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Abstract: Large soil samples are often necessary to represent areas where analytes are distributed as particulates. Proper processing of these large samples impose additional time, space, and equipment requirements on the laboratory community servicing environmental programs to investigate military training ranges. Part of this study evaluated the robustness of two methods used to process large soil samples for the determination of energetic munitions residues—whole sample mechanical grinding (comminution) and solvent dissolution. Both methods have been used successfully to reduce subsampling variance for samples collected on training ranges where particles of energetic residues have accumulated. However, two energetic compounds frequently detected in such samples—nitroglycerin (NG) and 2,4-dinitrotoluene (2,4-DNT)—may be susceptible to evaporative losses during solvent dissolution. Robustness experiments involved both lab-spiked and field-collected soils with various concentrations of energetic residue. An experiment utilizing field-collected soils involved the use of a rotary splitter. Even with this highly regarded equipment, the samples could not be split consistently, preventing a direct comparison of the two techniques in soils with residue concentrations less than 40 mg/kg. Two other investigations evaluated sample holding times and cross-contamination resulting from grinding processes. The results indicated that energetic compounds typically found on military training ranges were stable in air-dried soils for periods in excess of 53 days when stored in the dark at room temperature. A slight amount of cross-contamination from grinding was detectable using gas chromatography. The concentrations were below detectable levels when using liquid chromatography and were eliminated by adding a step of soaking the grinding bowl in a sonic bath filled with dilute cleaning detergent to the cleaning protocol.

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Preface

This report was prepared by Alan Hewitt, Susan Bigl, and Marianne Walsh, Environmental Sciences Branch, Cold Regions Research and Engineering Laboratory (CRREL), U.S. Army Engineer Research and Development Center (ERDC), Hanover, NH; Sylvie Brochu, Defence Research and Development Canada–Valcartier, NorthVal-Bélair, Quebec, Canada; Kevin Bjella, Force Projection and Sustainment Branch, CRREL/ERDC; and Dennis Lambert, Engineering Resources Branch, CRREL/ERDC.

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1 Introduction

A consequence of military testing and training activities with munitions is the buildup of energetic compound residues in impact ranges, at firing points, and where demolition operations are performed (Jenkins et al. 2006a). The secondary explosives residues frequently detected in surface soil samples from impact ranges are trinitrotoluene (TNT), 1,3,5-hexahydro-1,3,5-trinitrotriazine (RDX), and octrahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). These residues are consistent with the common high-explosive charges in munitions: TNT, Composition B (“Comp B”, 39% TNT and 60% RDX), Tritonal (80% TNT and 20% aluminum), Octol (30% TNT and 70% HMX). In addition, HMX typically is a manufacturing impurity (10%) in RDX (U.S. Army 1984), and 2 amino-4,6-dinitrotoluene and 4 amino-2,6-dinitrotoluene (2ADNT and 4ADNT), two environmental transformation products of TNT, also are frequently detected (Walsh et al. 1993). With the exception of 2ADNT and 4ADNT, these munitions constituents are crystalline in composition. At firing points, nitroglycerin (NG) and 2,4-dinitrotoluene (2,4-DNT) are often detectable in surface samples (Jenkins et al. 2006a). These two energetic residues are impregnated into the nitrocellulose (NC) polymeric matrix, which is a major component of most propellant formulations. On demolition ranges all of these energetic compounds are often present.

On military testing and training ranges, energetic residues are heterogeneously distributed on the ground surface as particles of various sizes, shapes, and compositions (Jenkins et al. 2001, Radtke et al. 2002, Taylor et al. 2004). When the sampling objective is to estimate the mean concentration of energetic residues within a decision unit, the sampling strategy must involve the collection of constituents of concern in the same proportion as exists within the area under investigation for the results to be both reproducible and representative. The Engineer Research and Development Center – Cold Regions Research and Engineering Laboratory (ERDC-CRREL) has demonstrated that reproducibility is best achieved with samples of a mass of at least 1 kg comprising 30 or more increments (Jenkins et al. 2005). Accuracy (representativeness) can only be inferred from reproducibility, since we can’t obtain the true concentration. Collecting discrete samples has been discouraged for most applications, since this strategy often underestimates the mean concentration. Sets of discrete

values frequently are not normally distributed, invoking the requirement for a non-parametric statistical interpretation (Jenkins et al. 2005).

