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Identification of TNT Transformation Products in Soil

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PREFACE

This report was prepared by Marianne E. Walsh, Research Physical Scientist, Applied Research Branch, Experimental Engineering Division, and Dr. Thomas F. Jenkins, Research Chemist, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by the U.S. Army Waterways Experiment Station (AF25), Ann Strong, Project Monitor.

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CONTENTS

Preface ii
Introduction 1
Procedure 1
Results and discussion 3
Mass spectra of nitroaromatic compounds 3
Survey of dried soils 3
Analysis of undried soils 7
Comparison of transformation products identified using various extraction solvents 7
Analysis of soils contaminated with tetryl 10
Summary of transformation products identified in soil extracts 10
Literature cited 12
Appendix A: Mass spectra of TNT and potential contaminants 15
Appendix B: Fragmentation pathways for nitroaromatics 25
Appendix C: U.S. military explosives and propellants 29
Abstract 32

ILLUSTRATIONS

Figure

1. Chromatograms obtained using various liquid chromatographic parameters 2
2. Typical HPLC chromatogram obtained from a TNT contaminated soil showing the commonly occurring co-contaminants TNB, 2-A,4-A and 2,4-DNT 5
3. Whole propellant grains found in an EOD area 5
4. HPLC chromatograms showing detection of 2-A and 4-A 8
5. Mass spectrum of compound identified as nitrosodinitrotoluene 10
6. Mass spectrum of compound identified as 2,4-dinitroanthranil 11
7. HPLC chromatograms of extracts of soils contaminated with tetryl 11
8. Mass spectra of compounds found in tetryl-contaminated soils 12

TABLES

Table

1. Most abundant mass spectral fragment ions (m/e) for TNT and possible co-contaminants determined using electron impact ionization 3
2. Range of concentrations found in contaminated samples 4
3. Summary of compounds found by GC/MS analysis of acetone extracts of soils from Army installations 6
4. Summary of compounds found by HPLC and GC/MS analyses of acetonitrile extracts of soils from Mead, Nebraska 8
5. Kinetic study results using methanol or methylene chloride, or both, for soil 26 extraction 9
6. Kinetic study results using methanol or methylene chloride, or both, for soil 32 extraction 10

Identification of TNT Transformation Products in Soil

MARIANNE E. WALSH AND THOMAS F. JENKINS

INTRODUCTION

Soils at many U.S. Army installations are contaminated with explosives residues. Analytical methodology has been developed at CRREL to detect and quantify some of these residues in soil (Jenkins et al. 1989) and water (Jenkins et al. 1986, Miyares and Jenkins 1991). Once explosives enter the environment, however, they may be transformed by microbiological and photochemical processes (Burrows et al. 1989). Since some of the transformation products are also of environmental concern, analytical methodology will also be required for these by-products. 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 may be expected in soil (Pennington 1988, Walsh 1990).

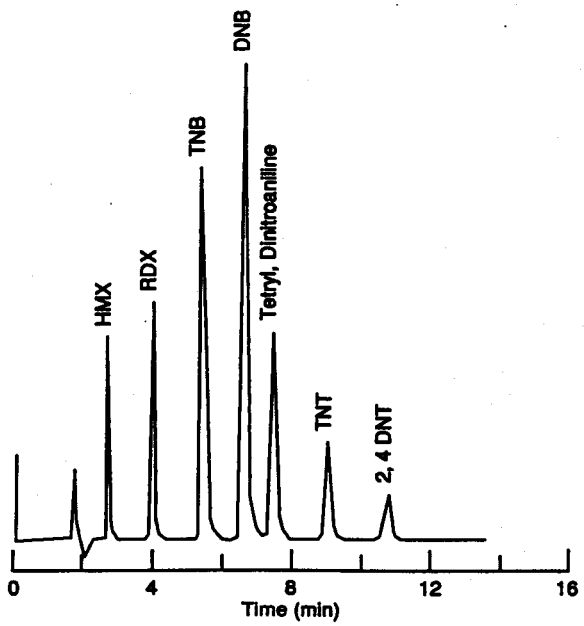
This paper will summarize the compounds present in U.S. military explosives, tabulate what residues have been found in soils collected at Army installations, and describe an initial study to investigate which solvent-extractable transformation products accumulate to detectable quantities in explosive-contaminated soils. Since the primary method of analysis for transformation products was gas chromatography/mass spectrometry (GC/MS), only thermally stable products compatible with gas chromatographic analysis were detected (primarily single ring nitroaromatic compounds). Some High Performance Liquid Chromatographic (HPLC) analyses for transformation products were also performed, but identification of transformation products was limited by the availability of analytical standards.

PROCEDURE

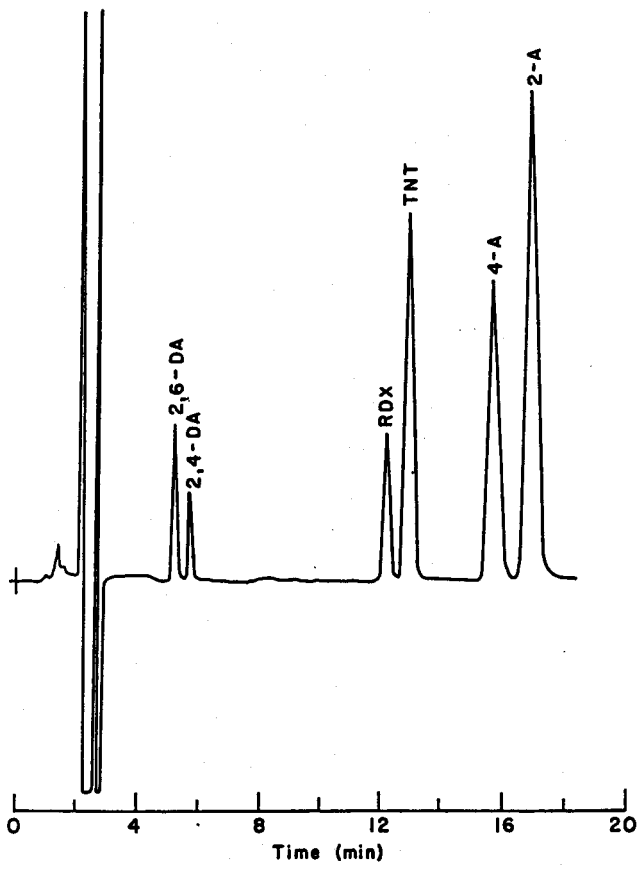
Soil samples were extracted in a sonic bath with either acetone, acetonitrile, methanol or methylene chloride. Both wet and dry soils were extracted. Soil-to-solvent ratios varied from 1:2 to 1:5 (mass [g]:volume [mL]); the smallest mass of soil extracted was 2 g and the largest was 20 g. Sonication times were from 1 to 48 hours. The sonic bath temperature was maintained below 25°C. After sonication, all extracts were filtered through disposable Millex SR filter units (0.5-µm pore size).

Extracts were analyzed by GC/MS or by RP-HPLC, or both. Samples were introduced into the Mass Selective Detector (MSD) through a Hewlett-Packard 5890 Series 2 gas chromatograph. An HP-5 (cross-linked 5% phenyl methyl silicone, 25-m × 0.20-mm × 0.33-µm film thickness) column was maintained at 75°C for 2 minutes and then the oven was temperature-programmed at 20°C/min to 240°C and held at 240°C for 10 minutes. The transfer line to the MSD was set at 280°C and the operating temperature of the source was 220°C. The injection port temperature was 250°C; splitless injections were used. The carrier gas was helium; linear gas velocity was 30 cm/s. GC/MS analysis was conducted using a Hewlett-Packard 5970 MSD. The mass spectra were obtained at an ionization voltage of 70 eV.

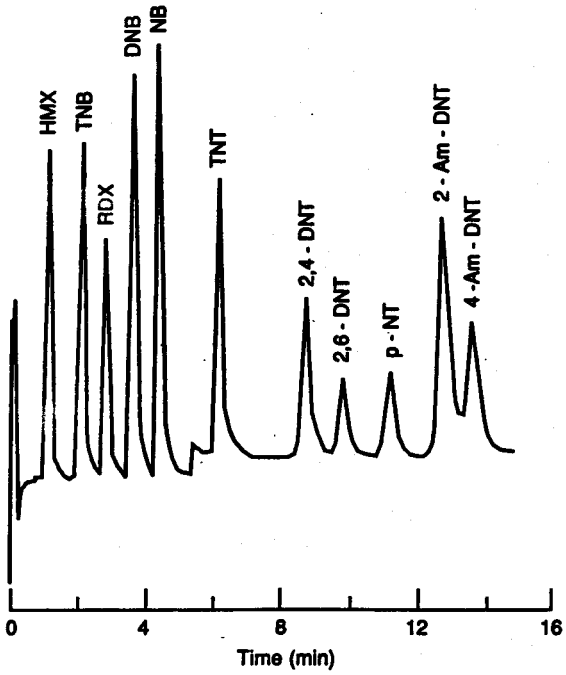
RP-HPLC determinations were conducted on a system containing a Spectra Physics 8800 pump and Spectra 100 variable wavelength UV detector. Samples were introduced onto the LC column through a 100-µL sampling loop. UV absorbances were measured at 254 or 238 nm. Chromatographic



a. LC-18 column (25 cm ×4.6 mm ×5 μm) eluted with 1.5 mL/min of 1:1 methanol–water.



b. LC-18 column (3.3 cm ×4.6 mm i.d.) in-line ahead of an LC-CN column (25 cm ×4.6 mm i.d.) eluted with 1.5 mL/min of 60.5:25:14.5 water–methanol–THF.



*c. LC-8 column (7.5 cm ×4.6 mm ×3 μm) eluted with 2 mL/min of 70.7:27.8:1.5 water–methanol–*THF.

Figure 1. Chromatograms obtained using various liquid chromatographic parameters.

data were collected on a Hewlett-Packard 3396A integrator and a Linear strip chart recorder. A variety of separation conditions was used with reversed-phase columns. Chromatograms with LC parameters are shown in Figure 1.

Analytical standards of 2,4,6-TNT (2,4,6-trinitrotoluene), 2,4-DNT (2,4-dinitrotoluene), 2,6-DNT (2,6-dinitrotoluene), TNB (1,3,5-trinitrobenzene), DNB (1,3-dinitrobenzene), TNBA (2,4,6-trinitrobenzaldehyde) and 2,4,6-trinitrophenol (picric acid) were prepared from Standard Analytical Reference Materials (SARM) obtained from the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, Maryland. All SARMs are at least 98 mole percent pure (USATHAMA 1990). Standards for 2-A (2-amino-4,6-dinitrotoluene), 4-A (4-amino-2,6-dinitrotoluene), 2,4-DA (2,4-diamino-6-nitrotoluene) and 2,6-DA (2,6-diamino-4-nitrotoluene) were obtained from Dr. David Kaplan at the U.S. Army Natick Laboratories. Standards for 3-nitroaniline, 4-amino-2-nitrotoluene, 2-amino-4-nitrotoluene and 2,4,6-trinitrobenzoic acid were obtained from Chem Service. The isomers of nitrotoluene, 3,5-dinitroaniline and 2,4-dinitrophenol were obtained from Aldrich and Kodak respectively. The various isomers of TNT were obtained from C. Ribaudo, Picatinny Arsenal, Dover, New Jersey. The identity of all standards that were not SARM was confirmed by GC/MS.

The methanol, acetonitrile, acetone and methylene chloride used to extract the soils, prepare standards or prepare mobile phases were either Baker or Mallinckrodt HPLC grade.

RESULTS AND DISCUSSION

Mass spectra of nitroaromatic compounds

Prior to analysis of soil extracts, standard solutions of known and potential TNT transformation products and commonly occurring co-contaminants were prepared. These standard solutions were analyzed by GC/MS to obtain retention times and mass spectra (Appendix A). The most abundant ions for each compound are listed in Table 1, and a description of fragmentation pathways for these nitroaromatic compounds is included in Appendix B.

Survey of dried soils

Over the past decade, CRREL has obtained contaminated soil samples from various Army sites. Each of these soils was analyzed by USATHAMA standard method SM02 (Jenkins et al. 1989); results are summarized in Table 2.

For soil samples collected at sites such as arsenals, depots and ammunition plants, the analytes TNT and RDX were found most frequently and at the highest concentrations (i.e., up to parts per hundred). When TNT was present in a soil, TNB, isomers of amino-DNT and 2,4-DNT were also generally present at detectable levels (Fig. 2). TNB is a phototransformation product (Burlinson 1980), the amino-DNTs are biotransformation products (Jerger et al. 1976) and 2,4-DNT is a manufacturing by-product (U.S. Army 1984). When RDX was found in a soil, HMX was also found but at a lower concentration. It is an impurity in munitions-grade RDX. Tetryl was infrequently found, perhaps because it is no longer used as a military explosive owing to its instability. The instability can also contribute to loss during sample preparation (Jenkins et al. 1989).

