0.32	0.32	122
Hawthorne AAP (Nev.)	A	TNT	4.53	4.75	95.4
	B	TNT	5.79	5.65	102
	C	TNT	0.79	0.90	87.3
Weldon Springs (Mo.)	A	TNT	0.96	1.26	76.2
	B	TNT	163	176	92.6
	C	TNT	0.075	0.077	97.4
Vigo Chem. Plant (Ind.)		TNT	11.7	13.4	87.3
Hastings East Ind Park (Neb.)		TNT	67.6	68.8	98.3
Sangamon Ordnance Pt. (Il.)		TNT	21.5	23.2	98.2
Raritan Arsenal (NJ)		TNT	71.7	80.6	98.0
Lexington-Bluegrass Depot (Ky)		TNT	5.90	7.11	83.0
Chicksaw Ordnance Works (Ind.)		TNT	0.21	0.16	131
Nebraska Ordnance Plant	A	RDX	13.6	14.1	98.3
	B	RDX	60.2	65.9	95.5
	C	RDX	1073	1080	99.7
	D	RDX	9001	10,455	92.6
Hawthorne AAP (Nev.)	A	RDX	1.97	2.01	99.0
	B	RDX	3.32	2.96	105
Lexington Bluegrass Depot (Ky)		RDX	9.10	9.37	98.5
Camp Shelby (Ms.)	A	2,4-DNT	3.4	4.2	80.9
	B	2,4-DNT	226	563	40.1
	C	2,4-DNT	6.7	7.3	91.8
Eagle River Flats (Ak.)	A	2,4-DNT	12.7	13.6	93.4
	B	2,4-DNT	7.4	7.7	96.1

*20 g soil shaken with acetone for 3 min.
†20 g soil extracted with acetone for 18 hours in sonic bath.
‡Relative to laboratory procedure.

since calibration depends on water content, we tested the method in the lab with air-dried soils wetted such that the moisture content was 10%. This moisture content was chosen since absorbance would be close to maximum, based on the previous experiment on the effect of water content. Only five soils were available that were contaminated primarily with 2,4-DNT. These soils were collected from explosive ordnance disposal sites. Results are given in Table 4. The field procedure severely underestimated the concentration of 2,4-DNT in one sample from Eagle River Flats, Alaska. This particular sample was also contaminated with copper (347 μg/g). As discussed previously, copper is a potential interferant since it may complex with 2,4-DNT or the Janowsky complex. Correlation between estimates for the remaining four samples was excellent (>0.999); however, the field procedure underestimated 2,4-DNT concentration by 15–25%.

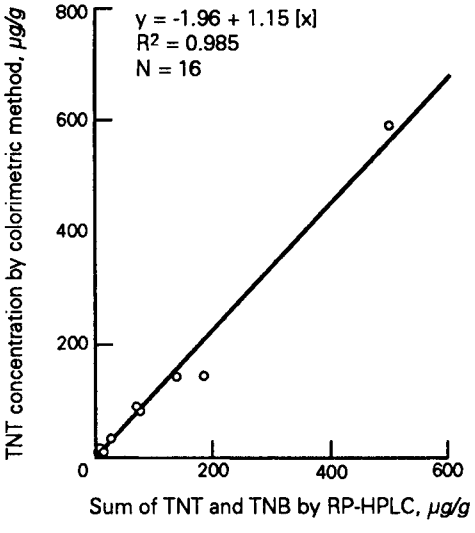

Fig. 6. Correlation of concentration estimates for TNT, using the field method with the sum of TNT and TNB by RP-HPLC.

To further explore the potential for false negatives, a series of soils from a number of Army installations that had been previously determined to be free of munitions residues were spiked with 2,4-DNT and analyzed by the field screening procedure. In all cases 2,4-DNT was easily detected, but as observed earlier, the measured concentrations were consistently lower than anticipated by up to 30%.[22] The magnitude of interference observed for the

Table 4. Comparison of colorimetric and RP–HPLC analysis of soil extracts

Sample origin	Colorimetric method, μg/g	RP–HPLC method, 2,4-DNT μg/g	RP–HPLC method, 2,6-DNT μg/g
Camp Shelby (Ms.)—A	3.3	3.4	0.6
Camp Shelby (Ms.)—B	203	226	12.1
Camp Shelby (Ms.)—C	5.0	6.7	0.2
Eagle River Flats (Ak.)—A	11.4	12.7	0.9
Eagle River Flats (Ak.)—B	0.8	7.4	0.5

Eagle River Flats sediment was not observed in any of these soils.

