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October 1991

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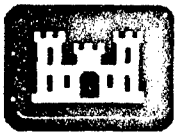
Special Report 91-17



U.S. Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

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Thomas F. Jenkins and Marianne E. Walsh

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Prepared for
U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
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PREFACE

This report was prepared by Dr. Thomas F. Jenkins, Research Chemist, Geochemical Sciences Branch, Research Division, and Marianne E. Walsh, Research Physical Scientist, Applied Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this research was provided by the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland (R-90, Multi-Analytical Services), Martin H. Stutz, Project Monitor.

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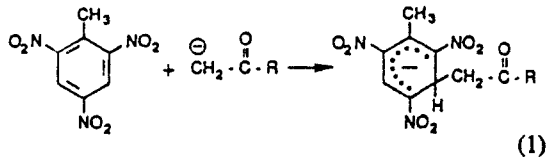
Field Screening Method for 2,4-Dinitrotoluene in Soil

THOMAS F. JENKINS AND MARIANNE E. WALSH

INTRODUCTION

2,4-Dinitrotoluene (2,4-DNT) is a major component of several munitions formulations used by the U.S. Army (Table 1). It is also one of the major impurities in production grade TNT (Leggett et al. 1977) and is often found in contaminated soils at army ammunition plants, depots and explosive ordnance disposal areas (Walsh and Jenkins, in press). Since 2,4-DNT migrates rapidly through the soil to groundwater and is thought to be toxic in water at quite low concentrations (Etnier 1987), methods are needed to locate sources of this contaminant in the soil. Laboratory procedures to quantify the concentration of 2,4-DNT in soil samples have been developed but no rapid field method is currently available to screen for this contaminant.

Field screening methods have recently been developed for TNT and RDX (Jenkins 1990, Walsh and Jenkins 1991). The TNT method involves extraction of the soil with acetone and generation of the red-colored Janowsky complex by addition of potassium hydroxide and sodium sulfite



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For qualitative screening, the reddish color can be detected visually or, for semiquantitative analyses, the color intensity can be obtained by measuring the absorbance at 540 nm using a battery-operated spectrophotometer. Many years ago, Bost and Nicholson (1935) observed that 2,4-DNT and many other dinitrated aromatic compounds react with a strong base to form a purplish-blue-colored solution, while trinitrated aromatics tended to form reddish-colored solutions. Jenkins (1990) reported that 2,4-DNT in soil extracts formed a blue-colored solution (λ_{max} = 570 nm) when reacted with potassium hydroxide and sodium sulfite. Field testing of the TNT procedure at two Explosive Ordnance Disposal (EOD) sites resulted in the observation that several soil extracts turned a bluish color when reacted with a strong base. Subsequent laboratory analysis revealed that these soil extracts contained 2,4-DNT as the principle munitions component. These results stimulated our interest in optimizing this reaction for field detection of 2,4-DNT in soils.

Table 1. U.S. Army munitions containing 2,4-dinitrotoluene.

Explosive (E) or Propellant (P)	*Percent 2,4-DNT in formulation*
M1 (P)*	10
M6 (P)*	10
IMR (P)*	8
Composition C (E)†	5–10

* U.S. Army (1984).
† Midkiff and Washington (1976).

OBJECTIVE

The objective of this research is to develop a simple field screening method for 2,4-DNT in soil based on the reaction of acetone solutions of 2,4-DNT with a strong base, which results in the development of a bluish-colored Janowsky complex. We hoped that the method could utilize an aliquot of the same acetone extract

obtained for the TNT and RDX field methods. The major intent of the research is aimed at detecting soils in which 2,4-DNT is a major munition component, rather than for soils where TNT is the major component and 2,4-DNT is present only as an impurity in TNT. The rationale for this strategy is that this method will be used in conjunction with the TNT field method, and soils in which TNT is detected will be subjected to further laboratory analysis where traces of 2,4-DNT will also be detected.

EXPERIMENTAL

Analytical standards

Analytical standards for 2,4-DNT, 2,6-dinitrotoluene (2,6-DNT) and TNT were prepared from Standard Analytical Reference Materials (SARM) obtained from the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, Maryland. The SARMs were dried to constant weight in a vacuum desiccator in the dark and stock standards were prepared in Alltech HPLC grade acetone. Test solutions of 2,4-DNT were prepared from reagent grade 2,4-DNT (Eastman Organic Chemicals) in either Alltech HPLC grade acetone or commercial grade acetone obtained at a local hardware store. The water added to simulate moisture in field soils was Type 1 reagent grade water. Test solutions of 2,6-DNT were prepared from SARMs in an identical manner.