Table 1. Most abundant mass spectral fragment ions (m/e) for TNT and possible co-contaminants determined using electron impact ionization.

Compound	*Molecular weight*	*Base peak*	*Other fragments (m/e)*
	TNT isomers		
2,4,6-TNT	227	210	89,63,30,180,193
3,4,5-TNT	227	30	227,63,89
2,4,5-TNT	227	210	30,51,63
2,3,4-TNT	227	134	30,210,63,180
2,3,5-TNT	227	210	180,30,63
2,3,6-TNT	227	30	210,63,51
	TNT transformation products		
2-Am-4,6-DNT ✓	197	180	197,78,104
4-Am-2,6-DNT ✓	197	180	197,104,78
2,4-Diamino-6-NT ✓	167	167	121,94,120
2,6-Diamino-4-NT ✓	167	167	121,94,28
TNB ✓	213	213	75,30,74
Dinitroaniline	183	183	64,63,91
TNBA ✓	241	30	74,75
	Other nitroaromatics		
2,4-DNT ✓	182	165	89,63,30,119
2,6-DNT ✓	182	165	63,89,90
4-Amino-2-NT	152	152	135,107,77
2-Amino-4-NT	152	152	106,77,79
DNB	168	168	30,76,75,50
3-nitroaniline	138	138	65,92,80
o-NT	137	120	137,65,92,89,39
m-NT	137	91	137,65,39,63,107
p-NT	137	91	137,65,39,107
2,4,6-trinitrophenol	229	229	62,91
2,4-dinitrophenol	184	184	63,53,15

Table 2. Range of concentrations (μg/g) found in contaminated samples.

Total no. of samples	*TNT*	*TNB*	*2-Am-DNT*	*2,4-DNT*	*DNB*	*Tetryl*	*HMX*	*RDX*
Nebraska Ordnance Works								
40	0.12–20,600 *n* = 14 median = 5.41	0.12–159 *n* = 13 median = 13.5	0.05–8.03 *n* = 8 median = 1.16	0.08–16.6 *n* = 10 median = 2.84	0.06–1.51 *n* = 5 median = 0.90	0.25–1260 *n* = 5 median = 230	1.1–115 *n* = 8 median = 7.72	0.5–1247 *n* = 10 median = 19.5
Umatilla Depot (Oregon)								
11	131–38,600 *n* = 11 median = 3990	9.52–63.5 *n* = 5 median = 19.6	ND	ND	0.29–29.8 *n* = 3 median = 11.4	ND	ND	ND
Newport, Indiana								
11	0.4 *n* = 1	ND	0.29 *n* = 1	ND	ND	ND	not analyzed	0.5–12,203 *n* = 11 median = 38.6
Weldon Springs Training Area (Missouri)								
29	0.12–13,400 *n* = 8 median = 210	0.3–60.7 *n* = 6 median = 12.4	0.05–2.30 *n* = 4 median = 0.11	0.08–0.7 *n* = 3 median = 0.4	0.06 *n* = 1	ND	1.1 *n* = 1	0.5 *n* = 1
Iowa AAP								
6	0.63–15,400 *n* = 6 median = 453	53.2–549 *n* = 3 median = 119	not analyzed	not analyzed	45.2 *n* = 1	346 *n* = 1	2.45–5700 *n* = 4 median = 28.7	97.4–13,900 *n* = 2 median = 7000
Raritan Arsenal (New Jersey)								
22	1.19–745 *n* = 5 median = 3.1	0.12–3.85 *n* = 2 median = 1.98	2.0–37.1 *n* = 2 median = 19.6	0.08–42.7 *n* = 3 median = 0.17	ND	ND	1.1 *n* = 1	0.5–4.38 *n* = 2 median = 2.44
Hawthorne AAP (Nevada)								
8	4.4–13,900 *n* = 5 median = 1910	3.2–116 *n* = 4 median = 95.4	ND	0.4–28.1 *n* = 4 median = 4.0	0.20–15.0 *n* = 4 median = 2.2	ND	56–2435 *n* = 3 median = 142	2.6–8112 *n* = 5 median = 127
Hastings East Park (Nebraska)								
24	0.12–10.6 *n* = 4 median = 231	2.7 *n* = 1	0.05 *n* = 1	2.6 *n* = 1	0.25 *n* = 1	ND	1.1 *n* = 1	0.5 *n* = 1
Milan (Tennessee)								
7	1.1–35 *n* = 4 median = 3.4	2.5–6.1 *n* = 2 median = 4.3	not analyzed	not analyzed	ND	ND	3.7–86 *n* = 4 median = 53	139–616 *n* = 3 median = 378
Louisiana AAP								
2	12.4–14.8 *n* = 2 median = 13.6	2.1–3.8 *n* = 2 median = 3.0	not analyzed	not analyzed	ND	ND	68–258 *n* = 2 median = 163	185–972 *n* = 2 median = 578
VIGO Chemical Plant (Indiana)								
2	0.56–7.61 *n* = 2 median = 4.10	ND	ND	ND	ND	ND	ND	ND
Chickasaw Ordnance Works (Tennessee)								
2	0.12 *n* = 1	ND	ND	ND	ND	ND	ND	ND
Sangamon Ordnance Plant (Illinois)								
2	103 *n* = 1	0.68 *n* = 1	4.9 *n* = 1	0.08 *n* = 1	ND	ND	ND	ND
Lexington-Bluegrass Depot (Kentucky)								
13	5.90 *n* = 1	ND	ND	ND	ND	ND	ND	ND
Eagle River Flats (Alaska) EOD site and impact area								
216	0.12–115 *n* = 12 median 0.24	not analyzed	0.05–0.731 *n* = 8 median = 0.20	0.08–84.0 *n* = 65 median = 0.62	ND	ND	ND	0.044–0.076 *n* = 4 median = 0.05
Camp Shelby (Missouri) EOD site and impact area								
7	ND	ND	DN	0.08–53.7 *n* = 4 median = 31.3	ND	ND	1.1 *n* = 2	0.5–3.83 *n* = 2 median = 2.2
TOTAL								
402	77	39	25	91	15	6	26	43

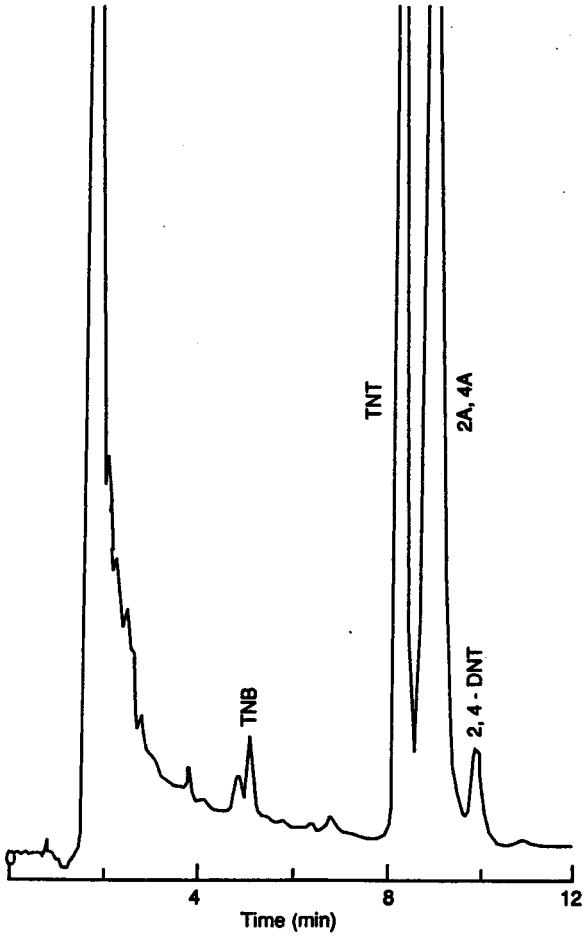


Figure 2. Typical HPLC chromatogram obtained from a TNTcontaminated soil showing the commonly occurring co-contaminants TNB, 2-A, 4-A and 2,4-DNT.

Two Explosive Ordnance Disposal (EOD) sites were sampled, and at both sites 2,4-DNT was detected at much higher concentrations than TNT. The source of this contamination was probably the improper demolition of excess propellant (i.e., it was blown up, not burned). In fact whole propellant grains were found scattered about each EOD area (Fig. 3). GC/MS analysis of acetonitrile extracts of soil samples and propellant grains confirmed the presence of diphenylamine and dibutylphthalate, which, along with nitrocellulose (Table C1), are the ingredients of M1 propellant.

For an initial study of the TNT transformation products present in soil, results of the HPLC analyses were used to select a series of soils representing a range of TNT concentrations (1 µg/g to 14 mg/g). The soils were obtained from the following locations: Weldon Springs (Missouri), Hawthorne (Nevada), Hastings East (Nebraska), Sangamon (Illinois), Raritan (New Jersey) and VIGO chemical plant (Indiana). Subsamples (20-g) were extracted with 100 mL of acetone by manually shaking for 3 minutes and equilibrating in an ultrasonic bath at 20°C for 14 hours. A portion (10 mL) of each extract was filtered through a Millex SR filter unit and a 1-µL aliquot analyzed by GC/MS, as described in the experimental section. Then, the 10-mL filtrate was concentrated under a gentle stream of nitrogen until the volume was approximately 0.5 mL and another 1-µL aliquot was analyzed by GC/MS.

As shown in Table 3, the most commonly

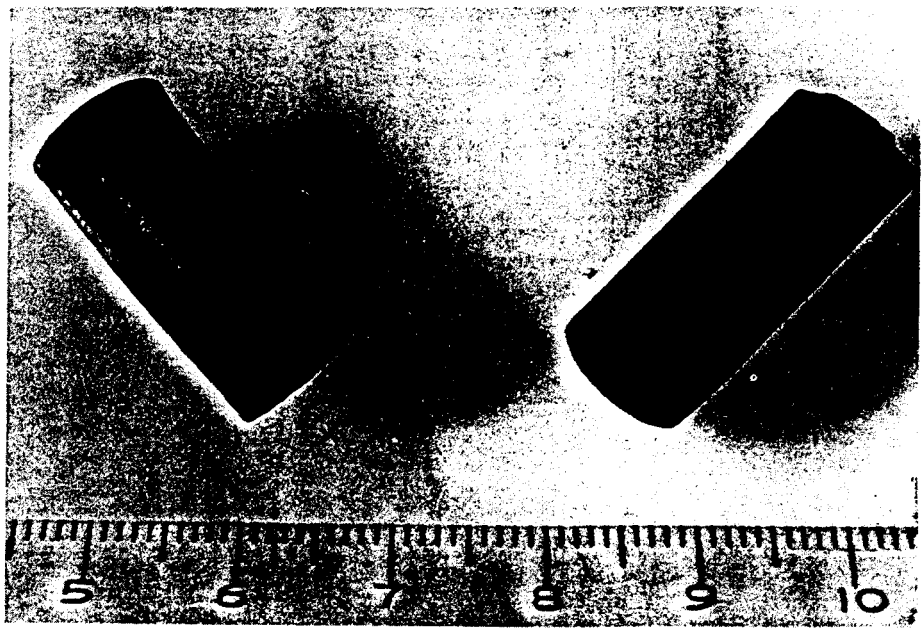


Figure 3. Whole propellant grains found in an EOD area. These grains are made up of nitrocellulose, 2,4-DNT, diphenylamine and dibutlyphthalate (scale in centimeters).

Table 3. Summary of compounds found by GC/MS analysis of acetone extracts of soils from Army installations.