The Strategic Environmental Research and Development Program “Distribution and Fate of Energetics on DoD Testing and Training Ranges: Characterization of Explosives Contamination” brought together several research laboratories to focus on an impending environmental problem confronting the armed forces (Pennington et al. 2001, 2002, 2003, 2004, 2005, 2006). Two groups have closely collaborated in studies addressing the distribution of energetic residues on military testing and training facilities: ERDC-CRREL and Defence Research and Development Valcartier (RDDC Valcartier). From the inception of this program there has been a concerted effort to develop sampling and sample processing protocols that would produce representative mean concentrations within areas where energetic residues were likely to accumulate. To achieve this goal, a sampling strategy has been used that involves gathering 30 or more increments to form a composite using a systematic-random sampling design [aligned square grids (Gilbert 1987) or systematic grid sampling (USEPA 2002)] throughout the chosen decision unit (population, exposure unit, or area of concern). Even when sampling only a couple of centimeters deep, the sample mass produced by collecting 30 or more increments with either small metal scoops or specially designed coring tools (Walsh, M.R. 2004) is between 0.5 and 1.5 kg.

Laboratory analysis of multi-increment samples and most other samples entails the removal of a small subsample for extraction. For a representative laboratory subsample, the constituents of interest must be evenly distributed throughout the entire sample (USEPA 2003). Presently, two procedures are being used to disperse energetic residues: mechanical pulverization (Walsh, M.E. et al. 2002) and solvent dissolution (Thiboutot et al. 1998). To process these large samples both groups embraced the theories and methods that Pierre Gy and Pitard developed to deal with the inherent heterogeneity of soils (Pitard 1993). Briefly, at ERDC-CRREL, soil samples are air-dried and sieved, and the fraction smaller than 2 mm is processed using a grinding mill, which reduces most of the sample particle size to less than 75 μm (Walsh, M.E. et al. 2002). Mechanical pulverizing is accomplished with a LabTech Essa LM-2 grinding mill and the B800 bowl. A subsample for analysis is then removed from the ground material. Following air-drying, researchers at RDDC Valcartier use a different technique; they use a minimal amount of acetone for solvent dissolution and

stir the slurry gently to disperse the energetic residues through the entire sample. Once the solvent has evaporated, the entire sample is passed through a sieve prior to subsampling for analysis.

Following their initial studies (Walsh, M.E. et al. 2002), ERDC-CRREL researchers determined that four additional grinding cycles are necessary for samples collected at firing points where propellant residues accumulate (Walsh, M.E. et al. 2004, 2005, 2007, Walsh and Lambert 2006). Walsh and Lambert (2006) also evaluated the robustness of the grinding protocol. Their initial study involved grinding a secondary source standard (Environmental Resource Associates, Arvada, CO) and Ottawa sand spiked with crystals of 2,4-DNT and Composition B (2,4-DNT Standard Reference Material; Composition B). The commercial standard contained RDX and TNT and was ground for 60 s. Grinding this standard significantly decreased the subsampling variance without altering the analyte concentration (Walsh and Lambert 2006). Grinding the spiked Ottawa sand, however, resulted in significantly decreased analyte concentrations in subsamples removed after an additional 240 s of continuous grinding compared to those removed after 60 s (Walsh and Lambert 2006, Walsh et al. 2007). They noted that the grinding bowl became noticeably warmer after 4 minutes of continuous grinding. The magnitude of losses were analyte dependent, i.e., the loss of HMX was less than RDX, which was less than TNT, which was less than 2,4-DNT. They surmised that warming enhanced the sublimation of the analytes with the highest vapor pressure or thermal degradation of these compounds.

In this study, we conducted several investigations to evaluate the current protocols. The first was a robustness evaluation of the grinding protocols using field-aged soils with previously estimated energetic residue concentrations. We also assessed the robustness of the solvent dissolution protocol using a combination of spiked and field-aged soils. In a third holding time investigation, we assessed the stability of two volatile energetic compounds in air-dried soils. A final investigation evaluated the effectiveness of our apparatus cleaning procedures to prevent cross contamination between samples. This work was ongoing during drafting of the revisions to Method 8330, which has been published subsequently as Method 8330B (USEPA 2006).

2 Methods for all Studies

Initial Sample Processing

Brief descriptions of the two laboratory protocols used in this study for distributing energetic residues throughout large samples are presented below. For consistency, all samples discussed in this report were air-dried and passed through a 2-mm (#10) sieve. The sieved fraction was then treated by pulverization or solvent dissolution. Appendix A presents the full protocol used at ERDC-CRREL for sample processing, grinding, and cleaning.

Energetic Residue Distribution Treatments

Pulverization Method

In the pulverization method, samples from firing points or demolition ranges were ground for five 60-s intervals with at least a one-minute cool-down period between each grind cycle; samples from impact ranges were ground for a single 60- or 90-s period. Samples larger than 500 g were ground in multiple batches of 300–500 g each, then stirred completely. Figure 1 shows the grinding mill, 800-cm-capacity bowl, and puck used for sample pulverization.



a. LabTech Essa LM-2 grinding mill.



b. Bowl (B800).

