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A New Method for Determining Residues Generated During Munition Demilitarization Activities: Analysis of Environmental Soil and Water Samples

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ocedures are presented for qualitative screening and subsequent quantitation of munitions nd related compounds present at sites contaminated by open burning/open detonation (OB/OD) isposal of munitions. Methods were developed to recover munitions and polycyclic aromatic ydrocarbons (PAHs) from soil via sonic extraction into acetonitrile, and munitions from ater via trapping onto C18 disposable cartridges and eluting with methanol. Complementary PLC procedures were used for identification and quantification of these compounds. A ualitative HPLC gradient method was developed, and used to screen samples for a wide range f munitions and PAHs. Quantitation of munitions and their environmental reduction products as accomplished using an HPLC isocratic method. Recoveries of munitions and degradation roducts spiked into sandy loam soil were greater than 90% in all cases. Corresponding ecoveries from aqueous samples were comparable for the nitroaromatics, but were poorer for he nitramines. Critieria of detection for individual muntions ranged from 0.067 mg L^{-1} to .37 mg L^{-1}.

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INTRODUCTION

Out-of-date and out-of-specification munitions have commonly been disposed of by burning and detonation on unprotected ground (1). This practice, open burning/open detection (OB/OD), generates a mixture of contaminants into the immediate area at high concentration (2). The mixture consists primarily of unburned munitions but environmental weathering and microbial action are known to produce modifications (3). Brueggemann's analysis (4) of the ash from munitions burned in incinerators revealed substantial concentrations of polycyclicaromatic hydrocarbons (PAHs) but these compounds are not mentioned in Jenkin's report describing a method for quantitation of explosive residues in soil (5).

Nitroglycerin (NG) is a component of several military munitions (6) but is not generally found as a contaminant at OB/OD sites. Failure to detect NG may be attributed either to an actual absense of this compound or to an inability of current detection methods. Failure to detect NG could be due to its weak absorbance at UV wavelengths greater than 220 nm, where most munition analyses are performed.

Nitroguanidine (NQ) is used exclusively in M30 propellant, which is a mixture of NQ, NG and nitrocellulose. Since NQ is more polar than other munitions, it will leach rapidly and may therefore have a short residence time at the soil surface. It is also readily degraded by ultraviolet (UV) light (7). In addition, because of its high polarity, methods which utilize reversed phase high performance liquid chromatography (HPLC) and UV absorbance often have difficulty separating NQ from extractable natural soil components (8).

The nitramine munitions cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) are chemically similar and are widely used as explosives and as propellants. Industrial synthesis methods of these munitions do not produce pure compounds. All military grades of HMX contain RDX as an impurity and most RDX contains HMX (6). They are normally found together as environmental contaminants. Nitramines are easily extracted from soil samples and readily lend themselves to quantitation by reverse phase HPLC and UV absorbance.

Trinitrotoluene (TNT) and other nitroaromatics are the most common contaminants at many OB/OD sites. These compounds are less polar than the preceding and have excellent UV absorbance. They are readily quantitated by reverse phase HPLC and UV detection methods. Nitroaromatics undergo a variety of modifications in the environment but tend to remain identifiable as related forms because frequently their ring structure is not degraded (3).

MATERIALS AND METHODS

The method employed for sample preparation and extraction was adapted from the method developed and extensively tested by Jenkins (9, 10, 11). The modified procedure entailed grinding dried soil samples, and extracting into acetonitrile with 18 hours of sonication at 20 ^{o}C. Extracts were centrifuged at 3900 X G for 15 min, passed under piston pressure through a Gelman 0.45 Mm

Acrodisc-CR disposable filter, and analyzed by HPLC. The latter portion of the sequence differs from Jenkins method in that a step requiring mixing the acetonitrile extract with an aqueous floculating solution was eliminated, and that an internal standard (1,3-dinitrobenzene, DNB) is incorporated.