TNT† conc. (µg/g)	Analyte																
	DNB	*2,6-DNT*	*Dinitrophenol*	*2,4-DNT*	*3,5-DNT*	*Unknown**	*TNB*	*2,4,6-TNT*	*Unknown**	*2,3,6-TNT*	*2,4,5-TNT*	*Trinitrophenol*	*TNBA*	*4Am-DNT*	*DNA*	*2Am-DNT*	*Dinitronaphthalene*
Weldon Springs (Missouri)																	
1.4	—	—	—	—	—	√	—	√	√	—	—	—	—	—	—	—	—
186	—	—	—	—	—	—	√	√	—	—	—	—	—	—	—	√	—
800	√	—	—	√	—	—	√	√	—	—	—	—	√	√	√	√	—
2320	—	√	—	√	—	—	√	√	—	—	—	—	√	√	—	√	—
13400	—	√	—	√	—	—	—	√	—	—	—	—	√	—	—	√	—
Hawthorne (Nevada)																	
4.4	—	—	—	—	—	√	—	√	√	—	—	—	—	—	—	—	—
5140	—	√	—	√	√	—	√	√	—	—	—	—	—	√	√	√	—
13,900	—	√	—	√	—	—	—	√	—	—	—	√	—	—	—	—	—
6.3	—	—	√	—	—	√	√	√	√	—	—	—	—	—	—	—	—
Hastings East (Nebraska)																	
89.2	—	—	—	—	—	—	—	√	—	—	—	—	—	—	—	—	—
373	—	√	—	√	—	—	—	√	—	—	—	—	—	√	√	√	—
Sangamon (Illinois)																	
103	—	—	—	—	—	—	—	√	—	—	—	—	—	√	—	√	—
Raritan (New Jersey)																	
1.4	—	—	—	—	—	√	—	√	√	—	—	—	—	—	—	—	—
140	—	—	—	—	—	—	—	√	—								
745	√	√	—	√	√	—	—	√	—	√	√	—	√	√	√	√	√
VIGO (Indiana)																	
7.6	—	—	—	—	—	—	—	√	—	—	—	—	—	—	—	—	—

*Base peak of 195, tentatively identified as an isomer of aminodinitrobenzoic acid.
†Determined by HPLC.

found reduction products were 2-amino-4,6-dinitrotoluene (2A) and 4-amino-2,6-dinitro-toluene (4A). They were present in samples containing TNT, ranging in concentration from 186 to 2300 µg/g. Neither 2A nor 4A was found in the soil with 13,900 µg/g of TNT. This could be a result of TNT toxicity to the microorganisms responsible for this transformation. Other transformation products identified were trinitrobenzene (TNB), trinitrobenzaldehyde (TNBA) and 3,5-dinitroaniline (DNA).

In the chromatograms of 4 of the 16 soil samples, we observed two peaks eluting on either side of TNT. These peaks were observed only in those samples with levels of TNT less than 6 µg/g. The mass spectra for these peaks were consistent with the structure of aminodinitrobenzoic acid. The isomer 2-amino-4,6-dinitrobenzoic acid has been identified as a stable phototransformation product of TNT (Spanggord et al. 1983). Thus, we have tentatively identified these compounds as isomers of aminodinitrobenzoic acid.

Analysis of undried soils

The results discussed thus far were obtained from extraction of soils that had been air dried. There is the possibility that the drying process plays a role in the formation of the transformation products that we observed or results in the destruction of other unidentified products. The receipt of fresh soil samples from Mead, Nebraska, gave us an opportunity to investigate these possibilities by extracting soils that had not been previously dried. A 10-g subsample of each wet soil was placed in a 40-mL vial, and the remainder of the soil sample was air dried and ground with a mortar and pestle.

Subsamples (2-g) of the dried soils were extracted with 10 mL of acetonitrile in a sonic bath for 18 hours at 20°C. An aliquot of each extract was filtered, then analyzed by GC/MS. Another aliquot of each extract was diluted 1:3 v/v with water prior to analysis by HPLC using an LC-8 column (7.5 cm × 4.6-mm × 3 µm), eluted with 70.7:27.8:1.5 water–methanol–THF (Miyares and Jenkins 1991). Peak identities were confirmed on an LC-CN column eluted with 1:1 methanol–water.

Subsamples (10-g) of the wet soils were extracted with 25 mL of acetonitrile in a sonic bath for 18 hours at 20°C. The extracts were diluted 1:2 v/v with water and separated on a tandem arrangement of LC-18 and LC-CN columns eluted with 60.5:25:14.5 water–methanol–THF. This separation scheme permits the detection of the isomers of diaminonitrotoluene that would coelute with HMX and RDX on the LC-8 column (Fig. 1). The disadvantage of this separation is that HMX coelutes with 2A (Fig. 1).

From the results of these analyses (Table 4), the following generalizations can be made. First, the diaminonitrotoluenes either were not present or were not extracted from the soil with acetonitrile. Anilines are known to bind to humic material in such a way that they are not recovered by simple solvent extraction (Bollaog and Loll 1983). Second, dinitroaniline was detected in most of the soils containing TNB. Third, when detected, 2A and 4A were either found together in almost equal amounts (Fig. 4) or 2A was detected but not 4A. Comparing the results from the extraction of dried and undried soils, it appears to us that the drying process does not play a role in the formation of the detected degradation products. No additional transformation products were detected from extraction of the undried soil. Thus, we conclude that air drying the soil prior to extraction is the preferred approach, since it enables sample homogenization prior to subsampling.

air drying optimal

Comparison of transformation products identified using various extraction solvents

In the two previous sets of soil sample extractions, polar solvents (acetone and acetonitrile) and lengthy extraction times (14 and 18 hours) were used. The transformation products 2A, 4A, DNA, TNB and TNBA were found in several soils. Some transformation products may not be stable in these solvents, especially when subjected to extended periods of sonication. Extraction with other solvents and with shorter or longer periods of sonication might reveal other products.

Subsamples (10 g) of two soils (26 and 32) from Weldon Springs and Mead, respectively, containing TNT and some transformation products (Tables 2 and 3) were extracted with 30-mL of methylene chloride, a less polar solvent than either acetone or acetonitrile. For comparison, subsamples were also extracted with methanol and with a mixture of methanol–methylene chloride. Samples were sonicated and, at various time intervals ranging from 1 to 48 hours, 3.00-mL aliquots of the extract were removed. Prior to analysis by GC/MS, the extracts were filtered and reduced in volume to 0.5 mL under a stream of nitrogen at room temperature. Integrated peak areas were obtained from the chromatograms and normalized to the peak areas for an internal standard (p-nitrotoluene). The results of these analy-

Table 4. Summary of compounds found by HPLC and GC/MS analyses of acetonitrile extracts of soils from Mead, Nebraska.

Soil no.	*Analysis*	*TNT*	*TNB*	*DNA*	*2A*	*4A*	*2,6DA*	*2,4DA*	*DNB*	*2,6DNT*	*2,4DNT*	*HMX*	*RDX*
32	HPLC:LC18/CN	2.6	0.45	ND	Int	2.4	0.07	ND	0.04	ND	ND	Int	429
	HPLC:LC8	3.5	Int	1.2	1.9	ND	ND	ND	ND	ND	ND	116	1140
	GCMS	present	ND	ND	present	ND	ND	ND	ND	ND	ND	—	—
34	HPLC:LC18/CN	2620	244	ND	Int	ND	ND	ND	ND	ND	2.2	Int	615
	HPLC:LC8	3200	Int	9.2	8.3	8.3	ND	ND	3.2	ND	4.1	114	845
	GCMS	present	present	present	present	present	ND	ND	present	present	present	—	—
35	HPLC:LC18/CN	79.6	89.6	ND	Int	ND	ND	ND	ND	ND	1.45	Int	41.5
	HPLC:LC8	77.2	Int	ND	0.14	0.92	ND	ND	0.79	0.14	1.23	11.9	46.6
	GCMS	present	present	present	present	present	ND	ND	present	present	present	—	—
37	HPLC:LC18/CN	4.85	102	2.0	Int	ND	ND	ND	ND	ND	3.4	Int	19.7
	HPLC:LC8	2.45	Int	1.5	0.35	ND	ND	ND	ND	0.17	2.7	3.9	16.7
	GCMS	present	present	prsent	present	ND	ND	ND	ND	ND	present	—	—
38	HPLC:LC18/CN	0.3	ND	ND	0.33	0.36	ND	ND	ND	ND	0.21	ND	ND
	HPLC:LC8	0.7	Int	ND	0.39	0.36	ND	ND	ND	ND	0.24	ND	ND
	GCMS	present	ND	ND	ND	ND	ND	ND	ND	ND	present	—	—
40	HPLC:LC18/LC	105	0.9	ND	6.7	7.9	ND	ND	ND	0.09	0.2	ND	ND
	HPLC:LC8	270	Int	ND	5.6	8.8	ND	ND	0.3	ND	0.8	ND	ND
	GCMS	present	ND	present	present	present	ND	ND	ND	ND	ND	—	—
41	HPLC:LC18/CN	5.7	0.1	ND	8.0	5.3	ND	ND	ND	0.08	0.2	ND	ND
	HPLC:LC8	5.2	Int	ND	6.7	3.7	ND	ND	0.04	0.08	0.3	ND	ND
	GCMS	present	ND	ND	present	present	ND	ND	ND	ND	present	—	—

Int = Interference, quantitation not possible.
— = HMX and RDX not detectable under GC conditions used.
ND = Not detected.

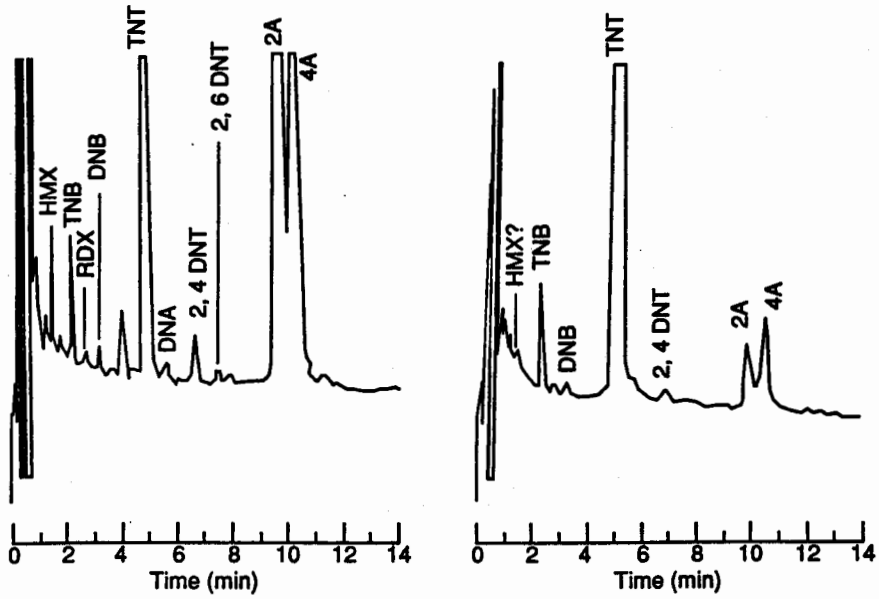


Figure 4. HPLC chromatograms (LC-8 column) showing detection of 2-A and 4-A.

Table 5. Kinetic study results using methanol or methylene chloride, or both, for soil 26 extraction.

	Normalized areas		
Hour	Methanol	MeOH/MeCl$_2$	MeCl$_2$
a. 2-amino-4,6-DNT			
1	0.0491	0.0501	0
2	0.0797	0.0539	0
6	0.113	0.0618	0.065
22	0.08	0.0729	0.0438
30	0.0768	0.0872	0
48	0.121	0.0658	0
b. 3,5-dinitroaniline			
1	0.0318	0.0388	0
2	0.0483	0.0438	0
6	0.08	0.0618	0.0506
22	0.0457	0.0468	0
30	0	0.0667	Present
48	0.0765	0.0534	0
c. Possible nitrosodinitrotoluene isomer			
1	0.254	0.320	0
2	0.365	0.336	0
6	0.677	0.399	0
22	0.312	0.34	0
30	0.564	0.508	Present
48	0.561	0.320	0
d. Trinitrobenzaldehyde			
1	0.0675	0.108	0
2	0.0528	0.132	0
6	0.174	0.0397	0
22	0	0.0247	0
30	0	0.123	0
48	0	0.00911	0
e. 4-amino-2,6-DNT*			
1	0.0603	0.0520	0
2	0.0391	0.0545	0
6	0.0737	0.0793	0.065
22	0.092	0.0857	0.0356
30	0.12	0.122	0.030
48	0.154	0.0858	0

	Normalized areas		
Hour	Methanol	MeOH/MeCl$_2$	MeCl$_2$
f. Possibly 4,6-dinitroanthranil			
1	0.116	0.103	0
2	0.131	0.104	0
6	0.181	0.116	0
22	0.165	0.104	0.0371
30	0	0.137	0.0738
48	0.214	0.143	0
g. TNB and TNT combined			
1	11.0	14.2	6.06
2	17.4	14.3	15.6
6	18.2	13.7	13.0
22	17.6	13.9	13.7
30	23.5	12.7	13.6
48	18.5	13.9	17.3
h. 2,4-DNT			
1	0.0181	0	0
2	0	0	0
6	0.0342	0.0239	0
22	0	0.0147	0.0142
30	0.057	0.0485	0.018
48	0.0447	0.0433	0
i. DNB and 2,6-DNT			
1	0	0	0
2	0	0	0
6	0.0262	0	0
22	0	0.0278	0.0167
30	0	0.0215	0
48	0.018	0.04	0

*A phthalate coeluted with 4A.

ses are shown in Tables 5 and 6.