Figure 1. Grinding apparatus used for pulverization.



c. Grinding puck.

Figure 1 (cont.). Grinding apparatus used for pulverization.

Solvent Dissolution Method

For the solvent dissolution method, the sample was placed in a 23- × 33-cm (9- × 13-in.) glass dish in a fume hood; then the dish was leveled. Acetone was slowly poured onto the surface until the liquid entirely covered the soil. Then the slurry was stirred for a couple of minutes before allowing the acetone to evaporate (Fig. 2). Drying periods ranged between 4 and 18 hours, depending on the soil type.



a. Initial dry sample.



b. Addition of acetone.

Figure 2. Acetone dissolution procedure.



c. Final acetone-soil slurry.

Figure 2. Acetone dissolution procedure.

Subsampling, Extraction, and Analysis

Following either of these energetic residue distribution treatments, samples were processed with the same procedures for subsample collection, extraction, and analysis. The sample was thoroughly mixed, then spread to a 1-cm thickness over a new sheet of aluminum foil. Then, a 10.0-g subsample was built by collecting approximately 30 increments from randomly chosen locations with a stainless steel spatula and placing them into a 60-mL (2-oz) wide-mouth amber glass bottle. The energetic residues were extracted by adding 20 mL of acetonitrile and agitating the bottles for 18 hours on a shaker table set at 150 rpm (Walsh and Lambert 2006). Following extraction, each sample was vigorously shaken and then allowed to settle for 1 hour prior to withdrawing several milliliters from the particle-cleared solvent layer with a syringe and filtering 7 mL through a 0.45- μ m Millex FH filter. The first 1 mL or so of extract was dispensed into a waste container, the remainder into an amber 7-mL vial. The filled vials were subsequently stored in a freezer until analysis.

Sample extracts were analyzed by reverse-phase, high-performance liquid chromatography (RP-HPLC) following Method 8330B (USEPA 2006). Samples were mixed at a ratio of one part extract (acetonitrile) with three parts reagent-grade (de-ionized) water. RP-HPLC analysis was conducted on a modular system from Thermo Finnigan composed of a SpectraSYSTEM Model P1000 isocratic pump, a SpectraSYSTEM UV2000 dual wavelength UV/VS absorbance detector set at 210 and 254 nm (cell path 1 cm), and a SpectraSYSTEM AS300 auto sampler. Separations were made on a 15-cm $\times$ 3.9-mm (4- μ m) NovaPak C-8 column (Waters Chroma-

tography Division, Milford, MA) eluted with 15:85 isopropanol/water (v/v) at 1.4 mL/min.

Analysis by gas chromatography with an electron capture detector (GC-ECD) was performed on only the Ottawa Sand samples used to assess carryover between grinding operations. These analyses were performed on an HP 6890 gas chromatograph equipped with a micro ECD detector utilizing Method 8095 (USEPA 2002). Primary separation was conducted on a 6-m x 0.53-mm-ID fused-silica column with a 1.5- μ m film thickness of 5% (phenyl)-methylsiloxane (Rtx-5 from Restek, Bellefonte, PA). Confirmation GC-ECD analysis was performed using a 6-m x 0.53-mm-ID column having a 1.5- μ m film thickness of a proprietary polymer (Rtx-TNT-2 from Restek). A more detailed description of the GC-ECD operating parameters is available elsewhere (Walsh and Ranney 1999). Estimated reporting limits for these two instrumental methods in analysis of soil samples are listed in Table 1.

Table 1. Estimated reporting limits for energetic compounds in soil.

Analyte	Soil (mg/kg)	
	RP-HPLC	GC-ECD
HMX	0.04	0.01
RDX	0.04	0.006
TNB	0.04	0.003
TNT	0.04	0.002
2,6-DNT	0.08	0.002
2,4-DNT	0.04	0.002
2ADNT	0.08	0.002
4ADNT	0.08	0.002
NG	0.1	0.01
DNB	0.04	0.002
Tetryl	0.04	0.01
PETN	0.2	0.016

3 Experimental Studies, Results, and Discussion

Grinding Study

Methods

Three samples from Holloman Air Force Base (AFB) and three soils from Canadian Forces Base (CFB) Petawawa were selected to evaluate the potential influence of extended grinding (i.e., grinding times greater than 60 s). The Holloman AFB samples were collected in an area where Tritonal residues from air-to-surface bombs were observed. These samples were initially ground for 60 s and were determined to contain 0.33, 4.0, and 36 mg/kg TNT when analyzed in May 2005 (Jenkins et al. 2006b). After analysis, the ground soil samples had been individually archived in plastic bags contained in cardboard boxes and stored at room temperature. In June 2006, five replicate subsamples were removed from the archived samples. The remaining sample was ground for five 60-s intervals with a one-minute cool-down period between grinds before removing a second set of five replicate subsamples. All subsamples were prepared and analyzed as a single batch in an order that alternated between the two grinding treatments. The results are shown in Table 2 along with the original (May 2005) estimated concentrations.

