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LABORATORY AND ANALYTICAL METHODS FOR EXPLOSIVES RESIDUES IN SOIL

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ABSTRACT

Standard analytical methods have been developed to characterize explosives residues in soil at U.S. Department of Defense installations. The laboratory analysis is conducted using RP-HPLC, and the most commonly found analytes are TNT and RDX. Other analytes commonly detected are the environmental transformation products of TNT including TNB, dinitroaniline, and the isomers of amino-DNT, and the manufacturing by-products DNB and the isomers of amino-DNT. Field methods designed to detect TNT and RDX have enhanced site characterization by providing rapid on-site results for a greater number of samples than would be economically feasible by depending solely on off-site laboratory analyses for all samples. Attempts may be made to use both laboratory and field methods to analyze treatment matrices such as incinerator ash and compost, but further analytical method development is needed to enhance extraction and minimize interferences.

INTRODUCTION

Soils at many U.S. Department of Defense installations are contaminated with explosive residues. The sources of these residues include the manufacture of secondary explosives, the fabrication of finished munitions, the destruction of out-of-specification material, the destruction of out-of-date bombs, rockets and ammunition, and the utilization of munitions at Army training sites. Disposal of munitions

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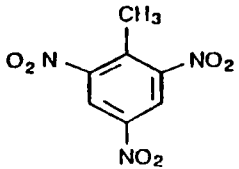
wastes during World War I, World War II, the Korean War and the Viet Nam War was accomplished by means that did not protect groundwater, such as unlined lagoons. Leaching mobile contaminants are migrating with groundwater at several installations. The areal extent and severity of explosives contamination is determined using standard analytical methods for soil and water matrices.

To date, remediation of contaminated soil has been primarily by incineration. But due to high costs and negative public perception, alternatives to incineration are under investigation. Currently, bioremediation of munitions-contaminated soil is the focus of intensive investigation.

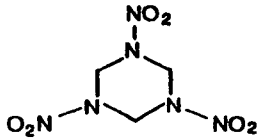
The purpose of this paper is to provide an overview of the explosives contamination problem at some Department of Defense facilities from an analytical chemistry perspective, with emphasis on the compounds found in explosives-contaminated soils, and the laboratory and field methods that are being used for site characterization. Problems encountered when these methods are used to characterize treatment matrices such as incinerator ash, compost, or slurry reactor effluent are discussed.

COMPONENTS OF EXPLOSIVES RESIDUES

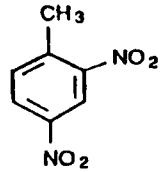
TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) (Figure 1) are major ingredients in nearly every munition formulation (Table 1) and are the secondary explosives used in the greatest quantities. Several other organic chemical explosives have also been used in specific munition formulations, including 2,4-DNT (2,4-



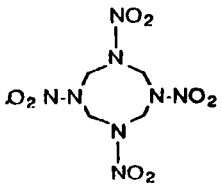
TNT



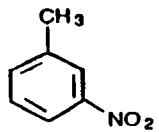
RDX



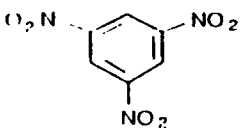
2,4 - DNT



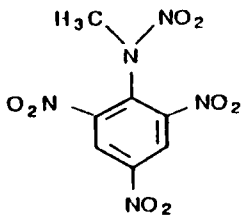
HMX



m - NT



1NB



Tetryl

FIGURE 1

Chemical Structures for Nitroaromatics and Nitramines

TABLE 1

Summary of Explosive Chemicals Present in Various Military Munitions [1, 2]