The transformation products previously found in acetone extracts of soil 26 included 2A, 4A, DNA, TNBA and TNB. These compounds were also found in the methanol extracts, and, with the exception of TNBA, in the methylene chloride extracts as well. Instability of TNBA in certain solvents has been reported elsewhere (Jenkins et al. 1989). Two additional transformation products were tentatively identified in the methanol and methylene chloride extracts. One compound eluted at 13.1 minutes and had a mass spectrum (Fig. 5) consistent with the structure for an isomer of nitrosodinitrotoluene. Liu et al. (1984) identified nitrosonitrotoluene as a reduction product of DNT. The other compound eluted at 11.1 minutes and had a base peak of 209. This compound was tentatively identified as 4,6-dinitroanthranil (Fig. 6), reported to be a photoproduct of TNT (Burrows et al. 1989).

The only transformation products previously found in soil 32 were 2A and TNB. Both of these products were found in the methanol extracts, but not in the methylene chloride extracts. Methylene chloride may be a poor soil extraction solvent when these analytes are present at low levels and possibly associated with strong binding sites (Leggett 1985, 1991). Overall, methylene chloride

Table 6. Kinetic study results using methanol or methylene chloride, or both, for soil 32 extraction.

	Normalized areas		
Hour	*Methanol*	*MeOH/MeCl$_2$*	*MeCl$_2$*
a. 2-amino-4,6-DNT			
1	0.0214	0	0
2	0	0	0
6	0	0	0
22	0.08	0	0
30	0.0768	0	0
48	0.121	0	0
b. TNB			
1	0.0692	0	0
2	0	0	0
6	0	0	0
22	0.19	0.22	0
30	0.0861	0.167	0
48	0	0	0
c. TNT			
1	0.1654	0.0346	0.053
2	0.1434	0.1655	0.1215
6	0.0954	0.222	0
22	0.487	0.479	0
30	0.271	0.199	0.1797
48	0.3211	0.7547	0

was a much poorer extraction solvent than either methanol or methanol–methylene chloride for degradation products of TNT.

Analysis of soils contaminated with tetryl

Owing to its instability, tetryl is rarely observed in environmental samples. However, four soil samples from Mead, Nebraska, contained relatively high concentrations of tetryl (52–1260 µg/g), as determined by HPLC. Using an LC-8 separation (Fig. 1), we observed the same pattern of peaks in the chromatograms for the four contaminated soils (Fig. 7). With the exception of tetryl, the retention times for these peaks did not match the retention times of other nitroaromatic or nitramine compounds frequently found in munition-contaminated soils.

Gas chromatographic analysis of tetryl is problematic in that tetryl thermally degrades to N-methyl picramide. Tamiri and Zitrin (1986) speculate that this transformation occurs in the hot injection port. When the extracts from the tetryl-contaminated soils were analyzed by GC/MS, three compounds were identified: N-methyl picramide, 4-amino-2,6-dinitro-N-methylaniline and 2,4,6-trinitroaniline (Fig. 8).

SUMMARY OF TRANSFORMATION PRODUCTS IDENTIFIED IN SOIL EXTRACTS

In summary, for soil samples collected at Army sites such as ammunition plants, depots and arsenals, TNT and RDX were the most frequently found contaminants. The TNT transformation products TNB, TNBA, 2-amino-4,6-DNT and 4-amino-2,6-DNT were generally found in concert with TNT. Additionally, dinitroaniline, the reduction product of TNB, was confirmed by GC/MS in several soils. Other transformation products such as the tetranitroazoxytoluenes could also be present, but standards are needed to develop analytical methodology for the extraction and detection of these compounds.

It should be emphasized, however, that transformation products other than those identified by GC/MS could be present in these soils. This is particularly true for degradation products of RDX and HMX, which are themselves difficult to analyze by GC/MS (Belkin et al. 1985). Methods such

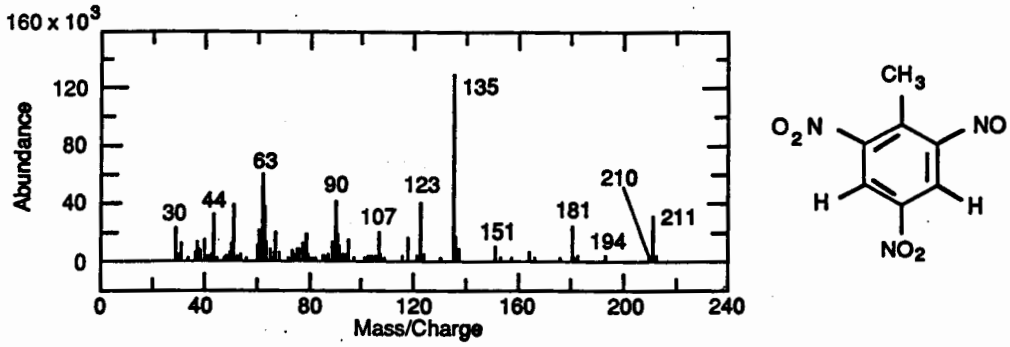


Figure 5. Mass spectrum of compound identified as nitrosodinitrotoluene.

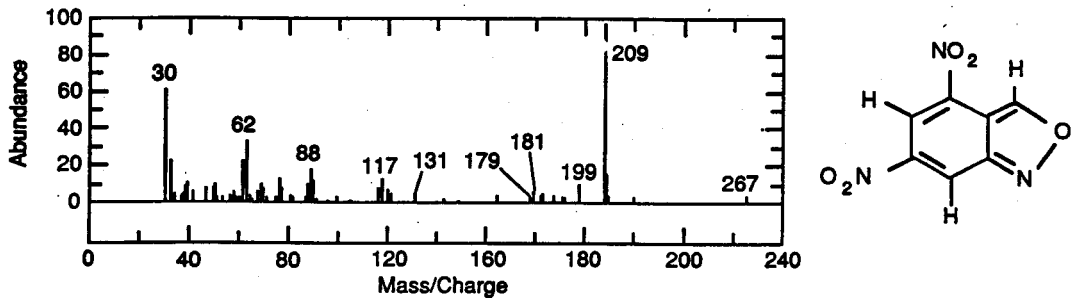


Figure 6. Mass spectrum of compound identified as 2,4-dinitroanthranil.

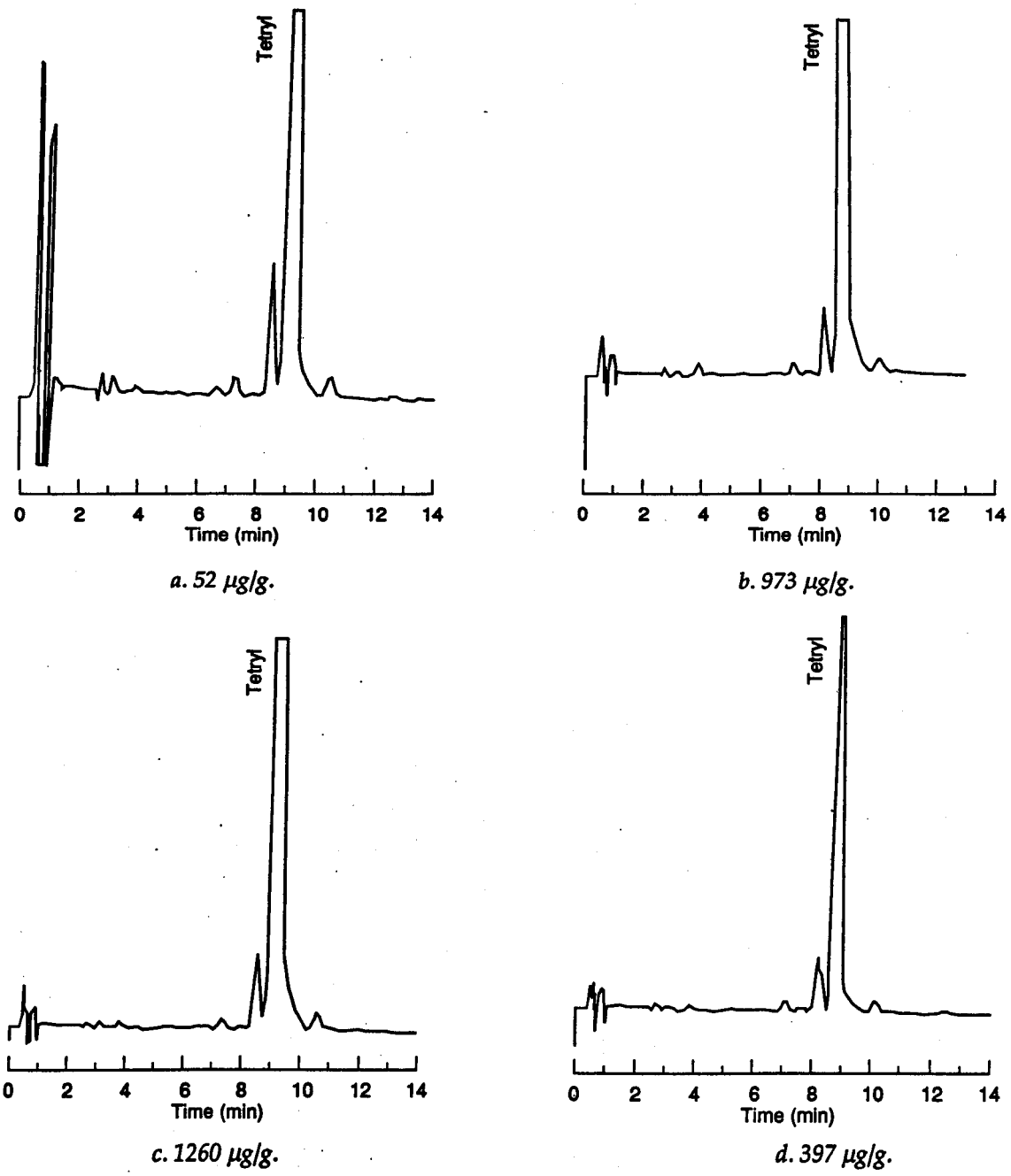
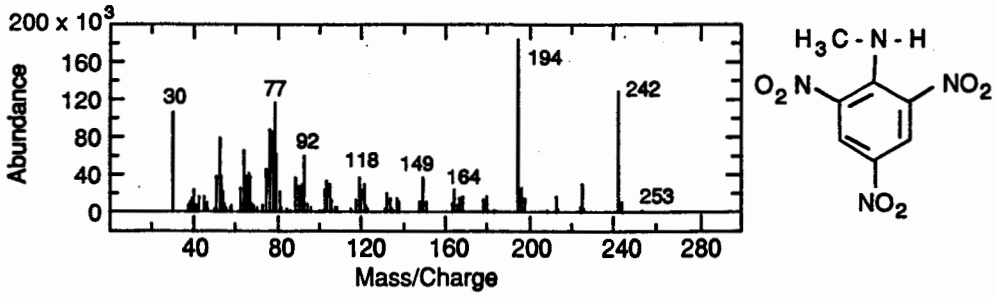
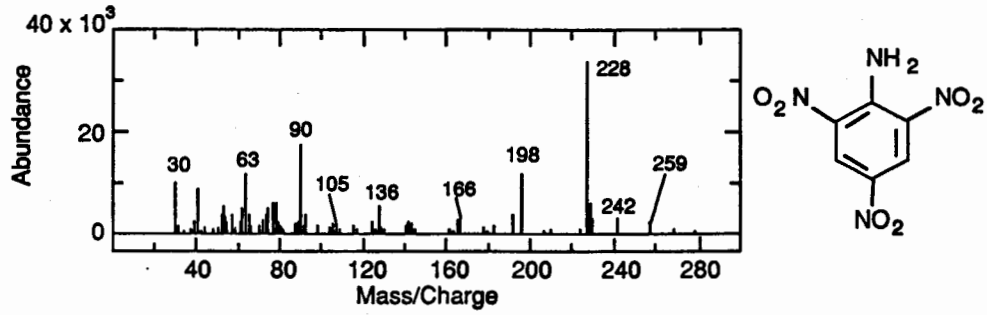


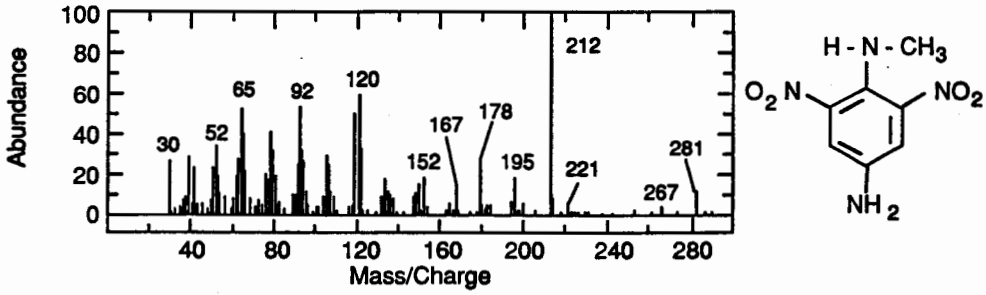
Figure 7. HPLC chromatograms of extracts of soils contaminated with tetryl.



a. N-methyl picramide.



b. 2,4,6-trinitroaniline.



c. 4-amino-2,6-dinitro-N-methylaniline.