Table 2. Energetic residue concentrations (mg/kg) in soils ground for 60 s (analyzed May 2005 and June 2006) and after an additional five 60-s periods (June 2006).

Sample	TNT (mg/kg)		
	60 s		5 × 60 s
	May 2005	June 2006*	June 2006*
H #2	4.0	4.25±0.020	4.25±0.048
H #4	0.33	0.370±0.023	0.346±0.005
H #10	36.0	37.4±0.385	37.1±0.502

* Mean of five replicates

Samples from CFB Petawawa were from two hand grenade ranges and from an area behind a fixed firing point on an anti-armor training range. One hand grenade range sampled had not been used for more than 30 years. The other hand grenade range and the anti-armor range are active.

When initially prepared for analysis in October and November 2005, samples from hand grenade ranges (Pet05-20 and -26) were ground for 60 s; the firing point sample (Pet05-22) was ground for five 60-s periods with intermittent cool-down periods. Table 3 shows the energetic residue concentrations determined during the initial analyses in November 2005. These soils were archived in the same manner as the Holloman AFB samples.

Table 3. Initial energetic residue concentrations (mg/kg) in field samples.

Sample	Type of range	HMX	RDX	TNT	NG	2,4-DNT	2AmDNT	4AmDNT
Pet05-20	Hand grenade*	0.052	0.12	0.18	<0.10	0.044	0.41	0.35
Pet05-26	Hand grenade	0.35	1.2	0.12	<0.10	0.056	<0.08	<0.08
Pet05-22	Anti-armor firing point	BD	BD	BD	140	4.3	<0.08	<0.08

* not active

BD = below detection

As with the Holloman AFB samples, the first step was to remove five replicate subsamples from the archived CFB Petawawa samples. The remaining portion of the sample was then ground for five 60-s intervals. The soil surface temperature was measured before and after grinding and showed an average temperature increase from 20 ± 1 to $28 \pm 1^\circ\text{C}$. After a second set of five subsamples was collected, the remaining sample was ground for five continuous minutes (with no cool-down period). After this grinding cycle, the average soil temperature was $33 \pm 2^\circ\text{C}$. A third set of five subsamples was collected. All subsamples were prepared and analyzed as a single batch, in an order alternating between the three grinding treatments. Table 4 presents results from the three sets of five replicates.

Results

The F-test established unequal variances between all of the data sets for the TNT concentrations determined for the two grinding treatments of the Holloman AFB samples. A t-test assuming unequal variances was applied to determine if the means were significantly different at the 95% confidence interval for the different grinding periods. This analysis indicated no statistical differences. Therefore, the additional grinding had not caused any significant loss of TNT (Table 2).

Table 4. Energetic residue mean concentrations (mg/kg) and standard deviations for field samples following three grinding treatments. Treatment: A – 1 or 5 × 60 s; B – 5 × 60 s; C – 300 s

Sample	Treatment	HMX	RDX	TNT	NG	2,4-DNT	2AmDNT	4AmDNT
Pet05-20	A	0.060 ±0.002	0.180 ±0.006	0.130 ±0.008	0.111 ±0.030	0.037 ±0.003	0.282 ±0.014	0.274 ±0.012
	B	0.066 ±0.004	0.181 ±0.006	0.146 ±0.013	0.103 ±0.013	0.064 ±0.044	0.344 ±0.007	0.328 ±0.011
	C	0.068 ±0.003	0.181 ±0.004	0.158 ±0.006	0.117 ±0.022	0.046 ±0.008	0.376 ±0.012	0.353 ±0.008
Pet05-26	A	0.298 ±0.003	1.03 ±0.004	0.041 ±0.003		0.062 ±0.021		
	B	0.288 ±0.004	0.976 ±0.011	0.043 ±0.004		0.060 ±0.014		
	C	0.268 ±0.007	0.904 ±0.015	0.043 ±0.005		0.058 ±0.005		
Pet05-22	A				136 ±2.80	4.68 ±0.188		
	B				131 ±1.15	4.64 ±0.136		
	C				127 ±1.25	4.64 ±0.032		