Eleven field-contaminated soils were used to compare the RDX concentrations estimated by the field method with those obtained by RP–HPLC analysis. The results from the field method were correlated with those obtained by the HPLC method for both RDX alone and the sum of RDX and HMX. The best correlation was obtained with RDX plus HMX and resulted in a slope of 0.9 and an R^2 of 0.995 (Fig. 7). Paired t-tests indicated that the estimates of RDX concentration obtained by the field procedure were not significantly different (0.05 significance level) from those obtained by the HPLC procedure for RDX alone or for the sum of RDX and HMX.

Estimation of detection capability

The reporting limits of TNT and RDX concentrations with these field procedures were established with the method of Hubaux and Vos[26] as adapted by the US Army Toxic and Hazardous Materials Agency.[27] The calculated certified reporting limits were 0.72 and 1.4 μg/g for TNT and RDX, respectively.

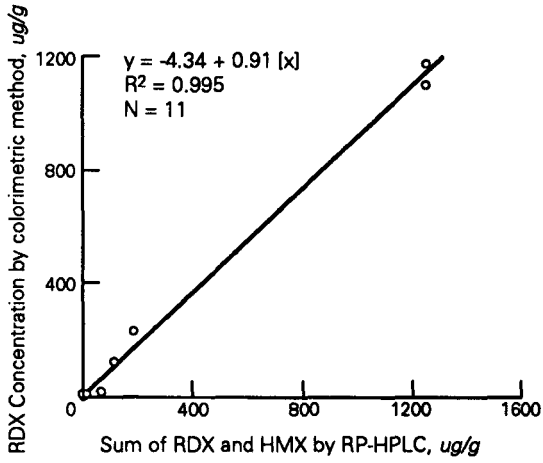

Fig. 7. Correlation of concentration estimates for RDX, using the field method with the sum of RDX and HMX by RP–HPLC.

The reporting limit for 2,4-DNT was 2 μg/g based on a certification procedure for methods that simply screen for contamination.[27] For the certification procedure four soils were spiked at a chosen concentration, in this case 2 μg/g. These soils, along with four soil blanks, were processed according to the method. After color development, four individuals were asked to distinguish the soil spikes from the blanks. Certification was performed three times, each at a different soil moisture content (10, 25 and 50% wet weight basis). In all cases, the soil spikes could be distinguished from blanks with 100% accuracy at 2 μg/g.

Field testing

Both the TNT and RDX procedures have been field tested and the concentration estimates obtained in the field compared with those obtained on separate subsamples processed by the standard RP–HPLC procedure.[3] Results are presented in Table 5.

The TNT procedure was initially tested at Umatilla Army Depot, Oregon. Since TNT concentrations were expected to be very high, a smaller subsample of soil was used and the extracts diluted before reaction with potassium hydroxide and sodium sulfite. This field test was conducted before the importance of reagent contact time was understood. Contact times of 10 min were used. Except for one sample, the results of laboratory analysis were higher than those obtained with the field method. This sample had a TNT concentration an order of magnitude higher than any of the other samples and was not included in this correlation. Correlation analysis was conducted comparing the field and laboratory results on the remaining 10 samples. This analysis resulted in an R^2 value of 0.865 which was significant at the 99% confidence level. The slope of the best fit relationship was 0.627, indicating the field procedure, on the average, gave results only about 63% as high as the laboratory results.