Figure 8. Mass spectra of compounds found in tetryl-contaminated soils.

as LC (Liquid Chromatography)/MS and SFC (Supercritical Fluid Chromatography)/MS may be very useful for identifying transformation products of these two compounds, as well as additional products from TNT and tetryl.

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APPENDIX A: MASS SPECTRA OF TNT AND POTENTIAL CONTAMINANTS

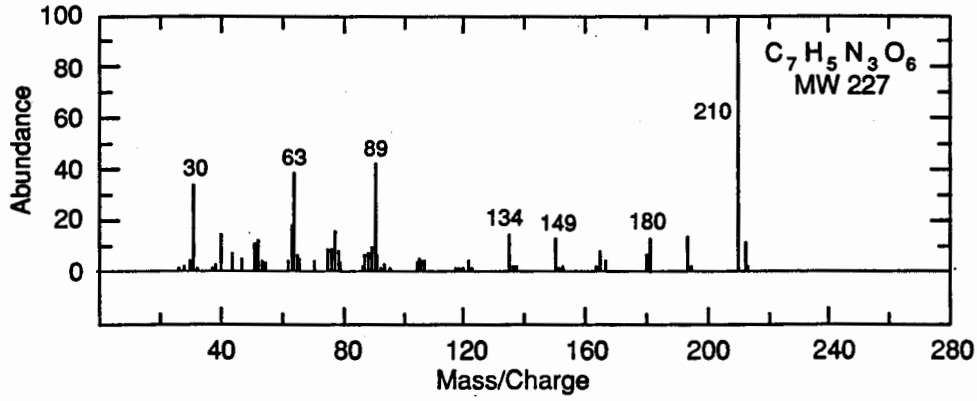


Figure A1. 2,4,6-TNT.

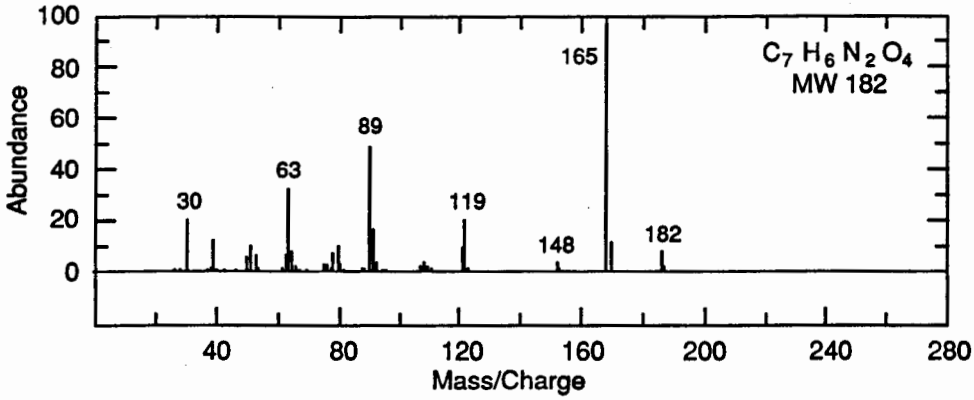


Figure A2. 2,4-DNT.

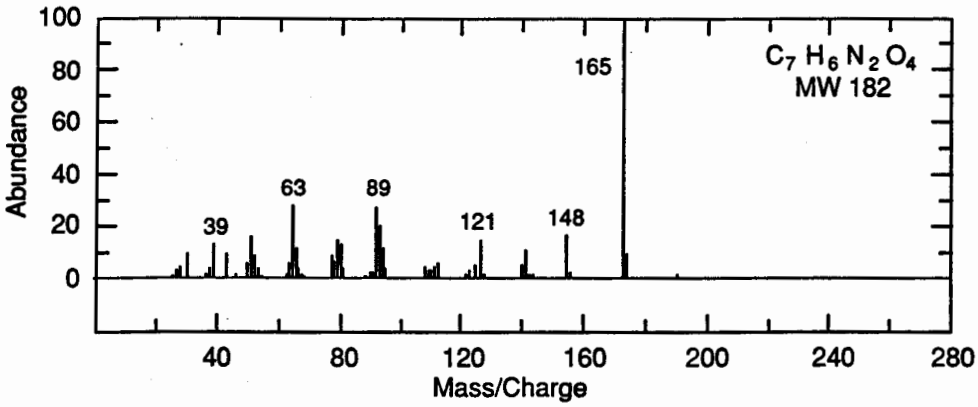


Figure A3. 2.6-DNT.

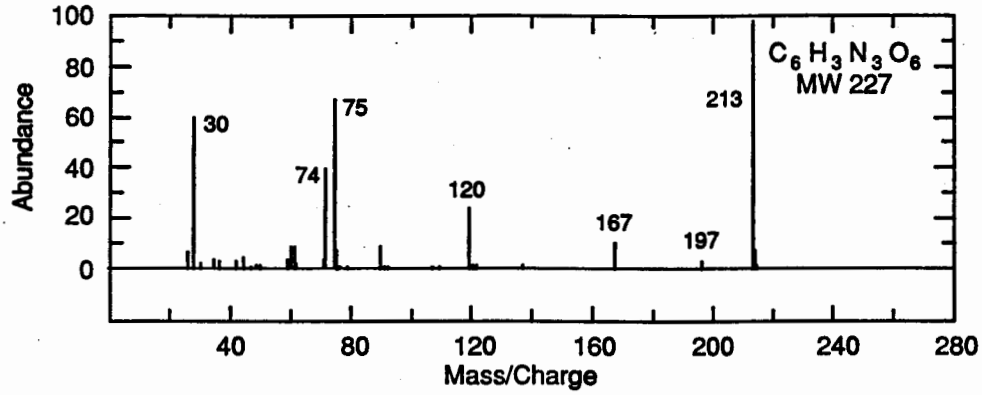


Figure A4. 1,3,5-TNB.

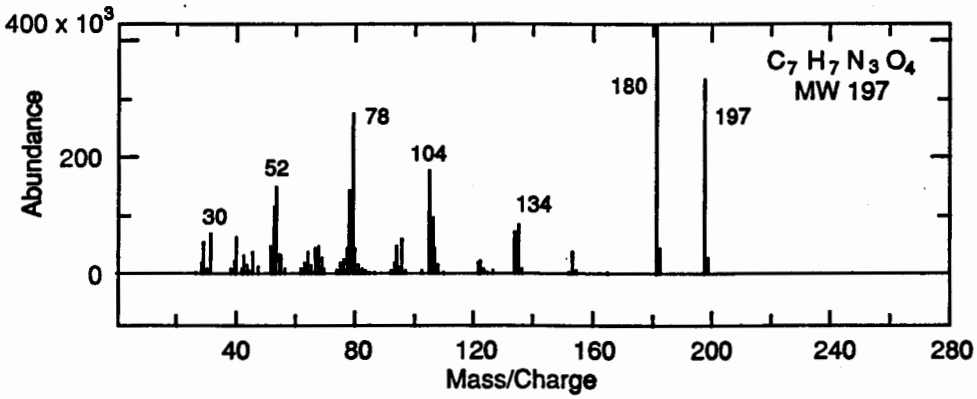


Figure A5. 2 Am-4,6-DNT.

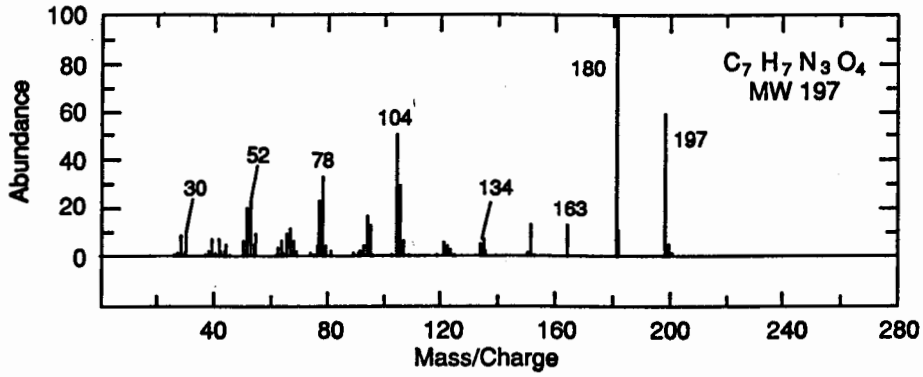


Figure A6. 4-Am-2,6-DNT.

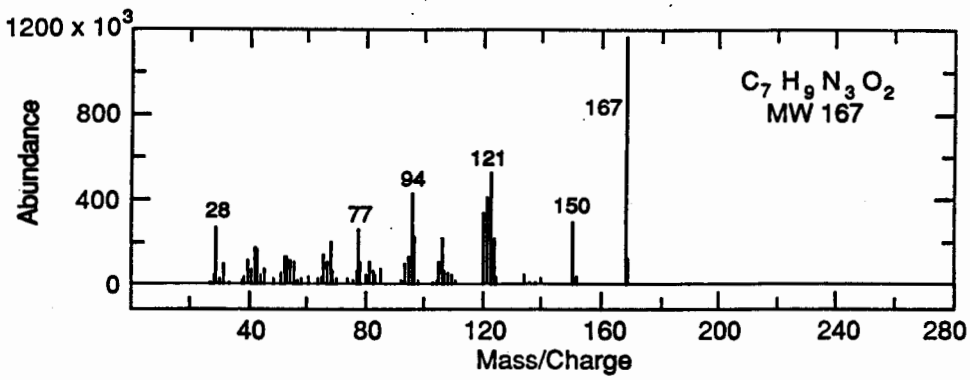


Figure A7. 2,4 Diamino-6-NT.

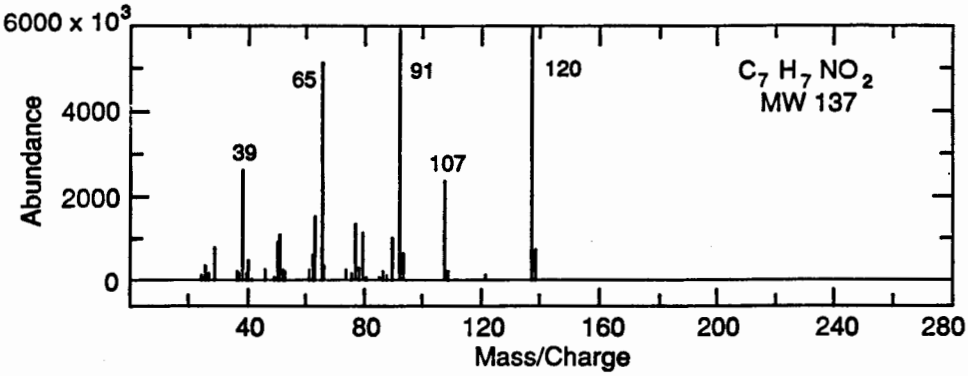


Figure A8. p-NT.

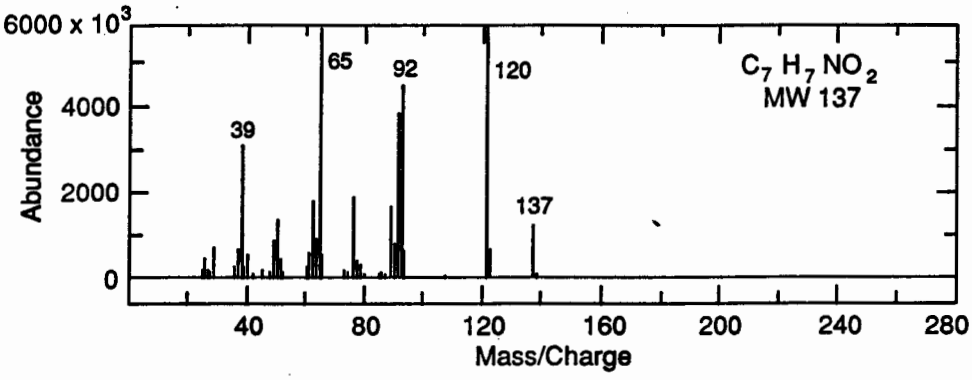


Figure A9. o-NT.

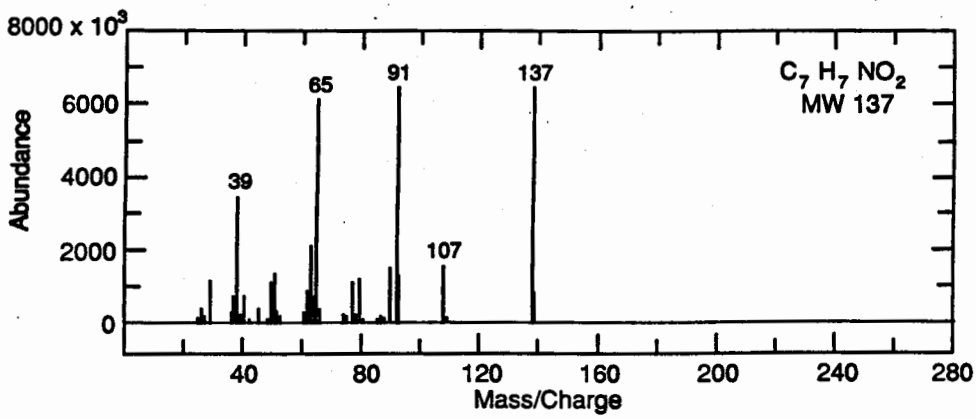


Figure A10. m-NT.