An estimation of the efficiency of extraction of each compound was obtained by doping subsamples of uncontaminated surface soil (A horizon, Wheeling sandy loam [fine-loamy, mixed, mesic Ultic Hapludalfs]) with acetonitrile containing a mixture of selected OB/OD compounds plus DNB. The soil was dried and extracted as above and the efficiency of extraction was calculated from the amount of each compound recovered. Because the efficiency of extraction of the OB/OD components at our test sites was similar to that of DNB, a simplified recovery correction system was possible. All soil samples were extracted with acetonitrile containing 5 mg L^{-1} (ppm) of DNB as an internal standard. Concentrations of OB/OD components observed in the extraction mixture were corrected for any observed loss of internal standard during the extraction process. Corrections were also made for any increases in concentration due to evaporation of the extraction solvent, acetonitrile. Corrections for losses or gains were generally minor.

Aqueous leachates from soil columns were collected and subsamples were adjusted to pH 6.00 ± 0.05, then made to contain 300 g L^{-1} NaCl. Two hundred mL of the resultant solution was put through a J.T. Baker 40 µm Sep-Pak Octadecyl (C18) disposable cartridge at a rate of 1.8 mL min^{-1}. Cartridges were prepared for use by wetting with 2 mL methanol, followed by 2 mL water. Munitions were eluted from the cartridges with 2 X 1-mL additions of methanol and eluates were analyzed by HPLC. Efficiencies of recovery were also determined for this procedure using aqueous standards of munitions.

HPLC analyses were performed with a Hewlett-Packard (HP) 1050 HPLC system that consisted of an autoinjector, pumping module, and UV detector. Signal integration was performed with an HP 3396A integrator. All analyses except screening tests for the presence of NG were done by UV absorbance at 244 nm. NG was determined at 220 nm. Extracts of uncontaminated (background) and highly contaminated surface soils (A horizons) were screened by a gradient (Table I) method developed for this investigation. This method was developed to identify a broad range of munitions, environmentally modified unitions, and polycyclicaromatic hydrocarbons (PAHs). A 15-µL sample was injected onto a 4.6 X 250 mm Rainin Microsorb C18 column with a 5 µm particle size, in series with a 4.6 X 250 mm Supelcosil LC-PAH column. Elution was accomplished with a methanol:water gradient (Table I). This method was used for preliminary identification of the components present in contaminated soils from OB/OD sites. A simpler isocratic method developed by Jenkins et al. (12) was used to substantiate the identification of contaminants, and for quantitation. A mobile phase of 70.7 percent water, 27.8 percent methanol and 1.5 percent tetrahydrofuran was utilized at a flow rate of 2 mL min^{-1} with a 4.6 X 75 mm Supelco LC8 column of 3 µm particle size. This mobile phase and column combination were also used to screen for the presence of NG.

Table I. HPLC Time/Gradient (Methnol:Water Mixture) for Initial Screening of Samples for a Broad Range of Munition-Related Analytes and PAHs

Time, min	Percent Methanol (% MeOH)
0	30
1.5	33.5
6.0	47.5
24.0	51.0
35.0	54.5
60.0	100.0
80.0	100.0

Table II. Efficiencies of Recovery of Munitions from Soil and Water

	Percent Munition Recovered (%), ±s		
	From soil extracted with acetonitrile		From aqueous leachate concentrates in MeOH
Compound	doped uncontam.	doped contam.	
HMX	99 ± 6	112 ± 4	29 ±10
TNB	102 ± 2	114 ± 3	123 ± 3
RDX	95 ± 1	91 ± 2	38 ± 1
TNT	107 ± 1	94 ± 9	90 ± 4
2,4-DNT	103 ± 1	110 ± 5	108 ± 7
2,6-DNT	103 ± 1	103 ± 2	104 ±20
2-Amino-DNT	100 ±<1	103 ± 1	112 ±15
4-Amino-DNT	98 ± 3	102 ± 4	137 ±40

DISCUSSION

Jenkins (5,9,12) has provided a workable method for the extraction and analysis of explosive residues in soils. It is quick and provides good resolution of contaminants common to OB/OD sites. However, several problems remain. His isocratic HPLC method was designed primarily for use with nitramine and nitroaromatic compounds. More polar munitions tend to coelute with a complex mixture of natural soil components. Acetonitrile elutes as a large negative peak immediately prior to or coeluting with HMX, which complicates the quantitation of this compound. Compounds which elute later than the dinitrotoluenes suffer from peak broadening, which impairs their quantitation.