Composition	Use	Explosives Present (%) TNT	RDX	HMX	DNT	Others
Anatols	a,b	20-50				Ammonium nitrate
Comp A	c,d,e,f		91-98			
Comp B	b,e,f,j	40	60			
Comp C	k		88			
Comp C2	k	5	79		12	m-Nitrotoluene, Nitrocellulose
Comp C3	h,k	4	77		10	m-Nitrotoluene, Nitrocellulose, tetryl
Comp C4	g		91			
Cyclotol	b,e,f,i	25	75			
HBX-3	m	29	31			
H-6	m	30	45			
HTA-3	a,b	29		49		
Minol-2	a,l	40				Ammonium nitrate
Torpex	a,f,l	40	42			
DBX	l	40	21			Ammonium nitrate
PBX			0-95	0-95		Trinitrobenzene
Baratol	a	33				Barium nitrate
Baranal	a	35				Barium nitrate
Black powder	n,o					Potassium nitrate
Explosive D	a,b					Ammonium picrate
PTX-1	g,p	20	30			Tetryl
PTX-2	f,i		28-33	41-44		PETN
Comp CH6	d		98			
Ednatols	a,c,i	40-50				Ethylene dinitramine
LX-14				96		
Octols	a,b,f,i	25-35			70-75	
Pentolite	f,g,i	25-90				PETN
Picratol	h					Ammonium picrate
Tetrytols	i,k	65-80				Tetryl
Tritonal	a	80				
Amatex 20	c	40	40			Ammonium nitrate
HBX-1	m	40	38			

Footnotes

a Bombs
b High energy projectiles
c Projectile filler
d Boosters
e Grenades
f Shaped charges
g Demolition explosives
h Ammunition
i Bursting charges
j Fragmentation charges
k Formerly used demolition explosives
l Depth charges
m High energy charges
n Igniter powder
o Time fuses
p Land mines

dinitrotoluene), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), m-NT (m-nitrotoluene), tetryl (methyl-2,4,6-trinitrophenyl nitramine), and TNB (1,3,5-trinitrobenzene). While some of these chemicals, such as tetryl, are no longer used in current munitions, residues from their manufacture and use remain at contaminated sites.

In addition to chemicals intentionally added to explosives formulations, munitions residues often contain chemicals which were impurities in production grade material or environmental transformation products of major or minor constituents. For example, military grade TNT contains a number of impurities, including 2,4-DNT and other isomers of dinitrotoluene, 1,3-dinitrobenzene (DNB), and other isomers of trinitrotoluene, especially 2,4,5- and 2,3,4-TNT [1, 3] (Table 2). In addition, TNT is subject to photo and microbial degradation from which a variety of transformation products have been identified in laboratory studies (Table 2). The major impurity in production grade RDX is HMX, which is present in concentrations as high as 12% [1]. The major environmental transformation products of RDX have been less well characterized but they include the mononitrosodinitro-, dinitrosomononitro- and trinitrosotriazines as well as several hydrazines, formaldehyde and methanol [11, 19, 20].

TOXICITY AND CLEANUP CONSIDERATIONS

The toxicity of explosive chemicals has been studied extensively by the U.S. Army Biomedical Research and Development Laboratory (Fort Detrick, Maryland) and a summary of the results of these investigations has been published [21]. Based on these studies, the U.S. Environmental

TABLE 2
Summary of Major Impurities and Environmental Transformation Products Associated with Military Grade TNT

Compound	Source*	Reference
2,4-dinitrotoluene	I	1, 3, 4
2,6-dinitrotoluene	I	2-4
1,3-dinitrobenzene	I	1, 4
2,4,5-trinitrotoluene	I	1, 3
2,3,4-trinitrotoluene	I	1, 3
2-amino-4,6-dinitrotoluene	M	4-14
4-amino-2,6-dinitrotoluene	M	4-17
Tetranitroazoxytoluene isomers	M	6, 7, 12, 15
2,4-diamino-6-nitrotoluene	M	7, 9, 12
2,6-diamino-4-nitrotoluene	M	9, 12
2-hydroxylamino-4,6-dinitrotoluene	M	7
4-hydroxylamino-2,6-dinitrotoluene	M	6, 7
1,3,5-trinitrobenzene	I,P	1, 4, 10, 12, 18, 19
1,3,5-trinitrobenzaldehyde	I,P	1, 4, 10, 12, 18, 19
1,3,5-trinitrobenzoic acid	I,P	1, 12
3,5-dinitroaniline	P	10
2-amino-4,6-dinitrobenzoic acid	P	13
3,5-dinitrophenol	P	18
3,5-dinitrocatechol	P	18
3,5-dinitrohydroquinone	P	18
4,6-dinitroanthranil	P	12
2,4,6-trinitrobenzonitrile	P	12

* I - impurity in production grade TNT; M-microbial transformation product of TNT; P-photodegradation product of TNT.