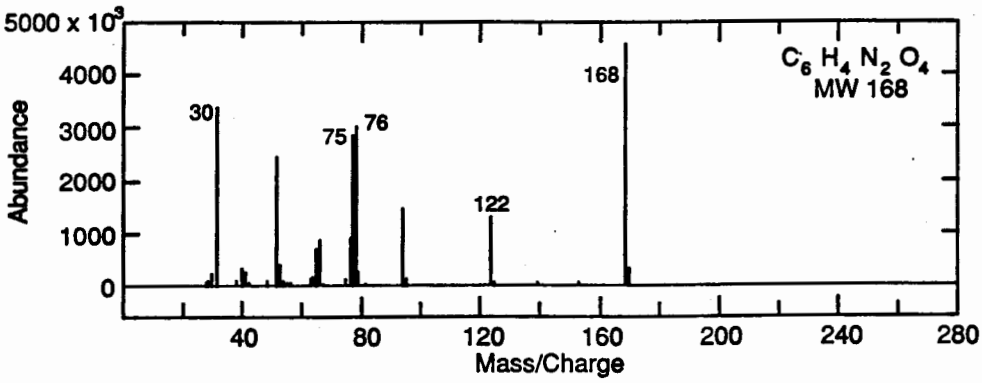


Figure A11. 1,3-DNB.

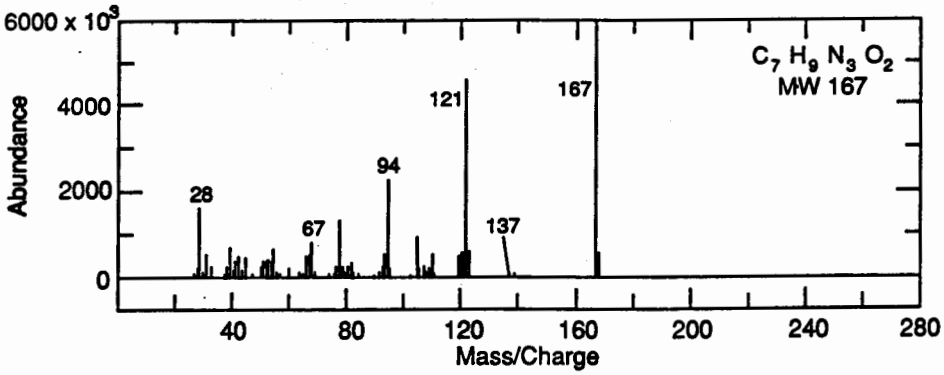


Figure A12. 2,6-Diamino-4-NT.

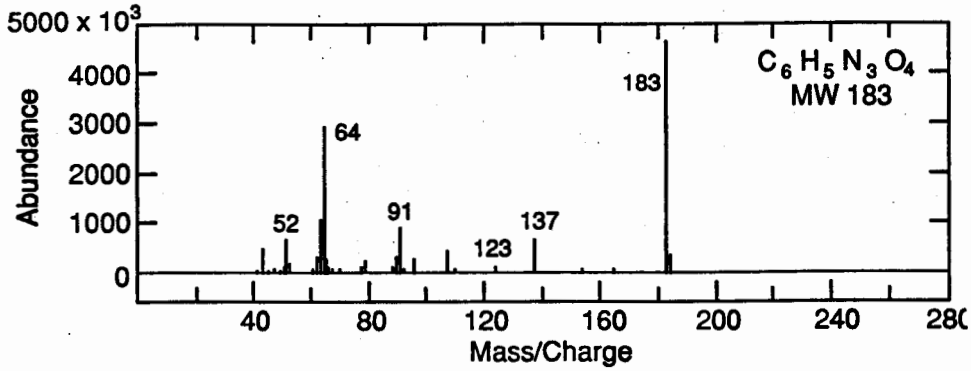


Figure A13. 3,5-Dinitroanaline.

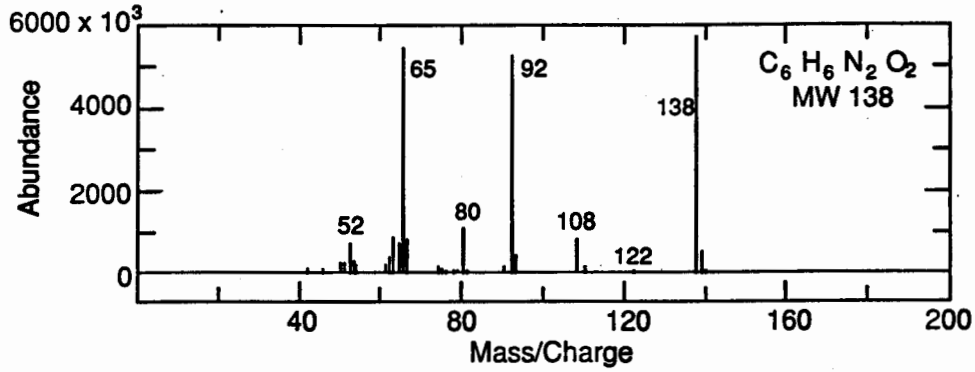


Figure A14. 3-Amino-nitrobenzene.

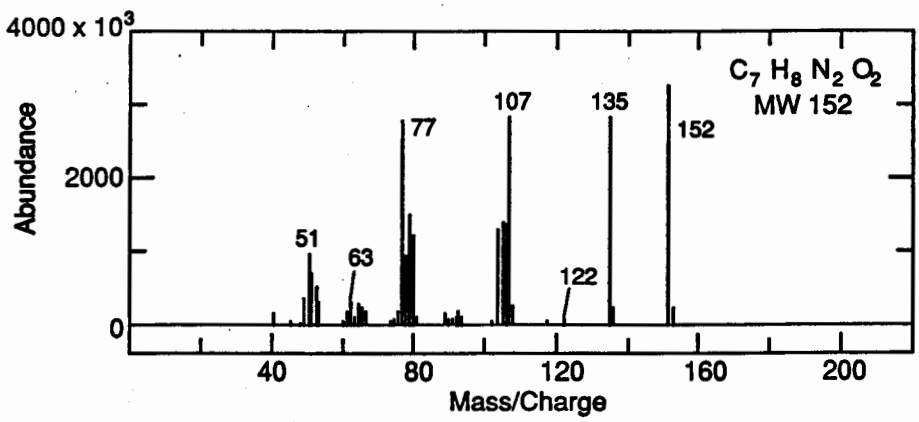


Figure A15. 4-Amino-2-nitrotoluene.

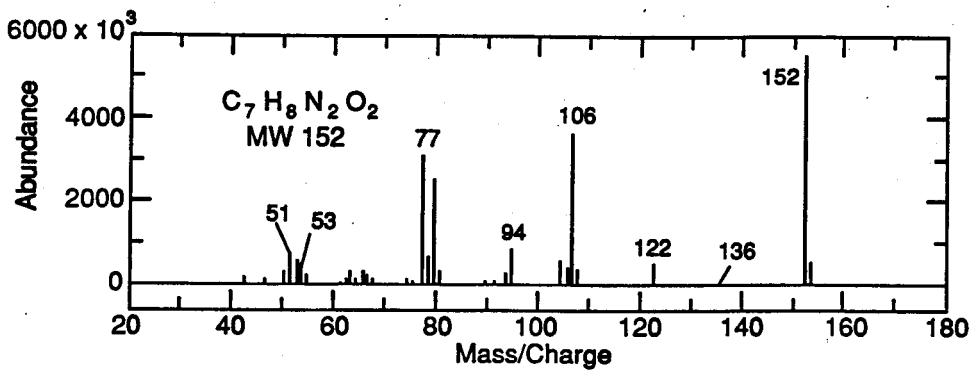


Figure A16. 2-Amino-4-nitrotoluene.

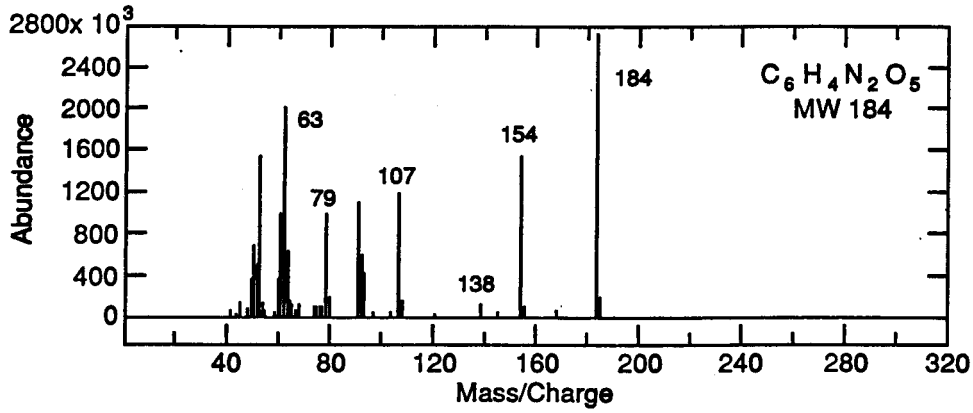


Figure A17. 2,4-Dinitrophenol.

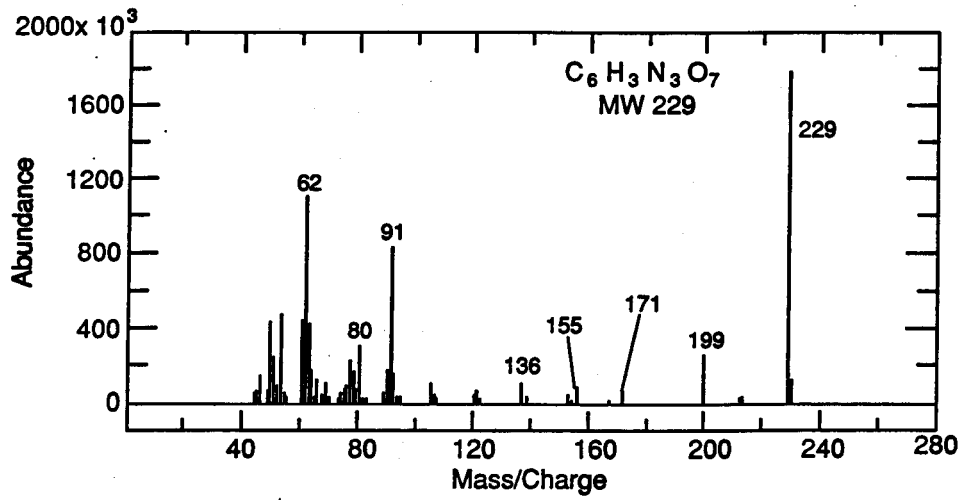


Figure A18. Picric acid or 2,4,6-trinitrophenol.

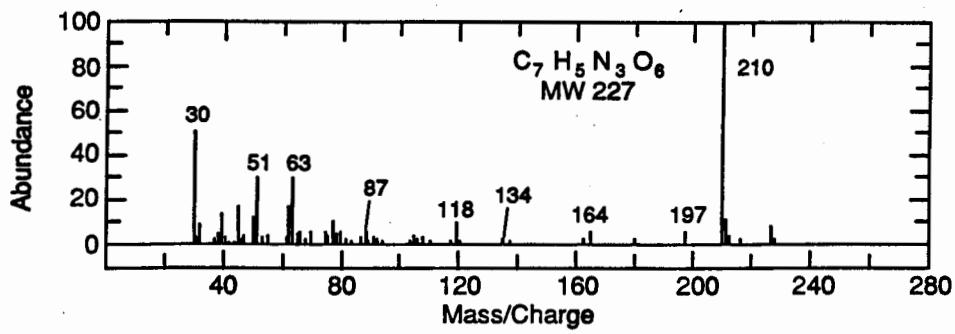


Figure A19. 2,4,5-TNT.