Soils

Soils used for laboratory extraction studies included field-contaminated and uncontaminated soils from a number of present and former military installations in 10 different states. Certification testing of the method was conducted using USATHAMA standard soil. Interference tests utilized a commercial potting soil obtained locally that was rich in humus and soils from military installations that were negative for munitions as determined by RP-HPLC.

Soil extraction

2,4-DNT is extracted from 20-g subsamples of wet soil by manual shaking with 100 mL of acetone in a 250-mL glass bottles. Samples are allowed to settle for 5 minutes, then a 25-mL aliquot of each acetone extract is filtered through a Millex SR 0.5-µm membrane.

Spectrophotometer

Absorbance measurements at 570 nm were obtained on a Hach DR/2000 spectrophotometer (bandpass 12 nm) operated in the battery-powered mode. Measurements were made using 25-mm matched cuvettes containing acetone to set zero absorbance.

Generation of Janowsky complex

Two pellets of potassium hydroxide (KOH) and approximately 0.75 g of sodium sulfite (Na_2SO_3) were added to 20–25 mL of solutions of DNT. Solutions were manually shaken periodically over a 30-minute period, then filtered through a Millex-SR filter unit into a cuvette. Absorbance was read at 570 nm.

RESULTS AND DISCUSSION

Absorbance spectrum for the Janowsky complex from 2,4-DNT

A 2.9-mg/L solution of 2,4-DNT was prepared in 95% acetone/5% water and Janowsky complexes were generated by addition of KOH and Na_2SO_3. The solution was filtered and the absorbance spectrum was obtained from 400 to 650 nm on a Hach spectrophotometer (Fig. 1). The absorbance maximum (λ_{max}) was observed at about 570 nm with a molar absorptivity of 1.12×10^4 L cm^{-1} mole^{-1}. The solution was initially blue and slowly changed to purple on standing. Colors and λ_{max} for other nitroaromatics, nitramines and nitrate esters subjected to the same reagents are given in Table 2.

Clearly, a colorimetric-based method will not be able to distinguish 2,4-DNT from several other dinitroaromatics, including 2,6-DNT. However, the objective of this work is to develop a field screening method with a low incidence of false negatives. The presence of one of the other dinitroaromatics would be of interest to anyone screening for 2,4-DNT and subsequent laboratory analysis can easily distinguish 2,4-DNT from these potential interferences.

The molar absorptivity obtained for the 2,4-DNT anion at 570 nm is somewhat lower than that obtained for TNT at 540 nm (1.12×10^4 vs 1.77×10^4). The back-

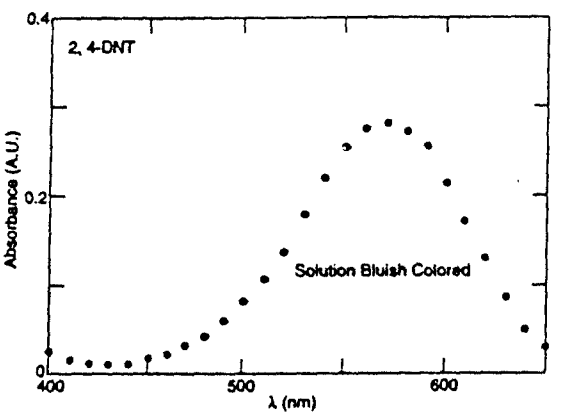

Figure 1. Absorbance spectrum of Janowsky reaction product of 2,4-DNT.

Table 2. Colors and λ_{max} obtained for acetone solutions of compounds treated with KOH and sodium sulfite.

Compound	Color observed: Jenkins (1990)	Color observed: Bost and Nicholson (1935)	λ_{max} (400–600 nm)
Nitrobenzene	None	None	—
o-nitrotoluene	None	None	—
m-nitrotoluene	None	None	—
p-nitrotoluene	None	None	—
1,3-dinitrobenzene	Purple	Purplish-blue	570
2,4-dinitrotoluene	Blue	Blue	570
2,6-dinitrotoluene	Pinkish-purple	—	550
1,3,5-trinitrobenzene	Red	Red	460,560
Tetryl	Orange	—	460,550
2-amino-DNT	Pale yellow	—	400
4-amino-DNT	None	—	—
Nitroglycerine	None	—	—
PETN	None	—	—
RDX	None	—	—
HMX	None	—	—
Picric acid	—	Reddish-orange	420
2,4-dinitrophenol	—	Yellowish-orange	430
TNT	Red	Red	462–540

ground absorption due to humic organics extracted from soil, however, is significantly lower at 570 nm than at 540 nm. Thus, the detection limit obtainable should be similar to the 1-µg/g level achieved for TNT using this colorimetric approach (Jenkins 1990).