An analysis of variance (ANOVA) was performed at the 95% confidence level for each of the analytes detected in the three samples from CFB Petawawa (Table 4). In sample Pet05-20 from the inactive hand grenade range, mean concentrations of RDX, NG, and 2,4-DNT showed little change with additional grinding; however, HMX, TNT, 2AmDNT, and 4AmDNT concentrations increased significantly. The two TNT breakdown products increased by about 30%: TNT increased by 20% and HMX by 15%. One explanation for these concentration increases is that the additional comminution made more analyte available for extraction from this soil. Because this range has been inactive for about 30 years, crystalline residues initially deposited from incomplete detonations likely have weathered. In the dissolved state, residues may have penetrated soil micro-pores or become sorbed by organic matter. The prolonged grinding increased the surface area of the soil matrix, which probably increased the availability of this sequestered fraction to solvent extraction. This phenomenon (i.e., an increase in analyte recoveries, particularly 2AmDNT and 4AmDNT) was also observed by Walsh and Lambert (2006) when samples were extracted for extended periods. Additional grinding of the active hand grenade range sample, Pet05-26, resulted in no significant

change in either TNT or 2,4-DNT concentrations; however, both HMX and RDX concentrations decreased by about 10% (significant at 95% confidence level). Samples from the anti-armor firing point sample, Peto5-22, showed no significant change in 2,4-DNT concentration with grinding; however, the NG concentration decreased by about 6% (significant at 95% confidence level). The two active range surface samples were from locations where it is anticipated that the energetic residues exist mostly as small crystalline or polymeric particles. In this physical state, prolonged grinding appeared to have caused small losses of energetic compounds, as shown previously by Walsh and Lambert (2006).

Discussion

Comparing the results obtained when these samples were initially processed and analyzed with those from this study shows that analytes were not lost over a storage period greater than one year. Mean TNT concentrations from the earlier analyses are very similar to the present results for the Holloman AFB samples (Table 2). Comparing the results in Table 3 (previous) and Table 4 (present) shows some discrepancies in the concentration estimates for the samples from the two hand grenade ranges. The largest discrepancies were for those energetic residues with low concentrations. In these cases the discrepancies can likely be attributed to the poorer precision associated with the subsampling and analysis of samples with low analyte concentrations.

Acetone Dissolution – Analyte Recovery in Spiked Samples

Two experiments were conducted to assess recoveries of energetic compounds when spiking samples and performing an acetone slurry treatment. The first experiment involved two trials in which 500 g of sand was placed in a glass dish and wetted with acetone. In trial one, commercial play sand (purchased at a local hardware store) was first wetted with 100 mL of acetone spiked with two commercial standards; immediately afterward, more acetone was added to completely wet the soil (70 mL). A second trial followed the same general format, except that Ottawa Sand was used; the total volume of acetone needed to wet this coarser material was 120 mL. After air drying, five or more replicate subsamples were obtained from each treatment. Table 5 presents the average percent recoveries of spiked analytes resulting from the two trials.

Table 5. Average percent recoveries of analytes spiked into acetone slurry.

Sample	HMX	RDX	TNT	NG	2,4-DNT
Trial 1	93.5	100	91.8	83.5	90.1
Trial 2	100	96.2	91.6	64.8	66.6

In the second experiment, commercial play sand was spiked with known amounts of crystalline and polymeric energetic residues. Several small pieces (38.4 mg) of weathered Composition B were added to 250 g of sand and ground for 60 s. Previous experiments that involved dissolving similar-sized chunks of weathered Composition B produced inconsistent results when attempting to establish the composition of these energetic materials. The discrepancy between the determined and theoretical concentrations for pieces of Composition B were attributed to the weathered surface, which failed to completely dissolve in either acetone or acetonitrile (dark particles remained). Therefore, to establish the concentrations of HMX, RDX, and TNT in the 250-g sample, five subsamples were removed for analysis.

Several small propellant pieces cut from a 105-mm howitzer propellant grain (70.7 mg, $9.1 \pm 0.1\%$ 2,4-DNT w/w, $n = 5$) and a chunk of LAW rocket propellant (53.8 mg, $33 \pm 1\%$ NG w/w, $n = 4$) were added to a separate 200-g portion of sand. This treated sand was also ground for 60 s.

Next, the remaining 200 g of soil treated with Composition B was mixed with the 200 g of soil spiked with propellant residues. The 400-g soil sample was placed in a Pyrex dish under a fume hood, and the dish was leveled. Then, 200 mL of acetone was slowly added to the soil, the acetone slurry was stirred, and the sample was allowed to air-dry overnight. The results for the five replicate subsamples removed for analysis are shown in Table 6.

Table 6. Average percent recovery of energetic residues spiked into soil sand treated by the acetone slurry protocol.