The gradient chromatography method presented here can accurately detect munition compounds and PAHs with a very broad range of polarities if they are present at >1.0 mg L^{-1} (ppm). This method was used in our Laboratory for the first analysis (screening) of the most highly contaminated surface samples from munition contaminated OB/OD sites. When very polar munitions and PAH compounds were not present, the isocratic method was used for substantiation of compound identification and for quantitation.

PAH compounds have occasionally been detected in the waste products from munition incinerators, but detectable quantities of these compounds were not found in the ash or soils from OB/OD sites. A possible explanation for this difference is that the high energy intermediates responsible for ring fusion may accumulate at higher concentrations in contained combustion, or may arise from residual petroleum products associated with shell casings and bursting devices.

TNT remaining on the surface at OB/OD sites is converted to TNB, with the latter's concentration often exceeding that of the parent compound (16). Quantitation of TNB in acetonitrile extracts of soil was somewhat limited by background absorption due to material coextracted from contaminated soils. But the quantitation of TNB in the methanol concentrates of the aqueous leachates contained compounds that often severely interfered with this determination. TNT is also microbially degraded, by reduction to aminodinitrotoluenes, and may also be transformed into phenolic compounds and diazo forms (3). Although the aromatic ring structure of these compounds is resistant to degradation, evidence exists of other environmental processes in which these compounds become strongly bound to soil (3). Unlike the nitroaromatics, nitramine munitions and NQ undergo reactions which may leave little trace of the original compound (16, 3). Therefore, it is not surprising that recovery of munitions from soil is generally poor, after aging under simulated field conditions. Green et al.(17) were able to recover only a small fraction of added TNT after soil columns were leached. Banwart and Hassett (18) found that extractable TNT declined from 2000 mg kg^{-1} (ppm) to <20 mg kg^{-1} when plants were grown for 90 days in soil amended with straw. Care must be taken in the design of experiments to determine the fate of munition residues within soil columns, to ensure that concentrations in leachates and extracts remain within the detection limits of the analytical method. However, it is also important to note that soils differ in their binding capacities and that loading a soil in excess of its binding capacity for any given compound may yield remarkably high initial rates of movement.

RESULTS

The above procedures have proven effective in recovering and quantitating munitions at moderate to high concentrations in sandy loam soil (Table II); they have the additional advantage of being simple and reproducible. However, several shortcomings were encountered. Efforts to identify minor components of the OB/OD soil contaminant mixture were not successful due to interferences from natural soil components.