Effects of variable water concentrations in acetone extracts

Extraction of field soils with acetone results in extracts with concentrations of water that can vary significantly. For the TNT field method, both the rate of color development and the maximum absorbance obtained were related to the percentage of water in the acetone (Jenkins 1990). To minimize this effect for TNT detection, the weight of soil and volume of extraction solvent were set at 20 g and 100 mL, respectively, so that moisture levels in the acetone extracts were maintained within acceptable bounds.

An experiment was conducted to determine the extent of this problem for 2,4-DNT detection. Three solutions of 2,4-DNT (2.88 mg/L) were prepared with water concentrations corresponding to soil extracts (20 g soil/100 mL acetone) containing 10, 25 and 50% moisture (wet weight of soil basis). Eight replicate aliquots of each solution were reacted with KOH and Na_2SO_3 in glass vials using reagent contact times varying from 1.5 to 60 minutes. Each vial was manually shaken periodically during the contact time, filtered through a Millex SR filter and the absorbance obtained at 570 nm. Results are shown in Figure 2. The time to reach maximum absorbance varied from 15 minutes for the low water content solution to 60 minutes for the highest water content solution. In general, the absorbance obtained at 30 minutes was at least 90% of the maximum and the 30-minute contact time was selected for future experiments.

To explore the effect of variable water concentrations on color intensity, acetone solutions of 2,4-DNT at 0.86 and 5.76 mg/L were prepared containing water concentrations that corresponded to soil moisture levels ranging from 0 to 75% (wet weight of soil basis), assuming that a 20-g subsample was extracted with 100 mL of acetone. Aliquots of these solutions were reacted with KOH and Na_2SO_3 for 30 minutes with periodic shaking and then filtered. Absorbances were obtained at 570 nm and the

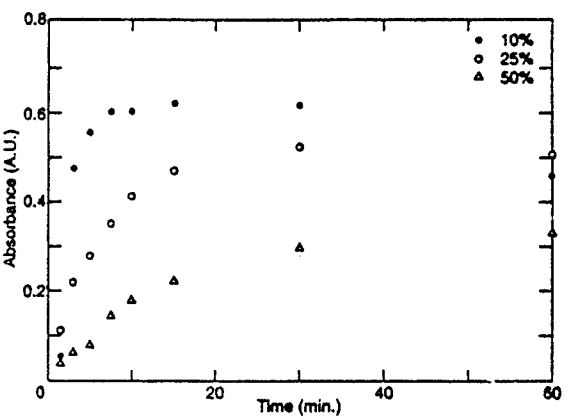

Figure 2. Effect of variable water concentrations in acetone on rate of color development.

Table 3. Absorbance of acetone solutions at 570 nm as a function of soil moisture content and 2,4-DNT concentration (30-minute reagent contact time).

Soil moisture content (% on wet weight basis)	Absorbance (A.U.) 2,4-DNT concentration (mg/L) 0.86	2.88	5.76
0	0.056	—	0.036
5	0.158	—	1.239
10	0.189	0.620	1.221
25	0.169	0.526	0.991
50	0.110	0.298	0.824
75	0.072	—	0.321

Table 4. Stability of absorbance (570 nm) with time for filtered solutions of 0.86 mg/L 2,4-DNT following reaction with KOH and Na_2SO_3.

Time after filtration (min.)	Absorbance (A.U.) soil moisture (% of wet weight) 5	10	25	50	75
0	0.158	0.189	0.169	0.110	0.072
6	0.154	0.189	0.172	0.109	0.080
30	0.150	0.194	0.179	0.122	0.087
60	0.167	0.175	0.167	0.125	0.091

results are presented in Table 3. When no water was added, the resulting solution was colorless to yellowish. In all other cases, the resulting solution was light purple. Absorbances at 570 nm for both 2,4-DNT concentrations varied significantly, with low absorbance obtained at very low or very high water concentrations. Since water contents will be neither controllable nor easily measurable in the field, the variation of absorbance with moisture level will be a limiting factor for use of the method to obtain semiquantitative results. The vast majority of surface soils have moisture contents in the range of 5–50% (wet weight basis) and in this range the absorbance varied from 0.110 to 0.189 A.U. for the 0.86-mg/L concentration and from 0.824 to 1.239 A.U. for the 5.76-mg/L concentration. Because of this variability, this procedure to determine 2,4-DNT will be less quantitative than the corresponding procedure for TNT.