Sample	HMX	RDX	TNT	NG	2,4-DNT
Rep-1	4.14	37.2	25.8	34.0	14.5
Rep-2	4.14	36.4	25.4	33.6	14.3
Rep-3	4.12	36.0	25.2	33.2	14.2
Rep-4	4.28	37.8	26.0	34.8	14.6
Rep-5	4.20	37.0	25.6	34.2	14.3
Mean	4.18	36.9	25.6	34.0	14.4
Std Dev*	0.065	0.701	0.316	0.607	0.190
%Rec'd**	101%	99.9%	101%	76.5%	89.3%

* Standard deviation

** Percent recovered

NG and 2,4-DNT consistently showed the poorest and most variable recoveries for the three trials. These results were independent of the spiking treatment or the matrix type (play sand or Ottawa Sand). NG and 2,4-DNT have the highest vapor pressures among the energetic compounds most frequently detected on military training ranges. The average recoveries and standard deviations for these two analytes were $75 \pm 9.4\%$ and $82 \pm 13\%$, respectively. The recoveries of HMX, RDX, and TNT were consistently greater than 91%, and the overall average recovery and standard deviation for these three analytes was $97 \pm 4\%$. These results suggest that compounds with higher vapor pressures are susceptible to evaporation losses when the solvent slurry protocol is used to disperse energetic residues throughout a sample.

Acetone Dissolution in Field Samples - Robustness of Sample Splitting

Another experiment in this study investigated the robustness of sample splitting along with a continued comparison of the grinding and solvent dissolution sample treatment protocols using 12 large (>1 kg) samples collected at CFB Petawawa. Four samples came from impact areas, six from firing points, and two from an ordnance demolition range. All the samples were split using a Labtech Essa rotary sample divider (Model RSD5) with twelve collection chambers. To form two equal splits, contents of every other bucket were combined. One sample split was prepared by mechanical grinding (using the appropriate number of cycles for different residues) and the other by acetone dissolution. Once processed, 12 subsample replicates were removed from each split, then extracted and analyzed. Each sample was analyzed in a batch, alternating subsamples from the two preparation methods. Table 7 lists statistical parameters determined for each split—average, median, standard deviation, percent relative standard deviation, and concentration range.

The rotary (spinning riffle) sample divider used in this experiment is recognized as the most precise method for dividing a sample equally with regard to particle size, density, and other physical factors (Cross 2000, Gerlach et al. 2002). At concentrations above 40 mg/kg for HMX, RDX, and TNT, three compounds that are not subject to loss during acetone dissolution, mean analyte concentrations obtained for the two sample splits processed by both protocols were often not significantly different. The average relative percent difference (RPD) was less than 5% ($n = 4$). Below 40 mg/kg, the RPD was inconsistent and averaged 33% ($n = 6$). Indeed, the results were significantly different (t-test at 95% confidence

Table 7. Concentration estimates for 12 replicates of split samples from firing points and processed by pulverization and by acetone slurry.