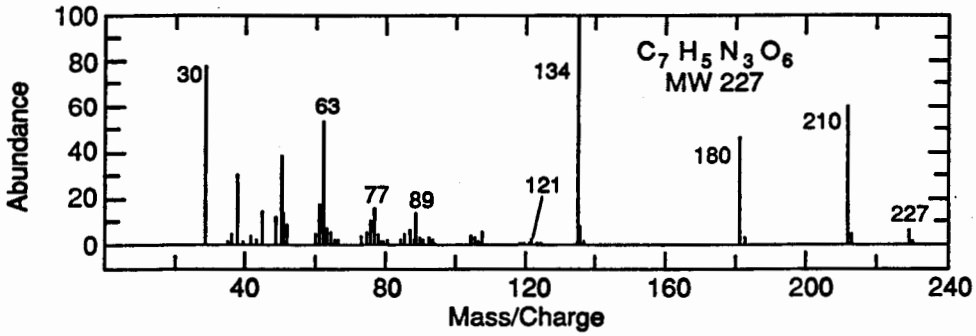


Figure A20. 2,3,4-TNT.

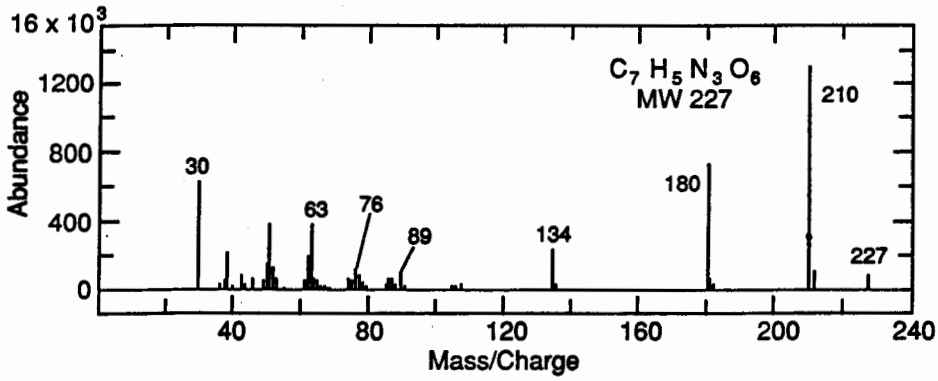


Figure A21. 2,3,5-TNT.

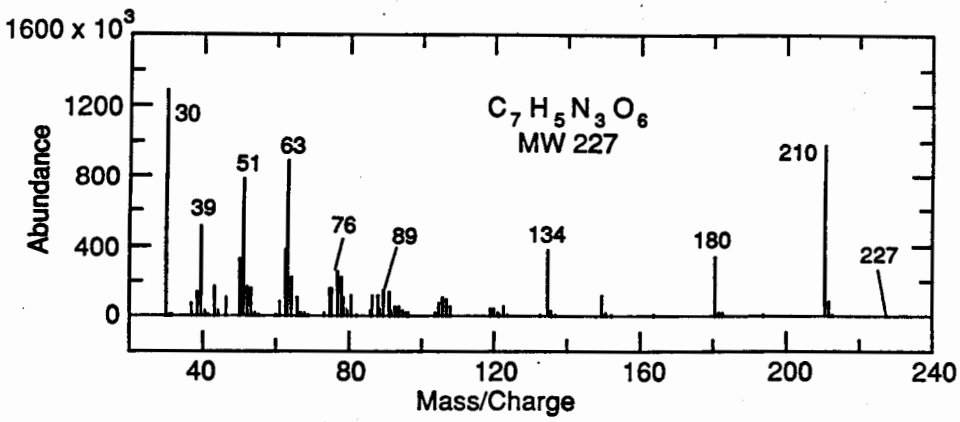


Figure A22. 2,3,6-TNT.

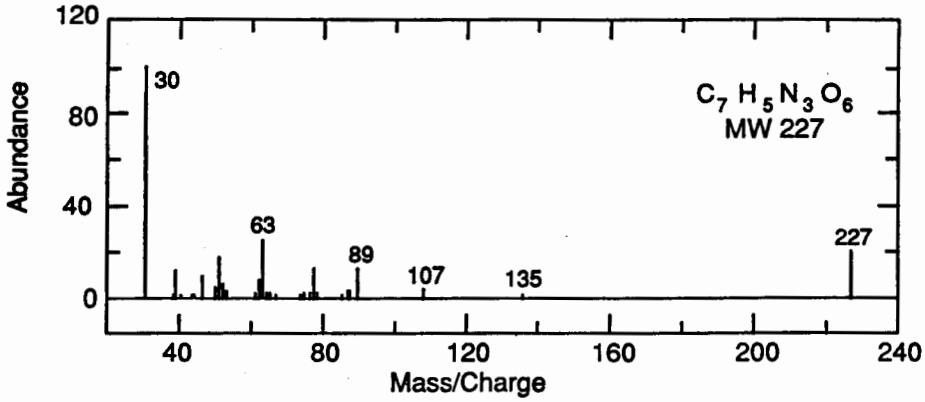


Figure A23. 3,4,5-TNT.

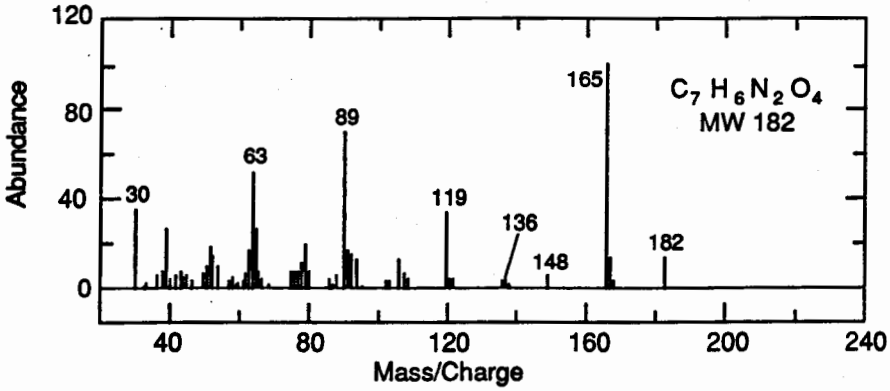


Figure A24. 2,5-DNT.

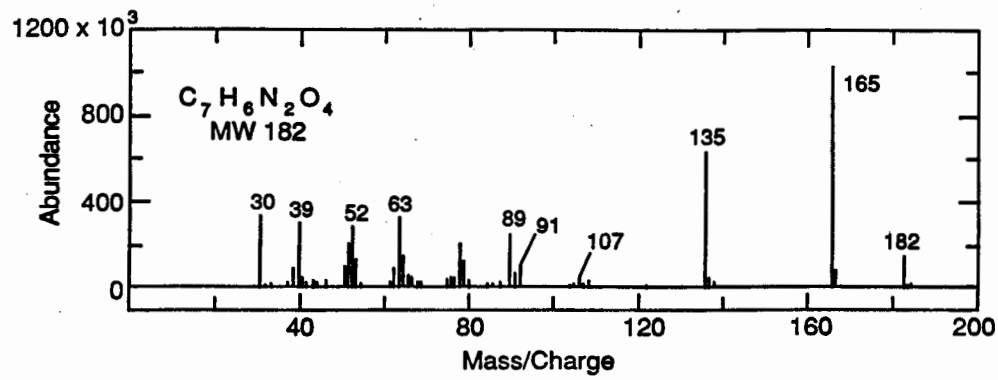


Figure A25. 2,3-DNT.

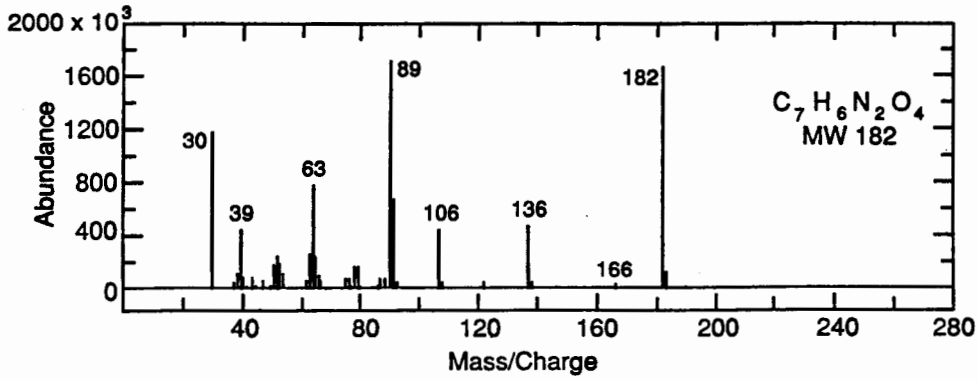


Figure A26. 3,5-DNT.

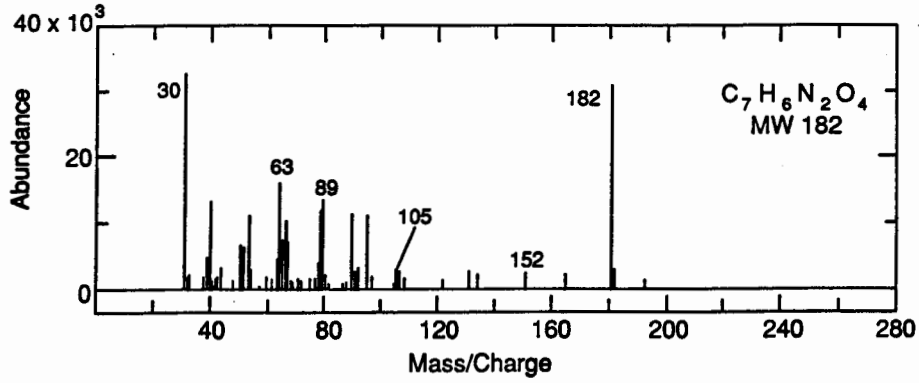


Figure A27. 3,4-DNT.

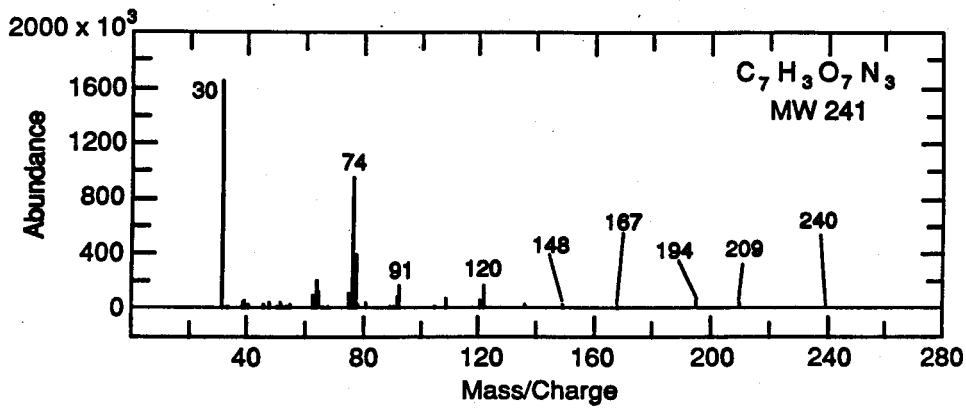
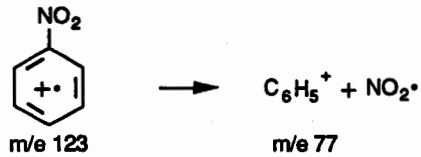


Figure A28. TNBA.

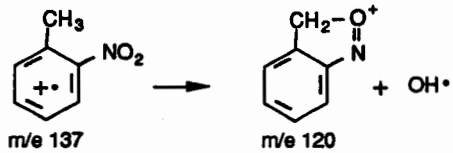
APPENDIX B: FRAGMENTATION PATHWAYS FOR NITROAROMATICS

The fragmentation pathways for mono-substituted nitroaromatics in electron impact mass spectrometry have been discussed elsewhere (Budzikiewicz et al. 1967). For nitrobenzene, for example, there is a relatively abundant molecular ion at m/e = 123 and a loss of NO_2 to give the base peak in the spectrum at m/e = 77 (eq B1).



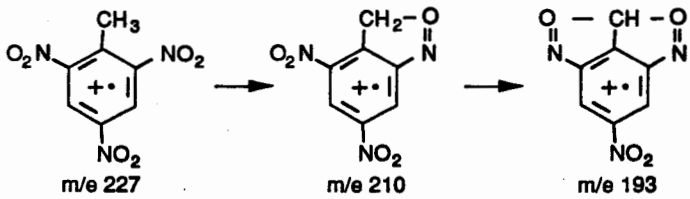
(B1)

When a methyl group is also present on the aromatic ring—ortho to a nitro substituent—the mass spectrum is modified in two ways. First, the intensity of the molecular ion [M] is substantially reduced and initial fragmentation is dominated by loss of a hydroxyl radical [M-17] as shown for o-nitrotoluene in eq B2.



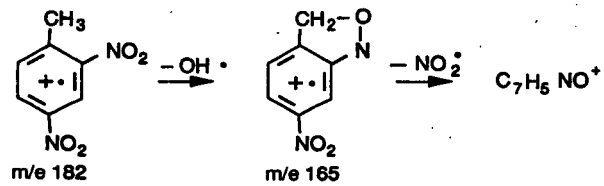
(B2)

Even when multiple nitro groups are also present, the base peak in the spectrum is generally this [M-17] ion (Jenkins et al. 1973). For nitroaromatic compounds in which the methyl group is ortho to two nitro groups, this loss of hydroxyl can occur twice to give an [M-34] ion as shown for 2,4,6-trinitrotoluene (eq B3).