Stability of filtered solution

A test was conducted to determine how long the absorbance was stable after extracts are filtered. A series of solutions was prepared with 2,4-DNT at 0.86 mg/L, but with variable water concentrations corresponding to extracts from soils with water contents ranging from 5–75% (wet weight basis). Aliquots of each solution were reacted with KOH and Na_2SO_3 and shaken periodically for 30 minutes and then filtered. Absorbance measurements were made over a period of 60 minutes after filtration (Table 4). Over the moisture range of 5–50%, absorbances were stable to within 15% of the highest reading obtained. Thus, absorbance measurements can be made up to an hour after filtration without substantially affecting results.

Extraction efficiency of field procedure

The extraction efficiency of the field procedure (3 minutes of manual shaking in acetone) was assessed for TNT and RDX (Jenkins 1990, Walsh and Jenkins 1991). In both cases the field procedure was compared with the laboratory method, which consists of an 18-hour extraction with acetonitrile in an ultrasonic bath (Jenkins et al. 1989). The mean extraction efficiency for the 3-minute field method was 96% for TNT and 98% for RDX, indicating that the procedure was clearly adequate for field screening.

To assess the extraction efficiency of the field method for 2,4-DNT, an experiment was conducted with six field-contaminated soils from Eagle River Flats, Alaska, and Camp Shelby, Mississippi. These were the only soils available that contained 2,4-DNT but comparatively little or no TNT. All were collected from EOD sites. A 20-g portion of each soil was placed in a 200-mL glass bottle, and 2.0 mL of deionized water and 100 mL of acetone were added. The water was included since the soils had been previously air dried. The samples were manually shaken for 3 minutes and allowed to stand for 30 minutes while the particles settled. A 22-mL aliquot was removed and the remainder of the suspension placed in an ultrasonic bath for 18 hours. The suspensions were then removed and allowed to stand for 30 minutes before we took a second 22-mL aliquot.

Both extracts were filtered through Millex SR disposable filter units and analyzed by reversed-phase HPLC (Jenkins et al. 1989). The results are presented in Table 5.

For all the samples, except Camp Shelby B and D, the results for the 3-minute field extraction method were at least 80% of the concentration obtained for the more

Table 5. Comparison of extraction efficiency for field procedure vs extended laboratory procedure.

Sample origin	2,4-DNT concentration (µg/g) Field extraction procedure	Laboratory extraction procedure
Camp Shelby (Miss.) A	3.4	4.2
Camp Shelby (Miss.) B	226	563
Camp Shelby (Miss.) C	6.7	7.3
Camp Shelby (Miss.) D	0.0	0.2
Eagle River Flats (Alaska) A	12.7	13.6
Eagle River Flats (Alaska) B	7.4	7.7
Spiked soil	19.5	19.8

exhaustive laboratory method. Camp Shelby B had a very high concentration of 2,4-DNT and the concentration obtained for the 3-minute field extract was only 40% of the value for the laboratory extraction method. Results from the 3-minute extraction did indicate that a fairly high level of 2,4-DNT was present, which is probably adequate for a field screening procedure. Camp Shelby D contained much lower levels of 2,4-DNT than the other soils tested and the 3-minute extraction time was not adequate. The field method, however, will probably not be sufficiently sensitive to detect concentrations below the microgram-per-gram level. Overall, the 3-minute extraction time appears to be acceptable for a field screening method.

Comparison of concentration estimates from colorimetric and RP-HPLC methods

Extracts from the 3 minutes of manual shaking (discussed in the previous section) were also analyzed by the field colorimetric method. Use of the same extracts enabled us to directly compare concentration estimates from the field colorimetric procedure to those obtained from the RP-HPLC laboratory method. Results are shown in Table 6.

Except for Eagle River Flats B, the results from the field method were 15–25% lower than the sum of 2,4-DNT and 2,6-DNT extracted by RP-HPLC. The Eagle River Flats B sample apparently contained a component that interfered with the generation of the Jackson–Meisenheimer anion. Analysis of this sample by inductively coupled argon plasma spectrometry revealed an unusually high concentration of copper (347 µg/g). For the 39 other soil samples taken from this and neighboring sites, copper concentrations were below a certified reporting limit (58.6 µg/g). Mean copper concentration in soil worldwide is about 25 µg/g (Sposito 1989). Copper, and other metal cations, could form complexes with either the unreacted DNT (Leggett, in press) or the Jackson–Meisenheimer anions (Fig.3).