TABLE 3
Drinking Water Criteria for Munitions-related Chemicals

Compound	Criteria (μg/L)	Reference
TNT	1.0*	22
RDX	2.0*	23
HMX	400*	24
2,4-DNT	0.17**	25
2,6-DNT	0.0068**	25
1,3,5-TNB	1.0*	26

* Lifetime exposure cancer risk level 10^{-6}.

** Recommended criteria for cancer risk of 10^{-6}

Protection Agency (EPA) and Oak Ridge National Laboratory have issued a series of Health Advisories and recommended drinking water criteria for several of these explosives (Table 3). Recommended maximum allowable concentrations range from 400 μg/L for HMX [24] to 0.0068 μg/L for 2,6-dinitrotoluene [25]. No general recommendations have been issued for contaminant levels in soil. Instead, soil levels have been evaluated on a site-by-site basis, depending on such factors as the proximity of the contaminated soil to locations of groundwater use [27]. For example, at Cornhusker Army Ammunition Plant, cleanup criteria of 5 μg/g for TNT, 10 μg/g for RDX and 15 μg/g for TNB were established for the protection of groundwater [28]. As part of an ecological risk assessment at Joliet Army Ammunition Plant, toxicity testing using early seedling growth and vigor tests, earthworm survival and growth tests, and Microtox® assays indicated that lowest-observable-effect concentrations of TNT were 7 to 19 μg/g [29]. These concentrations, which are based on toxicity tests, must be considered when an analytical method is chosen for the analysis of soil from a contaminated site or of treatment matrices such as compost, slurry reactor effluent, or incineration ash.

LABORATORY METHODS

A variety of analytical techniques have been examined for determining munitions residues in environmental matrices. Since numerous compounds are potentially present, many with similar physical and chemical properties (Table 4), analytical methods have generally included a chromatographic separation. Methods have included thin layer chromatography (TLC) [35, 44-46], gas chromatography (GC) with a

TABLE 4

Physical and Chemical Properties of Nitroaromatics and Nitramines.

Analyte	*Molecular Weight*	*Melting Pt. (°C)*	*Boiling Pt. (°C)*	*Water Solubility (mg/L)*	*Vapor Pressure at 20°C (torr)*	*Log K_{ow}*	*Henry's Law Constant Hc (torr M^{-1})*
TNT	227.13	80.1-81.6 [22]	240 (explodes) [30]	130 @ 20° [22]	1.1×10^{-6} [31]	1.86 [32]	0.18 [12]
RDX	222.26	204.1 [23]	(decomposes)	42 @ 20° [33]	4.1×10^{-9} [34]	0.86 [32]	2×10^{-5} [12]
HMX	296.16	276-280 [24]	(decomposes)	5.0 @ 25° [35]	3.3×10^{-14} [21]	0.061 [36]	
TNB	213.11	122.5 [37]	315 [38]	34 @ 20° [34]	2.2×10^{-4} [12]	1.18 [39]	1.5 [34]
DNB	168.11	89.6 [37]	300-303 [38]	460 @ 15° [37]	3.9×10^{-3} [34]	1.49 [39]	1.8 [34]
Tetryl	287.14	129.5 [40]	(decomposes)	80 [41]	5.7×10^{-9} @25° [21]	1.65 [32]	
2,4-DNT	182.15	70 [26]	300 (decomposes) [30]	270 @ 22° [42]	2.2×10^{-4} @25° [21]	1.98 [39]	3.4 [34]
2,6-DNT	182.15	64-66 [26]		206 @ 25° [21]	5.67×10^{-9} [21]	2.02 [32]	18 [34]
2-Am-4,6-DNT	197.17	176 [43]		2800 [43]	4×10^{-5} [43]	1.94 [32]	3×10^{-3} [43]
4-Am-2,6-DNT	197.17	171 [43]		2800 [43]	2×10^{-5} [43]	1.91 [32]	1×10^{-3} [43]

variety of detectors [17, 47-60], high performance liquid chromatography (HPLC) [4, 30, 38, 53, 57, 61-77] and supercritical fluid chromatography (SFC) [36, 78].