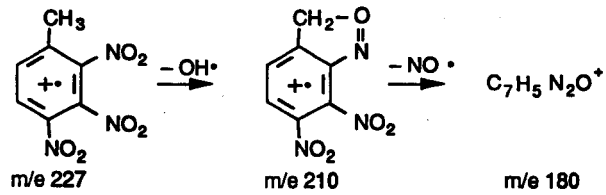
(B3)

For molecules where a methyl group is present, but not ortho to a nitro substituent, primary fragmentation generally occurs by loss of NO • or NO_2 •. The presence or absence of [M-17] and [M-34] ions can be used to differentiate between ortho and non-ortho substituted methyl nitroaromatics and mono- and di-ortho substituted methyl polynitroaromatics respectively. For example, there are measurable peaks at m/e = 193 [M-34] in the mass spectra of 2,4,6-TNT and 2,3,6-TNT, but no such ions are observed in the spectra of 2,4,5-TNT or 2,3,4-TNT. For polynitro compounds, secondary fragmentation of the [M-17] ions occurs primarily by loss of either NO • or NO_2 •. Loss of NO • is favored where intact nitro substituents are unhindered by other ortho substituents as shown for 2,4-DNT in eq B4. When



(B4)

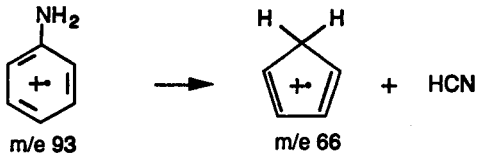
the intact nitro group is ortho to another substituent, such as the case with 2,3,4-TNT, loss of NO • is favored (eq B5).



(B5)

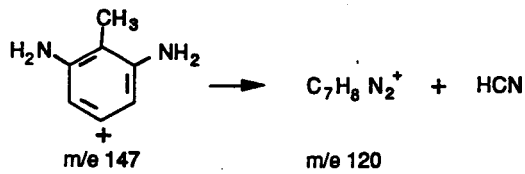
The presence of amino functionality on polynitaromatic compounds does not substantially alter primary fragmentation, as can be seen for 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene, which both show similar fragmentation patterns dominated by the [M-17] ion. Subsequent fragmentation of the [M-17] ion from 4-amino-2,6-dinitrotoluene shows a second loss of OH •, demonstrating that the two nitro groups are both positioned ortho to the methyl. The [M-17] ion from 2-amino-4,6-dinitrotoluene shows preferential further fragmentation by loss of NO_2•, demonstrating that nitro in the 4 position is not ortho to another ring substituent.

Once fragmentation of the nitro groups on the ring is complete, amino groups on the ring lose HCN, resulting in loss of 27. This was observed by Budzikiewicz et al. (1967) for primary fragmentation of the molecular ion from aniline (eq B6) and



(B6)

was observed by us in the further fragmentation of the m/e 212 daughter ion in 2,6-diamino-4-nitrotoluene (eq B7). This loss results in recognizable lower mass fragment ions in all amino-aromatics.



(B7)

The presence of a hydroxyl group on the ring of polynitroaromatic compounds produces a significant change in the mass spectra of these compounds. For both 2,4-dinitrophenol and 2,4,6-trinitrophenol (picric acid), the molecular ions are the base peaks in the spectra. In both cases primary fragmentation involves loss of NO • to

give large [M-30] fragment ions. In spite of the hydroxyl groups being ortho to nitro groups in both compounds, [M-OH] ions are not observed, unlike the methyl substituted analogs TNT and 2,4-DNT. The mass spectrum of 2,4,6-trinitrobenzaldehyde is unique in that neither the molecular ion or major fragment ions from simple losses of $NO\bullet$ or $NO_2\bullet$ are present in the 70-eV spectra. The dominant ions in the spectra are m/e = 30 (NO^+) and m/e = 74 ($C_6H_2^+$), which is the ion formed from loss of all ring substituents.

APPENDIX C: U.S. MILITARY EXPLOSIVES AND PROPELLANTS

Propellants

Propellants are divided into four classes, based on composition (U.S. Army 1984). These four classes are: single-base, double-base, triple-base and composite. Tables C1–C3 list the ingredients for the various compositions. Nitrocellulose is the chief ingredient in single-, double- and triple-base propellants. Diphenylamine is added as a stabilizer. Double-base propellants contain nitroglycerine, which acts as a gelatinizer for nitrocellulose, and triple-base propellants contain the explosive nitroguanidine in addition to nitrocellulose and nitroglycerin.

Composite propellants are a heterogeneous mixture of fuel such as metallic aluminum, a binder such as synthetic rubber and an inorganic oxidizing agent such as ammonium perchlorate.

Explosives

Most military explosive compositions contain either RDX, a nitramine, or TNT, a nitroaromatic, or both (Table C4 and C5) (U.S. Army 1984). Compositions can also contain nitramines such as HMX, nitroaromatics such as nitrotoluene and dinitrotoluene, nitrate esters such as nitrocellulose and PETN, salts such as ammonium nitrate and metals such as aluminum.

Table C1. Ingredients in single-base propellants (after U.S. Army 1984).

	Composition (%)			
Ingredient	*M1*	*M6*	*M10*	*IMR*
Nitrocellulose	85.0	87.0	98.0	100
Dinitrotoluene	10.0	10.0		8.0*
Dibutlyphthalate	5.0	3.0		
Diphenylamine	1.0*	1.0*	1.0	0.7
Potassium sulfate			1.0*	1.0*
Graphite			0.1*	

* Added.

Table C2. Ingredients in double-base propellants (after U.S. Army 1984).

	Composition (%)			
Ingredient	*M2*	*M5*	*M8*	*M18*
Nitrocellulose	77.45	81.95	52.15	80.0
Nitroglycerine*	19.5	15.0	43.0	10.0
Barium nitrate	1.4	1.4		
Potassium nitrate	0.75	0.75	1.25	
Ethyl centralite	0.6	0.6	0.6	
Graphite	0.3	0.3		
Dibutylphthalate				9.0
Diethylphthalate			3.0	
Diphenylamine				1.0

* Diethyleneglycol dinitrate sometimes substituted.

Table C3. Ingredients in triple-base propellants (after U.S. Army 1984).

Ingredient	*Composition (%)* M31	M30
Nitrocellulose	20.0	28.0
Nitroglycerine	19.0	22.5
Nitroguanidine	54.7	47.7
Dibutylphthalate	4.5	
Ethyl centralite	1.5	1.5
Graphite		0.1*
Cryolite	0.3	0.3

* Added.

Table C4. Explosives used in military explosive compositions (after U.S. Army 1984).

Compound	*(Formula)*	*Application*
HMX	($C_4H_8N_8O_8$)	Explosive charge, booster (octol), oxidizer in solid rocket and gun propellants
RDX (cyclonite)	($C_3H_6N_6O_6$)	Base charge in detonators, blasting caps, oxidizer in gun propellant, ingredient for projectile and bomb fillers
TNT	($C_7H_5N_3O_6$)	Bombs, HE projectiles, demolition charges, depth charges, grenades, propellant compositions
2,4-DNT	($C_7H_6N_2O_4$)	Ingredient of propellants, dynamites and plastic explosives
Tetryl	($C_7H_5N_5O_8$)	Boosters, ingredient of explosive mixtures, detonators and blasting caps, discontinued use in 1979
Ethylene dinitramineme (Haleite)	($C_2H_6N_4O_4$)	Booster
Ammonium nitrate	(NH_4NO_3)	Ingredient of mixtures used in bombs and large-caliber projectiles
Ammonium perchlorate	(NH_4ClO_4)	Ingredient of mixtures used in pyrotechnics and as projectile filler
1,2,4-Butanetriol trinitrate (BTTN)	$C_4H_7N_3O_9$)	Explosive plasticizer for nitrocellulose
Cyclotrimethylene trinitrosamine	($C_3H_6N_6O_3$)	Ingredient of projectile filler

Table C5. Explosive compositions (after U.S. Army 1984).

Composition	*Ingredients*	*Application*
Amatols	Ammonium nitrate and TNT (80/20, 60/40, 50/50)	Bombs, HE projectiles
Comp A	RDX (91–98.5%) coated with wax	Projectile filler, booster, grenades, shaped charges
Comp B	RDX (60%) and TNT(40%) Wax (1% added)	Fragmentation bombs, HE projectiles, granades, shaped charges
Cyclotols	RDX (60–75%) and TNT (25–40%)	Shaped charges, HE projectiles, grenades
Comp C	RDX (88.3%) and non-explosive plasticizer	Demolition explosive (replaced by C2)
Comp C2	RDX (78.7%), DNT (12%), meta-nitrotoluene (2.7%), TNT (5%), NC (0.6%), dimethylformamide (1%)	Demolition explosive (replaced by C3)
Comp C3	RDX (77%), DNT (10%), meta-nitrotoluene (5%), TNT (4%), tetryl (3%), NC (1%)	Demolition explosive, ammunition (replaced by C4)
Comp C4	RDX (91%),polyiso-butylene (2.1%), motor oil (1.6%), di(2-ethylhexyl) sebacate (5.3%)	Demolition explosive
Comp CH6	RDX (97.5%, calcium stearate (1.5%), graphite (0.5%) and polyisobutylene (0.5%)	Boosters and leads
Ednatols	Ethylene dinitramine and TNT (mixtures of 60/40, 55/45, and 50/50)	Bursting charges in ammunition, projectiles, bombs
LX-14	HMX (95.5%) and estane 5702-Fl (4.5%)	
Octols	HMX and TNT (mixtures of 75/25 or 70/30)	Fragmentation and shaped charges, oil well formation agent, HE projectile and bomb filler
Pentolite	PETN and TNT (mixtures of 50/50, 75/25, 40/60, 30/70, 10/90)	Shaped charges, bursting charge, demolition blocks
Picratol	Ammonium picrate (52%) and TNT (48%)	Ammunition
Tetrytols	TNT and tetryl (mixtures of 80/20, 75/25, 70/30 or 65/35)	Formerly used as demolition explosives or bursting charges (chemical shells and land mines)
Tritonal	TNT (80%) and flaked aluminum (20%)	Bombs
Amatex 20	RDX (40%), TNT (40%), and ammonium nitrate (20%)	Filler for ammunition
Ammonal	Ammonium nitrate (22%), TNT (67%), and flaked aluminum (11%)	Projectile filler
High blast explosives		
HBX-1	RDX (40.4%), TNT (37.8%) aluminum (17.1%), and wax and lecithin (4.7%)	HE charge
HBX-3	RDX (31.3%), TNT (29.0%), aluminum (34.8%) and wax and lecithin (4.9%)	HE charge
H-6	RDX (45%), aluminum (20%), TNT (30%), and D-2 Wax (5%)	HE charge
HTA-3	HMX (49%), TNT (29.0 or 28.65%), aluminum (22%), and calcium silicate (0.35%)	HE projectile and bomb filler
Minol-2	TNT (40%), ammonium nitrate (40%), and aluminum (20%)	Bombs (underwater depth, block buster, concrete fragmentation, general purpose)
Torpex	RDX (41.6%), TNT (39.7%), aluminum (18.0%) and wax (0.7%)	Shaped charges, depth charges, bombs
DBX	TNT (40%), RDX (21%), ammonium nitrate (21%), and aluminum (18%)	Depth charges
PBX	Several compositions containing either RDX (82-95%), diamino-trinitrobenzene (94%), or HMX (95%) mixed with a polymeric binder	
Baratol	Barium nitrate (67%) and TNT (33%)	Bomb filler
Baranal	Barium nitrate (50%) TNT (35%) and aluminum (15%)	Bomb filler
Black powder	Potassium nitrate (74%), sulfur (10.4%) and charcoal (15.6%)	Igniter powder, time rings (fuzes)
Explosive D	Ammonium picrate	AP projectiles and bombs
PTX-1	RDX (30%), Tetryl (50%), TNT (20%)	Land mines and demolition charges
PTX-2	RDX (41–44%), PETN (26-28%), and TNT (28–33%)	Shaped charges, Fragmentation charges

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Solvent-extractable TNT transformation products have been identified in explosive-contaminated soils. Soils from U.S. Army installations were extracted with a variety of solvents (acetonitrile, methanol, acetone and methylene chloride) and the extracts were analyzed by RP-HPLC-UV or GC/MS, or both. The TNT transformation products TNB, TNBA, 2-amino-4,6-DNT and 4-amino-2,6-DNT were generally found in concert with TNT. In additon, dinitroaniline, a reduction product of TNB, was also identified in several soils.

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