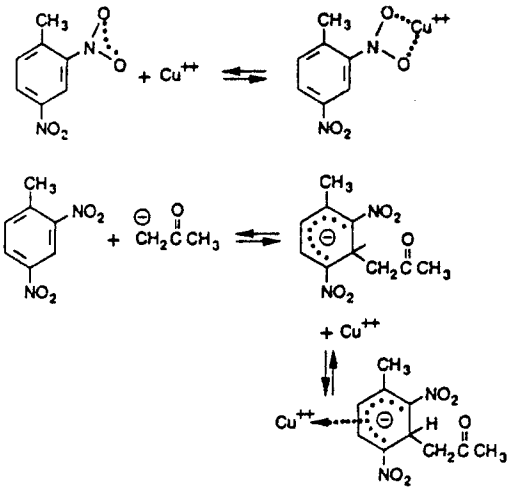

Figure 3. Possible complexes between copper cations and 2,4-DNT or the Janowsky reaction product.

To see if copper interfered with color formation, two 20.0-mL aliquots of a 4.0-mg/L 2,4-DNT solution were measured into separate vials. A 0.4-mL aliquot of water was added to one solution, and a 0.4-mL aliquot of a 1000-mg/L aqueous solution of copper sulfate was added to the other. After reaction with KOH and Na_2SO_3, the solution without added copper was purple, whereas the solution with added copper was a faint pink. Absorbances at 570 nm were 0.873 and 0.172 respectively. While this experiment does not prove that copper was responsible for the low estimate of 2,4-DNT concentration for the Eagle River Flats sample, the results are consistent with this interpretation.

To further explore the potential for false negatives, 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. Results are shown in Table 7. In all

Table 6. Comparison of colorimetric and RP-HPLC analysis of soil extracts.

	Colorimetric	*RP-HPLC Method*	
	method	*2,4-DNT*	*2,6-DNT*
Sample origin	*(µg/g)*	*(µg/g)*	*(µg/g)*
Camp Shelby (Miss.) A	3.3	3.4	0.6
Camp Shelby (Miss.) B	203	226	12.1
Camp Shelby (Miss.) C	5.0	6.7	a*
Camp Shelby (Miss.) D	<d†	<d	<d
Eagle River Flats (Alaska) A	11.4	12.7	0.9
Eagle River Flats (Alaska) B	0.8	7.4	0.5
Spiked soil	27.6	19.5	20.1

*Interference detected, unable to quantify.
†Below detection limits.

Table 7. Results using field screening procedure for soils spiked at 5.1 µg/g 2,4-DNT.

Sample origin	*2,4-DNT concentration found (µg/g)*
Keystone Ordnance Works (Pa.)	4.2
Fort Hancock (N.J.)	4.2
Hastings East Industrial Park (Neb.) A	4.2
Lake City Army Ammunition Plant (Mo.)	3.6
Lexington-Bluegrass Army Depot (Ky.)	3.6
Susquehana Ordnance Depot (Pa.)	3.8
Raritan Arsenal (N.J.)	4.2
Weldon Springs Training Area (Mo.)	3.5
Hastings East Industrial Park (Neb.) B	4.3

cases 2,4-DNT was easily detected, but, as observed earlier, the measured concentrations were consistently lower than anticipated by up to 30%. The severe interference observed for the Eagle River Flats soil was not observed in any of these soils.

Effect of total shaking time and shaking frequency on the extent of color development

While conducting studies on the effects of various reagent contact times, we observed that the amount of shaking a sample received while in contact with the solid reactants had an effect on the extent of color development achieved. The effect was most apparent at low water contents, where the reagents do not completely dissolve and the reactions may be taking place at the surface of the solid reactants. Since it would be impractical to manually shake the samples for the full 30-minute period in the field, an experiment was conducted to compare various shaking protocols. Each protocol was tested in duplicate using acetone solutions containing 4.0 mg/L of 2,4-DNT and 2% water (v/v). Descriptions of the protocols and results are shown in Table 8. ANOVA followed by a least significant difference test indicated that shaking protocols 1, 2 and 3 were not significantly different at the 0.05 significance level. Protocols 4 and 5 were significantly different from 1, 2 and 3 and from each other. Thus, it appears that it is important to shake the samples immediately after addition of the solid reactants (1 minute appears adequate) and probably additionally near the end of the reagent contact time. Without this initial shaking, as in protocols 4 and 5, lower results were obtained, even when actual shaking time was large. Thus, we recommend that, as a minimum, samples should be shaken 1 minute at the beginning and end of the reagent contact time to ensure maximum color development.