Sample	Analyte	Ground (mg/kg)				Acetone slurry (mg/kg)			
		Mean/ median	Std Dev.*	%RSD	Min/max	Mean/ median	Std Dev.*	%RSD	Min/max
Pet04-11	NG	3080/3030	250	8.11	2820/3780	2990/2980	98.5	3.30	2800/3160
	2,4-DNT	<4	--	--	--	<4	--	--	--
Pet04-19	NG	38.7/39.0	2.58	6.67	35.6/45.8	41.2/41.2	2.25	5.46	37.8/45.2
	2,4-DNT	4.12/4.08	0.42	10.2	3.72/5.34	4.17/4.13	0.25	6.04	3.80/4.60
Pet04-20	NG	43.0/43.4	1.34	3.13	40.6/44.4	37.6/38.0	1.93	5.14	34.2/40.2
	2,4-DNT	5.33/5.35	0.24	4.57	4.84/5.72	4.70/4.64	0.30	6.43	4.08/5.08
Pet04-36	NG	2.89/2.96	0.35	12.0	2.22/3.28	2.19/2.22	0.51	23.3	1.25/2.96
	2,4-DNT	0.700/0.654	0.144	20.6	0.514/0.964	1.17/1.22	0.24	20.4	0.44/1.37
Pet04-42	NG	4.18/4.17	0.22	5.28	3.84/4.57	3.42/3.41	0.15	4.49	3.16/3.76
	2,4-DNT	0.182/0.180	0.25	14.0	0.141/0.228	0.257/0.254	0.014	5.45	0.233/0.291
Pet04-53	NG	705/712	34.2	4.85	633/750	662/660	27.7	4.18	628/730
	2,4-DNT	<4	--	--	--	<4	--	--	--
Pet04-2	NG	1.03/1.03	0.125	12.2	0.802/1.22	0.718/0.716	0.031	4.32	0.664/0.772
	2,4-DNT	13.5/13.4	0.274	2.03	13.2/14.1	9.67/9.51	0.438	4.52	9.08/10.5
	2,6-DNT	0.436/0.437	0.009	2.02	0.420/0.456	0.292/0.294	0.011	3.93	0.274/0.308
	RDX	0.149/0.146	0.009	6.03	0.142/0.174	<0.04	--	--	--
Pet04-8	NG	0.114/0.099	0.058	51.5	0.040/0.202	<0.10	--	--	--
	2,4-DNT	0.529/0.498	0.064	12.1	0.466/0.638	1.35/1.33	0.101	7.49	1.17/1.55
	HMX	0.395/0.393	0.007	1.77	0.386/0.404	0.685/0.678	0.020	2.99	0.656/0.724
	RDX	1.49/1.48	0.047	3.15	1.43/1.60	4.37/4.09	0.749	17.1	3.84/6.52
Pet04-55	NG	4.20/4.13	0.898	21.4	2.44/6.22	3.13/3.22	0.327	10.5	2.20/3.48
	TNT	8.74/8.77	1.04	11.9	6.56/10.1	11.5/11.5	0.587	5.13	10.6/12.6
	HMX	401/402	20.3	5.05	354/430	386/382	36.0	9.34	9.34
	RDX	0.442/0.440	0.028	6.3	0.400/0.500	<0.04	--	--	--
Pet04-56	HMX	1440/1430	52.0	3.61	1380/1530	1450/1460	84.9	5.85	1310/1590
	TNT	189/190	9.0	4.74	168/202	202/203	7.25	3.59	190/212
Pet04-23	HMX	48.6/48.6	0.71	1.47	47.4/49.8	48.1/43.8	8.06	16.8	42.4/66.8
	RDX	3.43/3.36	0.19	5.55	3.28/4.00	3.64/2.99	2.32	63.6	2.84/11.0
	Tetryl	0.417/0.419	0.065	15.5	0.296/0.524	1.35/1.33	0.06	4.59	1.27/1.48
Pet04-27	HMX	0.146/0.147	0.010	7.0	0.132/0.172	0.137/0.140	0.009	6.48	0.120/0.146
	RDX	0.473/0.471	0.010	2.16	0.460/0.498	0.581/0.582	0.012	2.09	0.556/0.598
	TNT	0.103/0.100	0.012	11.5	0.092/0.134	0.099/0.100	0.006	5.7	0.082/0.104

* Standard Deviation.

interval) in half of the comparisons, and in a separate case, an energetic residue was detected in only one of the two sample splits. RDX was detected in only one of the Peto4-2 split samples. Therefore, even when

using a very precise laboratory method of sample splitting after drying and sieving to remove oversized particles (> 2 mm), energetic residues when present at low concentrations cannot necessarily be evenly divided with any degree of confidence. More trails, however, are warranted, because of the confounding experimental design. That is, this study should be repeated with only one method of processing the split sample prior to subsampling and analysis.

The inability to equally split the energetic residue within a field sample prevented further assessment of potential NG and 2,4-DNT loss during acetone dissolution. This study was performed because it is impossible to mimic physical and chemical properties of field samples with laboratory treated samples, so the loss of 2,4-DNT and NG during acetone dissolution remains speculative. Both treatments reduced the subsampling variance for the analytes of concern (that is, they addressed the compositional and distributional heterogeneity of the sample), so subsampling variance was small in the majority of cases. More important, however, this study indicates that splitting a sample prior to mechanical or solvent dissolution introduces indeterminate error that is inversely proportional to concentration.