For routine analysis of soils and waters from potentially contaminated sites, a suitable analytical method should provide for simultaneous determination of all common secondary explosives and their manufacturing impurities and environmental transformation products, utilize standard laboratory equipment, be sufficiently rugged so that minor deviations from the standard procedure do not produce significant changes in concentration estimates, and provide detection capability at or below criteria established for protection of human health and the environment. The Army and the USEPA have selected a reversed-phase high-performance liquid chromatographic (RP-HPLC) procedure, issued by the EPA Office of Solid Waste as SW846 Method 8330 [79]. This method is based on solvent extraction of analytes from soil using sonication, followed by an isocratic-HPLC separation and UV detection. Detection limits for 15 individual nitroaromatics, aminonitroaromatics and nitramines (HMX, RDX, TNB, DNB, tetryl, NB, TNT, 2-amino-4,6-DNT, 4-amino-2,6-DNT, 2,6-DNT, 2,4-DNT, 3,5-dinitroaniline, and the three isomers of NT) are all less than 1 μg/g. Method 8330 has been used extensively in our laboratory, in other Corps of Engineers laboratories, and in a number of commercial contractor laboratories conducting analyses for the Army. Similar protocols have also been accepted by the Association of Official Analytical Chemists [80, 81] and the American Society for Testing and Materials (ASTM) [82] as standard methods of

determining explosives residues in soil and water.

Our laboratory (CRREL) and the Corps of Engineers Missouri River Division Laboratory (MRD) have had extensive experience analyzing soils using Method 8330 [83]. Details of the research effort that went into the development of this method are presented elsewhere [4, 30, 32]. Much of the following information is summarized from a report we jointly published with the MRD [83].

ANALYTES DETECTED IN SOILS USING METHOD 8330

Using Method 8330, CRREL detected explosives residues in 175 out of 433 soil samples from 31 current or former DoD sites, and MRD detected these analytes in 144 out of 722 soil samples from 21 sites. For the combined data set, 28% of the samples analyzed were found to be contaminated with one or more target analytes (Table 5). Of these positive samples, 100% contained one or more of the following compounds: TNT, RDX, tetryl and 2,4-DNT. The analytes found in highest concentration varied with the type of site from which the samples were collected.

For soil samples collected at sites such as arsenals, depots, and ammunition plants, the analyte TNT was found most frequently (195 out of 243 positive samples or 80%) and at the highest concentrations (i.e. up to parts per hundred) [83]. Of these TNT-contaminated soils, 54% were also contaminated with TNB, a photo transformation product of TNT. DNB and 2,4-DNT, manufacturing byproducts of TNT, were present at detectable levels in 26% and 32%, respectively, of these samples, and 2-amino-DNT, a biotransformation product of TNT, was reported in 22% of these samples (although detection of this analyte was limited due to

TABLE 5
Frequency of Detection of Explosives Residues in Soil Samples Analyzed Using Method 8330 [83].

	CRREL	MRD	Total
Installations	31	21	46
Samples analyzed	433	722	1,155
Samples with detectable explosives	175	144	319
Analytes detected			
HMX	31	6	37
RDX	49	38	87
1,3,5-TNB	57	51	108
1,3-DNB	27	26	53
Tetryl	9	19	28
NB	0	0	0
TNT	106	103	209
4-Am-DNT	17	4	21
2-Am-DNT	39	15	54
2,6-DNT	22	1*	23
2,4-DNT	111	32	143
2-NT	0	0	0
4-NT	0	0	0
3-NT	0	0	0

*Didn't differentiate 2,4- and 2,6-DNT.

availability of standards). Conversely, over 94% of all detections of TNB, DNB, the isomers of DNT, and the isomers of amino-DNT were in samples contaminated with TNT. RDX was detected in 60% of the samples containing TNT. It is the main ingredient in several explosive compositions (Table 1), frequently with TNT. Samples contaminated with TNT and/or RDX accounted for 94% of all samples with detectable explosives residues.