Table 8. Absorbance obtained (570 nm) for various shaking protocols.

*Shaking protocol**	*Absorbance (A.U.)*		
	Rep 1	*Rep 2*	$\bar{X}$
1	0.902	0.865	0.898 a†
2	0.908	0.911	0.910 a
3	0.908	0.903	0.906 a
4	0.776	0.745	0.760 b
5	0.841	0.873	0.857 b

* 1. Shake for 1 minute; allow to stand for 28 minutes; shake for 1 minute.

2. Shake for 3 minutes; allow to stand for 3 minutes; repeat process throughout 30-minute period.

3. Shake for 15 minutes; allow to stand 15 minutes.

4. Allow to stand 15 minutes; shake for 15 minutes.

5. Allow to stand 7.5 minutes; shake for 15 minutes; allow to stand 7.5 minutes.

† Means annotated with the same letter are not significantly different at the 0.05 significance level.

Certification of screening procedure

Since the maximum absorbance obtained for a given concentration of 2,4-DNT varies with the percentage of water in the acetone extract, the results obtained from this procedure are more qualitative than quantitative. Therefore, the method was subjected to Class 2 certification, which is appropriate for methods that screen for the presence or absence of contaminants, rather than the Class 1 certification, which is appropriate for methods that quantify contaminants (USATHAMA 1990). For the certification procedure, four soils were spiked at a chosen Target Reporting Limit (TRL). 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. Calibration standards were prepared at the equivalent 2,4-DNT concentration for the spiked soils samples and at zero 2,4-DNT concentration.

Certification was performed three times, each at a different soil moisture content (10, 25 and 50% wet weight basis). In all cases, the calibration standards and soil spikes could be distinguished from blanks with 100% accuracy at 2 µg/g for 10, 25 and 50% soil moisture.

SUMMARY AND CONCLUSIONS

A simple colorimetric method was developed for the field screening of 2,4-DNT in soil. 2,4-DNT is extracted from soil by manually shaking a 20-g subsample with 100 mL of acetone for 3 minutes. A 20- to 25-mL portion of acetone extract is filtered through a Millex SR disposable filter assembly and the initial absorbance obtained at 570 nm. Two pellets of KOH and about 0.75 g of Na_2SO_3 are added, and the sample is shaken for 1 minute, allowed to stand for 28 minutes, then shaken again for 1 minute. The solutions are filtered and the absorbance read again at 570 nm. If 2,4-DNT is present in the soil subsample, the absorbance of the extract should increase by at least a factor of two. If the extract is colorless prior to adding KOH and Na_2SO_3, a blue color will form and then change to purple. If the extract is yellow initially, the color will change to green and then to purple or brown.

Color development is influenced by the moisture content of the soils. Therefore, the method cannot be calibrated for accurate quantitation in the field where the moisture content of the soils will be unknown. However, the method may be used for screening for contamination. The method was tested using the USATHAMA Class 2 certification procedure. A certified reporting limit of 2 µg/g was obtained for 10, 25 and 50% soil moisture. Since extracts from extremely wet soils give poor color development, we recommend that a smaller subsample be extracted with 100 mL of acetone if the moisture content appears to exceed 50% (wet weight basis).

The procedure described in this report is designed to complement similar procedures for TNT and RDX. The same soil extract may be used. These three procedures give the analyst the ability to detect contamination from high explosives (TNT and RDX) and propellants (2,4-DNT), as well as commonly occurring co-contaminants (TNB, DNB, HMX).

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APPENDIX A: METHOD DOCUMENTATION IN USATHAMA (1990) FORMAT

Certification
Field Method for the Detection of 24DNT in Soil

I. Summary

A. Analytes: This method is suitable for detecting 24DNT in the field using battery-operated equipment.

B. Matrix: This method is suitable for the detecting 24DNT in soil.

C. General method: 24DNT is extracted from soil by manually shaking a 20-g subsample with 100 mL of acetone for 3 minutes. A 20- to 25-mL portion of the acetone extract is filtered through a Millex SR disposable filter assembly and the initial absorbance obtained at 570 nm. Two pellets of KOH and about 0.75 g Na_2SO_3 are added, and the sample is shaken for 1 minute, allowed to stand for about 28 minutes, then shaken again for 1 minute. The solution is filtered and the absorbance read again at 570 nm. If 24DNT is present in the soil subsample, the absorbance of the extract should increase by at least a factor of two. A positive result can be detected visually and depends on the initial color of the extract. If the extract is colorless prior to adding KOH and Na_2SO_3, a blue color will form and then change to purple. If the extract is yellow initially, the color will change to green and then to purple or brown

II. Application

A. Calibration range: This procedure was subjected to a Class 2 certification using a standard concentration of 0.4 mg/L, which is equivalent to 2 µg/g if 20 g of soil is extracted with 100 mL of acetone.