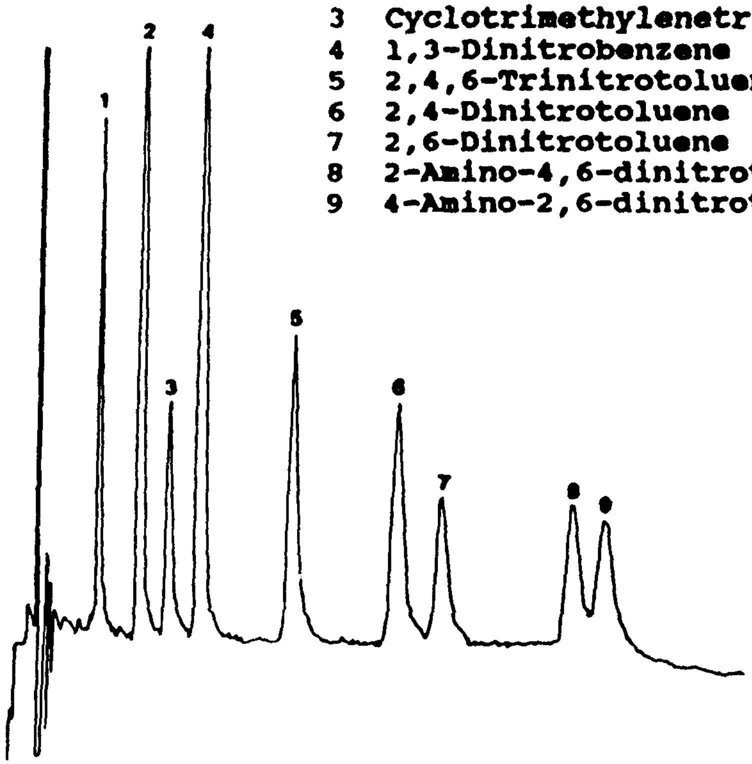
The isocratic HPLC method proved effective in quantitating intact munitions in water but performed less well with environmentally modified forms because they were later eluting and exhibited significant peak broadening (Figure 1). We also observed that this solvent and column combination was unusually sensitive to temperature. At temperatures above 23 °C retention times were shortened and at 30 °C the system no longer resolved the two aminodinitrotoluenes.

The gradient procedure presented here effectively separated components of a mixture that included most compounds likely to be encountered during analysis of soils from OB/OD contaminated sites (Figure 2). It was able to detect many compounds that would otherwise be missed by the isocratic method. However, this chromatographic procedure required 90 min to complete, and could not be run at high sensitivity because of problems with baseline drift.

Recovery of munitions doped into uncontaminated soil were nearly quantitative (Table II); whereas recoveries from the soil columns ranged from 20-25 percent for TNT, 2-5 percent for 2,4-DNT, and even less for 2,6-DNT. Due to the low recoveries from the soil columns, the munition concentrations in soil extracts and leachate water were often diminished to the extent that accurate quantitation was dificult at reported detection limits (Table III). These criteria of detection were calculated using the computerized Quality Assurance Program of the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), based on the methods of Hubaux and Vos (13, 14).

Concentration of the munitions in soil extracts was attempted by evaporating the acetonitrile into a stream of dry nitrogen at 60 °C. This procedure was not used because significant losses of TNT, the DNTs, and the early eluting PAH compounds occurred. Concentration of munitions by simple evaporation of the acetonitrile at ambient laboratory temperatures (20-25 °C) was also unsuccessful due to unacceptable losses of compound.

A procedure (15) developed by Brueggemann was used to concentrate munitions from our aqueous leachates. This method entails trapping munitions with disposable C18 columns, followed by elution with methanol. It was found to be useful for the nitroaromatics, however recoveries of the nitramine compounds were substantially lower (Table II). Passage of volumes of leachate greater than 30 mL had the effect of rinsing a portion of the nitramines from the column. In addition, this method concentrated naturally occurring soil components that interfered with determination of TNB and HMX.



1 Cyclotetramethylenetetranitramine (HMX)
2 1,3,5-Trinitrobenzene (TNB)
3 Cyclotrimethylenetrinitramine (RDX)
4 1,3-Dinitrobenzene (DNB)
5 2,4,6-Trinitrotoluene (TNT)
6 2,4-Dinitrotoluene (2,4-DNT)
7 2,6-Dinitrotoluene (2,6-DNT)
8 2-Amino-4,6-dinitrotoluene (2-Amino-DNT)
9 4-Amino-2,6-dinitrotoluene (4-Amino-DNT)

Figure 1. An example of the separation of a series of munitions and associated co-contaminants, by the isocratic HPLC method.