Of those samples contaminated with RDX, 37% also had HMX, generally at a lower concentration than RDX. HMX is an impurity in munitions-grade RDX, as well as an ingredient in several explosives compositions (Table 1). Tetryl was infrequently found, perhaps due to its instability. This instability can contribute to loss during sample preparation [4, 84]. NB and the isomers of NT were not found in these samples.

Soils from two Explosive Ordnance Disposal (EOD) sites were analyzed. At both sites 2,4-DNT was detected in all samples with detectable analytes [83]. The 2,4-DNT was present at much higher concentrations than TNT, the reverse of what is found at other types of sites. The source of this contamination was probably the improper demolition of excess propellant (i.e., it was detonated, not burned). In fact, whole propellant grains were seen scattered about each EOD area. GC/MS analysis of acetonitrile extracts of soil samples and propellant grains confirmed the presence of diphenylamine and dibutylphthalate, which along with nitrocellulose [1] are the ingredients of M1 propellant.

TRANSFORMATION PRODUCTS OF TNT DETECTED IN SOILS

As evidenced by the presence of TNB and the isomers of amino-DNT in the soils contaminated by TNT, explosives residues in soil may be transformed by photochemical and microbiological processes. While the transformation pathways of some explosives have been studied in cell cultures, composting systems and water, little research has been conducted to define what by-products are present in explosives-contaminated soil. Potential transformation products of TNT are

numerous. Of the compounds listed in Table 2, only TNB and the isomers of amino-DNT have been reported by previous investigators [43].

To determine if other TNT transformation products could be detected using gas chromatography-mass spectrometry (GC-MS), 11 soils that had been analyzed by Method 8330 were selected to represent a range of TNT concentrations (1 μg/g to 14 mg/g). The soils came from the following locations: Weldon Spring (MO), Hawthorne (NV), Hastings East (NE), Sangamon (IL), Raritan (NJ) and VIGO (IN). Subsamples were extracted with acetone and analyzed by GC/MS [83]. The most commonly found transformation products were 2-amino-DNT and 4-amino-DNT, the microbiological reduction products of TNT (Table 6). TNB, a

TABLE 6
Compounds Found by GC/MSAnalysis of Acetone Extracts of 11 soils from Various ArmyInstallations [83]

Analyte	Number Times Detected
2,4,6-TNT	11
2,3,6-TNT	1
2,4,5-TNT	1
2-Am-4,6-DNT	8
4-Am-2,6-DNT	6
TNB	5
Dinitroaniline (3,5-DNA)	4
Trinitrobenzylaldehyde (TNBA)	4
2,4-DNT	7
2,6-DNT	6
Dinitrophenol	1
DNB	2
Trinitrophenol	1
Dinitronaphthalene	1

photodecomposition product of TNT, was identified in 5 out of the 11 soils. Other transformation products identified in 4 out of the 11 soils were trinitrobenzaldehyde (TNBA) and 3,5-dinitroaniline (DNA). TNBA, like TNB, is a photodecomposition product of TNT, and converts to TNB by decarbonylation [10]. We have detected TNBA using Method 8330, but TNBA slowly converts to TNB in acetonitrile [4]. Because of this instability, the TNB concentration estimated using Method 8330 is the sum of the TNB and converted TNBA [19]. 3,5-DNA is a microbiological reduction product of TNB. The formation of 3,5-DNA from TNB in soil is consistent with the formation of 2-amino-DNT and 4-amino-DNT from TNT in soil.

Subsequent studies to determine maximum holding times for soil samples provided additional insight into the transformation potential of these analytes [85]. When aqueous solutions of HMX, RDX, TNB, TNT and 2,4-DNT were added to three soils and incubated for eight weeks, the nitramines were stable but the nitroaromatics were biotransformed at room temperature and under refrigeration (4°C). Reduction products of all three nitroaromatics were formed (3,5-dinitroaniline from TNB, the isomers of amino-DNT from TNT, and the isomers of amino-NT from 2,4-DNT). In contrast, when four field-contaminated soils were stored under similar conditions, nitroaromatics were quite stable. When three of these field-contaminated soils were subsequently fortified with aqueous solutions of TNT and TNB, rapid degradation was again observed for the added nitroaromatics[86]. The difference between fortified and field-contaminated soils in the rates of analyte transformation have implications beyond sample holding time estimates. When evaluating treatment

options, common practice is to add analyte of known concentration to the treatment matrix, sometimes with a radiolabel, and follow the change in analyte concentration with time. However, analyte-matrix interactions occurred over decades in field-contaminated soils; the results of these interactions, such as binding to the sample matrix, are difficult to mimic using spiked samples.