Table 5. Comparison of field estimates to lab estimates of concentration. Determinations made on separate subsamples

	Concentration, $\mu g/g$			
	TNT		RDX	
Site	Field*	Lab	Field*	Lab
Umatilla Depot, Oregon	1060	2250	NT†	NT
	3560	7430	NT	NT
	704	1180	NT	NT
	3180	4030	NT	NT
	4490	8590	NT	NT
	2530	3990	NT	NT
	84	131	NT	NT
	102,000	38,600	NT	NT
	6610	7690	NT	NT
	109	183	NT	NT
	716	1300		
Newport, Indiana	NT	NT	$<d$	0.05
	NT	NT	1.0	1.31
	NT	NT	1.7	3.15
	NT	NT	6.0	15.5
	NT	NT	6.8	8.4
	NT	NT	160	299
	NT	NT	38	38.6
	NT	NT	48	258
	NT	NT	660	1800
	NT	NT	2100	3170
	NT	NT	4300	12,200

*Not corrected for moisture.
†NT = not tested.

Two factors may have contributed to the low results for the field method. First, an excessively long reagent contact time prior to filtration was used for the samples. Thus the absorbance would have been reduced relative to its maximum value. Second, the TNT concentrations in the Umatilla soil were much higher than those in the other field-contaminated soils tested, and the percentage extracted in the short extraction time used by the field method could have been reduced compared to the 18-hr extraction with acetonitrile used in the laboratory procedure. Nevertheless, the field results were encouraging for a first test.

The RDX method was field tested in Newport, Indiana. Correlation between estimates for all 11 samples yields a correlation coefficient of 0.95. However, the slope of the best fit relationship is only 0.36. This low value for the slope is strongly influenced by the last data point, where the estimates of RDX concentration were 4300 and 12,000 μg/g for the field and laboratory procedures, respectively. If the comparison is made with only those soils that had absorbances for the field procedure within the linear range (less than 0.7 absorbance unit) without dilution of the acetone extract, the R^2 value is 0.94 and the slope is 0.95. We feel this comparison is justified since for a field screening test we wish to distinguish the boundary between uncontaminated and contaminated soil, making accuracy at the lowest concentrations most important.

The TNT and RDX methods were also field tested at Eagle River Flats, Alaska, and Camp Shelby, Mississippi. Forty samples were screened at Eagle River Flats; all gave negative tests. The samples were subsequently analyzed by RP–HPLC and no explosive residues were detected in any sample. Some practical information was gained from this field test. Both potassium hydroxide and sodium sulfite are hygroscopic and should be protected from moisture under humid conditions by keeping reagent bottles tightly closed. Low ambient temperatures caused two problems. First, glacial acetic acid freezes at 16.6°. Second, reagent contact times for the TNT procedure had to be extended. The optimum time which depends on temperature was determined by observing the color development in a spiked sample.

At Camp Shelby, 22 samples were screened. Three samples gave positive indications for the presence of TNT, but no TNT was observed in these three samples by RP–HPLC. All three contained 2,4-DNT, as did some of the other samples, one of which was observed to give a purple color in the field TNT test. Nineteen of the soils gave a positive field screening response

for the RDX test. RDX was only detected by RP-HPLC in one of these soils. However, the RDX tests will also give a positive response for NC. NC is the primary component of single, double and triple base propellants. 2,4-DNT is an additive of single base propellant and its widespread presence at this site probably indicates the NC is present as well at even higher concentrations. In fact, propellant grains were observed scattered about the area. However, the soils were not analyzed for NC, since there is no reliable analytical technique to determine this compound in soil. So the explanation for false positives for the Camp Shelby samples must remain speculation. It should be pointed out that soils from this site were taken from areas which served as both an explosive ordnance disposal area and an artillery impact area and could have traces of a wide variety of munition compounds.

CONCLUSIONS

Simple field screening methods were developed for detecting 2,4,6-TNT, 2,4-DNT and RDX in soil. The procedure involves the extraction of munition residues from a soil subsample with acetone. Three portions of the extract are then reacted to two sets of reagents that form colors in the presence of nitroaromatics or nitramines. Concentration estimates obtained by this colorimetric procedure compared favorably with those obtained by the standard laboratory procedure. Field tests were conducted and the methods were found to be suitable for use under field conditions.

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