1 Nitroguanidine (NQ)
2 2,4,6-Trinitrophenol (Picric acid)
3 1-Acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX)
4 Cyclotetramethylenetetranitramine (HMX)
5 1-Acetylhexahydro-3,5-dinitro-1,3,5-triazine (TAX)
6 Cyclotrimethylenetrinitramine (RDX)
7 1,3,5-Trinitrobenzene (TNB)
8 1,3-Dinitrobenzene (DNB)
9 2,4,6-Trinitrophenylmethylnitramine (Tetryl)
10 2,4,6-Trinitrotoluene (TNT)
11 4-Amino-2,6-dinitrotoluene (4-Amino-DNT)
12 2-Amino-4,6-dinitrotoluene (2-Amino-DNT)
13 2,6-Dinitrotoluene (2,6-DNT)
14 2,4-Dinitrotoluene (2,4-DNT)
15 Naphthalene
16 Acenaphthylene
17 Fluorene
18 Phenanthrene
19 Anthracene
20 Fluoranthrene
21 Pyrene
22 Benz(a)anthracene
23 Chrysene
24 Benzo(a)pyrene

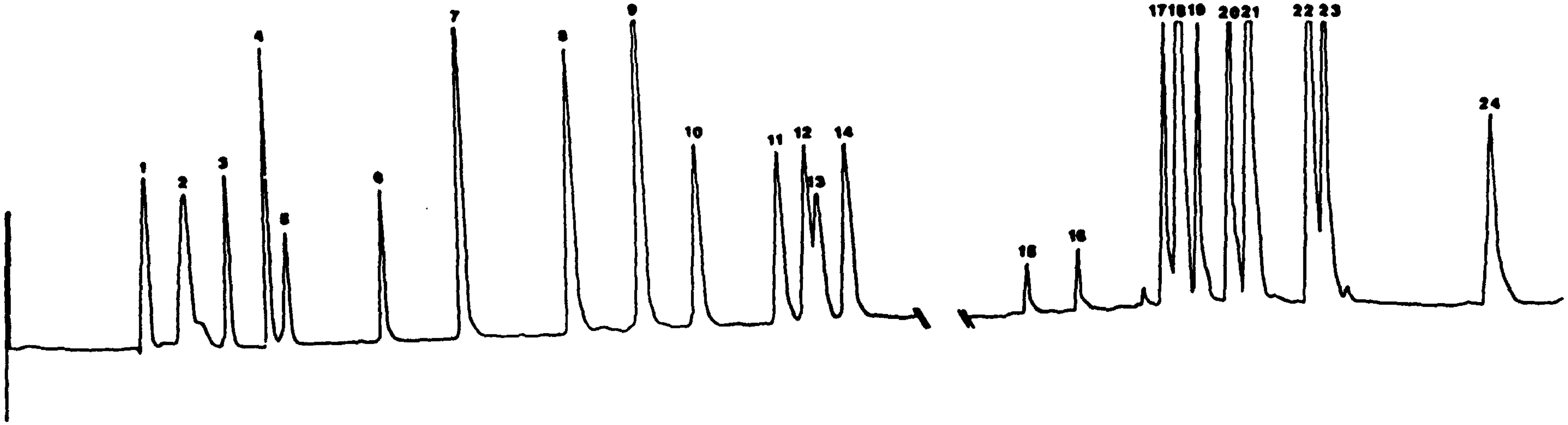


Figure 2. HPLC chromatogram showing the separation of a series of munitions, environmental degradation products of munitions, and PAHs, using the gradient chromatographic method.

Table III. Criteria of Detection* for Quantitation of Munitions Determined by HPLC

Compound	$mg\ L^{-1}$
HMX	0.15
TNB	0.15
RDX	0.067
DNB	0.15
TNT	0.093
2,4-DNT	0.17
2,6-DNT	0.37
2-Amino-DNT	0.14
4-Amino-DNT	0.12

* the x value on the standard regression line that has the same y value as y at x = 0 on the upper confidence limit (95% conf. level) curve (13).

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