FIELD SCREENING METHODS

Site characterization at explosives-contaminated sites has traditionally been conducted by soil sample collection and analysis at off-site commercial laboratories. Most of these laboratory analyses are conducted using Method 8330 and the results generally appear to have been satisfactory in terms of accurately identifying the various contaminants and their concentrations. Sometimes, however, the turnaround time for obtaining these results has been inadequate for optimum on-site decision making. In addition, per sample analytical costs have sometimes limited the number of samples that could be analyzed, resulting in insufficient spatial resolution of the boundary between contaminated and clean areas. This problem is further compounded by the cost of analyzing samples that are devoid of residues. On-site field screening has been suggested as a means of addressing some of the shortcomings resulting from exclusive reliance on analysis at off-site laboratories [87]. Since at least 95% of the soils found to be contaminated with residues of secondary explosives contained TNT and/or RDX, most secondary-explosives-contaminated soils could be identified if soils could be screened for these two analytes.

Colorimetric and enzyme immunoassay (EIA) field screening methods for TNT and RDX have been developed. Both procedures rely on extraction of soil with an organic solvent such as acetone . Colorimetric procedures for TNT and RDX are based on the classical Janowsky and Griess Reactions, respectively. EIA procedures have been developed for TNT and RDX. Commercial kits based on colorimetric reactions are available from EnSys Corporation, and EIA based kits are available from EM Science (DTECH), Quantix, Millipore and Ohmicron.

A study was conducted to compare two commercially available methods of field screening for TNT in soil [88]. The study utilized 99 soil samples from the Naval Surface Warfare Center, Crane, Indiana. All soil samples were analyzed using a commercial colorimetric method (EnSys) and a commercial enzyme immunoassay method (D TECH), and the results compared to those from the standard RP-HPLC laboratory method (Method 8330). Comparisons were made relative to numerical agreement of screening results with laboratory analysis by RP-HPLC, and usage in two distinct scenarios.

Of the 99 soil samples analyzed by the laboratory method, 25 had TNT concentrations greater than the RP-HPLC detection limit of 0.3 μg/g. Of these 25, 11 had concentrations in the range 0.3 - 1.0 μg/g and 14 had concentrations greater than 1.0 μg/g (the operating field screening detection limit for this study). Results were positive from both field screening methods for all 14 soils with TNT concentrations greater than 1.0 μg/g by RP-HPLC. Thus, no false negatives were observed by either method for samples above the field screening detection limit. Of the 11

samples with TNT concentrations in the range 0.3 - 1.0 μg/g, D TECH failed to detect 3 samples and EnSys failed to detect 2 samples. RP-HPLC analysis of 66 samples resulted in non-detects for TNT and other nitroaromatics. For these samples, the D TECH kit yielded 63 non-detects and 3 false positives and the EnSys method resulted in 64 non-detects and 2 false positives.

Quantitative results from both field methods were regressed against the numerical results of the RP-HPLC analyses. Somewhat better agreement was obtained between results from RP-HPLC and results from the EnSys method. These better results appear to be largely due to a decrease in sampling error achieved by air drying a fairly large portion of soil and homogenizing prior to subsampling. Both kits respond to the presence of other nitroaromatics in addition to TNT. With the D TECH kit, the nitroaromatics produce similar responses. However, EnSys kit may actually be used to identify the major nitroaromatic present since different colored solutions are produced for different nitroaromatics: TNT (pink-red), 2,4-DNT (blue-purple), tetryl (orange), and DNB (purple).