B. Tested concentration range: This procedure was subjected to a Class 2 certification using a soil concentration of 2 µg/g.

C. Interferences: A number of other nitroaromatics will develop a visible color as well as 24DNT. These compounds include: 26DNT (pinkish purple), TNT (red), TNB (red) and TETRYL (orange).

Soils with a high copper content will cause negative interference (i.e., prevent color development).

D. Safety information: The normal safety precautions associated with the use of a flammable organic solvent and potentially toxic chemicals should be employed. Eye protection is recommended when shaking bottles to protect against splash from poorly sealed containers.

III. Apparatus and Chemicals

A. Instrumentation:

1. Field portable, battery-operated colorimeter (HACH DR2000 Spectrophotometer or equivalent).
2. Triple pan balance, to measure soil weights.
3. Analytical balance for preparation of stock solution.

B. Analyte:

24DNT (2,4-dinitrotoluene)
MP: 70°C
Solubility in water at 25°C: 300 mg/L
Octanol/water partition coefficient: 95
CAS # 121-14-2.

C. Reagents and SARMs:

1. 24DNT (SARM quality).
2. Acetone, commercial grade.
3. Potassium hydroxide (KOH), reagent grade pellets.

4. Sodium sulfite (Na_2SO_3), reagent grade.
5. Water, distilled.

D. Glassware/equipment:

1. 8-oz (240-mL), Qorpak or equivalent glass bottles with caps, one per sample.
2. Glass volumetric pipets:
   - 1.00 mL
   - 3.00 mL
   - 25.00 mL.
3. 100-mL graduated cylinder.
4. Stopwatch or timer.
5. Cuvette bottles (25-mL capacity), 25-mm path length.
6. Glass volumetric flask (2)—250 mL.
7. Millex SR filter units, 0.5 µm, 2 per sample.
8. BD Plastipak syringes, 20-mL, 2 per sample.
9. Forceps.
10. Spatula or measuring spoon.
11. Glass vials, 25-mL, one per sample.

IV. Calibration

A. Initial calibration:

1. Preparation of standards: Solid 24DNT (SARM or reagent grade) is dried to constant weight in a vacuum desiccator in the dark. About 0.1 g is weighed out to the nearest 0.1 mg, transferred to a 250-mL volumetric flask and diluted to volume with acetone. The 24DNT concentration of this stock standard is about 400 mg/L. This stock standard should be prepared in the laboratory before going to the field.

A working stock standard is prepared by diluting 25.0 mL of the stock 24DNT standard to 250 mL in a glass volumetric flask and bringing to volume with acetone. The concentration of this working stock standard is about 40 mg/L.

The calibration solution (0.4 mg/L) is prepared by combining 1.00 mL of the 40-mg/L working stock standard, 99.0 mL of acetone, and 3 mL of water. Glass volumetric pipets are used to dispense the working stock standard and the distilled water, and a 100-mL graduated cylinder is used to add the acetone. The solution is prepared in an 8-oz (240-mL) glass bottle, capped and shaken.

2. Instrument calibration: About 20 mL of the 0.4-mg/L calibration solution is poured into a 25-mL glass vial. Then two pellets of KOH and about 0.75 g Na_2SO_3 are added, and the solution is shaken for 1 minute, allowed to stand for about 28 minutes, then shaken again for 1 minute. The solution should change from colorless to blue and finally to purple. The solution is filtered through a 0.5-mm Millex SR filter unit into a vial and the color noted.

Calibration standards are analyzed in triplicate at concentrations of 0 (blank) and 0.4 mg/L (equivalent to 2.0 µg/g). All blanks must yield negative results and all standards must yield positive results (i.e., develop a visible purple color).

B. Daily calibration: One blank and one calibration standard (0.4 mg/L) are analyzed each day before and after sample analysis.

V. Certification Testing

A. Preparation of spiking solutions: The spiking stock standard is prepared in an identical manner to the calibration stock standard described in Section IV-A-1. The soil spiking solution is prepared in an identical manner to the working stock standard also described in Section IV-A-1.