For some samples, the RP-HPLC results were consistently lower than either the EnSys or D TECH results. even when the concentrations of other nitroaromatic analytes are also added to the TNT concentration by RP-HPLC. We believe this is due to response of the two field methods to other transformation products of TNT which are not resolved by RP-HPLC, but retain the functionality required to react with the two field methods. These could be monomeric compounds of very different polarity than TNT or transformation products of TNT bound to humic substances.

Since a portion of the humic material extracts into acetone, bound residues can interact like free analyte if the requisite functionality is still present. If so, this color-forming reaction could be useful in studies to determine the fate of TNT in compost.

A second comparison[89] was conducted with 150 soil samples from Umatilla Army Depot in which TNT was present at concentrations greater than 0.5 µg/g. Soil samples were homogenized and subsamples analyzed by immunoassay procedures from D TECH and Quantix, and the colorimetric tests developed at CRREL[87] and commercialized by EnSys. Laboratory analysis using SW846 Method 8330 again was used to evaluate performance. Analytical accuracy and precision were estimated for each screening method. For samples with TNT concentrations less than 30 µg/g, correlation with the laboratory results was the highest using the D TECH method. For samples with TNT concentrations above 30 µg/g, correlation was better using the CRREL method. The costs of using the various screening tests were compared, as were other practical considerations such as space requirements, the amount of waste generated, power requirements, analysis time, analyst skill level, and flexibility with respect to variable sample lot size. Based on these criteria, no single screening method consistently out-performed the others over a range of soil concentrations.

ANALYTICAL CHALLENGES ASSOCIATED WITH TREATMENT MATRICES

Both the laboratory and field analytical methods have resulted in data that were generally acceptable when the methods were used to

analyze soils. When use of these methods has been extended to treatment matrices such as ash or compost, problems have been encountered.

For example, when incinerator ash was spiked with a solution of TNT , and the sample extracted and analyzed, poor recovery of TNT was observed. This poor recovery resulted from the high pH of the ash. In the presence of base, nitro compounds such as TNT are converted to Meisenheimer anions. TNT as the anion does not have the same RP-HPLC retention time as TNT, therefore it is not detected as TNT using the standard method. When the ash was neutralized, spiked TNT was readily recovered[90].

Two major problems are encountered when biotreatment matrices are analyzed using Method 8330. Many biotreatment matrices have polar components that are extracted with the analytes of interest and produce high background interferences. This problem may be solved by a clean-up step, gradient elution, or use of a more selective detector. Newer varieties of RP-HPLC columns are also available that may provide better resolution. The second problem, which is far more serious, is incomplete extraction of transformation products. To date, the ultimate fate of TNT and its metabolites in biotreatment matrices has not been established. While the amino reduction products are frequently detected and some laboratory studies have shown some mineralization to carbon dioxide, the sum of the metabolites have not accounted for the decline in TNT concentration. This lack of a material balance has been attributed to the binding of metabolites to organic matter. These bound metabolites are incompletely recovered by the solvent extraction procedure in Method

8330.

The common biotransformation products of TNT will be detected using Method 8330, but in situations where metabolites may accumulate, such as in a bioreactor, other methods will be needed to identify biotransformation products.

The field analytical methods may be prone to background interferences in matrices other than soil. For example, composts may contain additives such as manure and fruit/vegetable matter that will produce highly colored acetone extracts. A high background color will prevent the detection of a colored product. Amendments may also contain fertilizers that could affect the formation of colored products. Additionally, the efficiency of the extraction procedure for matrices other than soil has not been determined.

CONCLUSIONS

Characterization at explosives-contaminated sites relies on both on-site field screening and off-site laboratory analysis. Generally laboratory analysis is conducted using SW846 Method 8330, an RP-HPLC method developed to determine trace levels of nitroaromatics and nitramines in soil. Analytes most frequently detected in munitions-contaminated soils are TNT and RDX. Other analytes commonly detected include environmental transformation products of TNT including TNB, dinitroaniline, the isomers of amino-DNT, and the manufacturing by-products DNB and the isomers of DNT. Field screening is commonly conducted for TNT and RDX using colorimetric or enzyme immunochemical reactions. Attempts may be made to use both laboratory

and field methods to analyze treatment matrices, such as incinerator ash and compost, but further analytical method development is needed to enhance extraction and minimize interferences.

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