B. Soil spiking: Subsamples of 20.0 g of USATHAMA Standard Soil are placed in each of eight 8-oz (240-mL) glass bottles. A 3.00-mL aliquot of water is added to each since the standard soil has been previously dried. Four of the bottles are labeled "blank" and four are labeled "spike." A 1.00-mL

aliquot of the 40-mg/L 24DNT spiking solution is added to these bottles labeled "spike" to yield a spiked soil concentration of 2 µg/g. The spiked soils are allowed to stand for 1 hour capped prior to extraction.

C. Soil extraction and analysis: A 100-mL aliquot of acetone is added to each bottle labeled "blank," and a 99.0-mL aliquot of acetone is added to each bottle labeled "spike." Each bottle is capped and shaken manually for 3 minutes. Each sample is then allowed to stand for 5 minutes to allow the particles to settle, then a 20-mL aliquot of the extract is filtered through a 0.5-µm Millex SR filter into a 25-mL cuvette. Initial absorbance is obtained at 570 nm using a spectrophotometer. The solution is transferred to a 25-mL glass vial. Two pellets of KOH and about 0.75 g of Na_2SO_3 are added, and the sample is shaken for 1 minute, allowed to stand for about 28 minutes, then shaken again for 1 minute. The solution is filtered through a 0.5-µm Millex SR filter unit into a cuvette and the absorbance read again at 570 nm. For the spiked samples, the absorbance of the extract should increase by at least a factor of two. If the extract is colorless prior to adding KOH and Na_2SO_3, a blue color will form and then change to purple. If the extract is yellow initially, the color will change to green and then to purple or brown.

The results of these analyses are subjected to the rank sum test as described in USATHAMA (1990) Installation Restoration Quality Assurance Program (Appendix E).

VI. Sampling Handling

This method is designed to be used with field soils that have not been previously dried. If dried soils are used, add 3.0 mL of distilled water to the 20 g soil sample before extraction.

The soil sample is mixed as thoroughly as possible and a 20-g subsample added to a 8-oz (240-mL) glass bottle and the bottle capped until extraction is conducted. The samples should be kept cold (4°C) and in the dark until extraction takes place. Samples should be analyzed within a week of the day they are collected.

VII. Procedure

A 20-g subsample of undried soil is placed in a 8-oz (240-mL) glass bottle and 100 mL of acetone added. The bottle is capped and shaken manually for 3 minutes. Each sample is then allowed to stand for 5 minutes to allow the particles to settle, then a 20-mL aliquot of the extract is filtered through a 0.5 µm Millex SR filter into a 25-mL cuvette. Initial absorbance is obtained at 570 nm using a spectrophotometer. The solution is transferred to a 25-mL glass vial. Two pellets of KOH and about 0.75 g of Na_2SO_3 are added, and the sample is shaken for 1 minute, allowed to stand for about 28 minutes, then shaken again for 1 minute. The solution is filtered through a 0.5-µm Millex SR filter unit into a cuvette and the absorbance read again at 570 nm. If 24DNT is present in the soil subsample, the absorbance of the extract should increase by at least a factor of two. A positive result can be detected visually and depends on the initial color of the soil extract. If the extract is colorless prior to adding KOH and Na_2SO_3, a blue color will form and then change to purple. If the extract is yellow initially, the color will change to green and then to purple or brown.

XIII. Daily Quality Control

A blank and a spiked soil at 1X (2 µg/g) are analyzed each day as described in USATHAMA (1990) Installation Restoration Quality Assurance Program.

IX. References

Jenkins, T.F. and M. Walsh (1991) Field screening method for 2,4-dinitrotoluene in soil. USA Cold Regions Research and Engineering Laboratory, Special Report 91-17.

USATHAMA (1990) USATHAMA QA program. USA Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland 21010.

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13. ABSTRACT (*Maximum 200 words*)

A simple field screening method was developed to detect the presence of 2,4-dinitrotoluene (2,4-DNT) in soil. The method involves extraction of 2,4-DNT from the soil with acetone, generation of a bluish-purple Janowsky complex by addition of potassium hydroxide and sodium sulfite, and estimation of concentration by measuring the absorbance at 570 nm with a battery-operated spectrophotometer. While the extent of color development is also somewhat dependent on the moisture content of the soil, analysts can visually detect concentrations of 2 µg/g or greater in the soil. The acetone extraction step was shown to extract at least 80% of the 2,4-DNT present in a series of field contaminated soils. A 30-minute reaction time is required after addition of the reagents, and the color, once formed, is stable for at least 60 minutes after filtration. The presence of TNT, tetryl, TNB and 2,6-DNT will result in a positive interference with this method. High concentrations of copper in the soil may result in negative interference by inhibiting the formation of the Janowsky complex or by complexing with it to modify its visual absorbance characteristics.

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