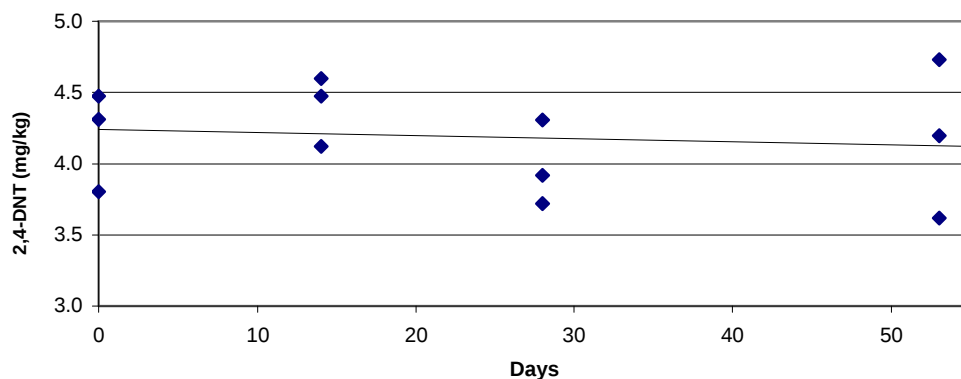
Holding Time Study

To evaluate holding times, we selected four archived firing point samples that contained either NG or 2,4-DNT or both when previously processed and analyzed. Since these two compounds have the highest vapor pressures among the energetic residues typically found on military training ranges, they would tend to have the greatest concentration decrease rate. Two samples had been collected in July 2002 at Donnelly Training Area (DTA), Alaska. When originally processed, these samples were only ground for 90 s and were determined to contain 2.3 and 6.8 mg/kg of 2,4-DNT (samples from firing point Mark and Audrey, respectively) (Walsh, M.E. et al. 2002). The other two samples, when processed after being collected at Canadian Forces Base (CFB) Petawawa in October 2005, were ground for five 60-s intervals. The first of these samples (Pet05-02) contained 9.2 mg/kg NG; the other (Pet05-19) contained 22.5 ± 0.2 mg/kg NG and 0.57 ± 0.06 mg/kg 2,4-DNT.

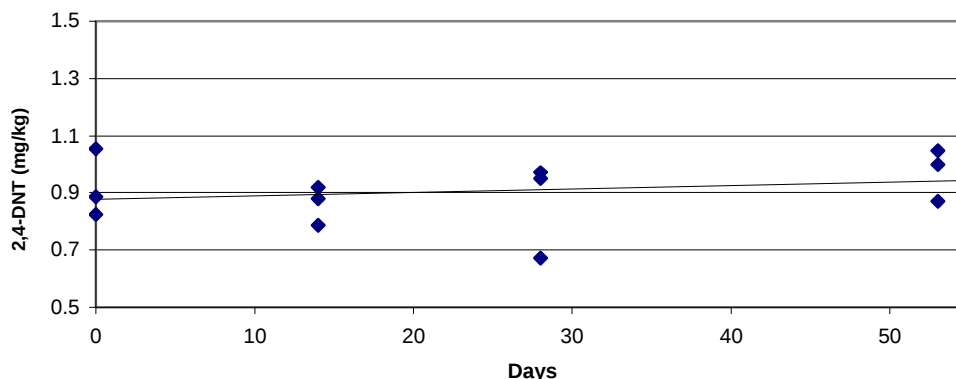
All four samples were re-ground for five 60-sec intervals, and 12 replicate subsamples were obtained from each one. On day zero, triplicate subsamples of each of the four samples were randomly chosen for freezer storage.

The remaining subsamples were held at room temperature. After room temperature storage periods of 14 and 28 days, four more sets of triplicate subsamples were placed in the freezer. On day 53, the last set of triplicates held at room temperature and all those placed in the freezer were extracted and prepared for analysis. A totally randomized order of analysis (random number generated) was performed with this batch of subsamples.

The results of this holding time experiment indicate that no analyte was lost during the 53-day period (Fig. 3). This conclusion was verified by an analysis of variance (ANOVA) performed at the 95% confidence level; slopes of linear regression models were not significantly different from zero. Indeed, the analyte concentrations from the two CFB Petawawa samples that had been ground with the revised protocol (5×60 s) when they were initially processed and analyzed in October 2005 did not appear to change markedly over a 6-month period (Pet05-02— 9.2 vs. 8.9 ± 0.3 mg/kg NG; Pet05-19— 22.5 vs. 21.6 ± 0.67 mg/kg NG and 0.57 vs. 0.48 ± 0.02 mg/kg 2,4-DNT). The samples from DTA had originally only been ground for 90 s, which is not adequate for propellant residues (Walsh and Lambert 2006, Walsh, M.E. et al. 2007).

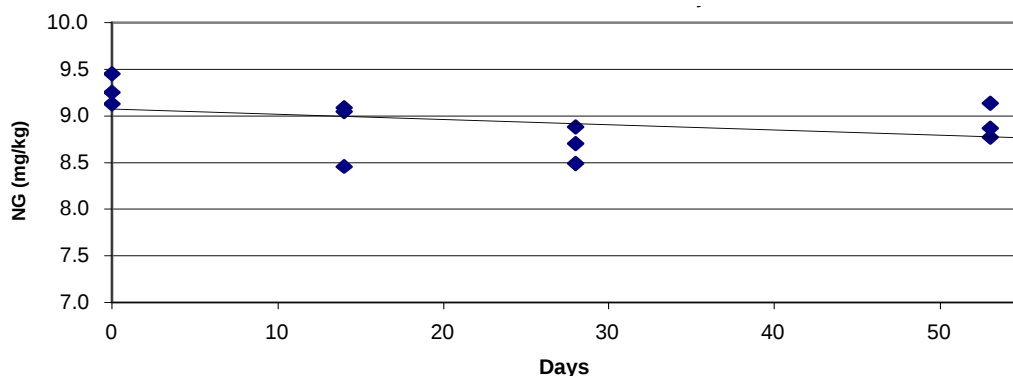


a. Sample collected at 105-mm Howitzer firing point Audrey, DTA, AK.

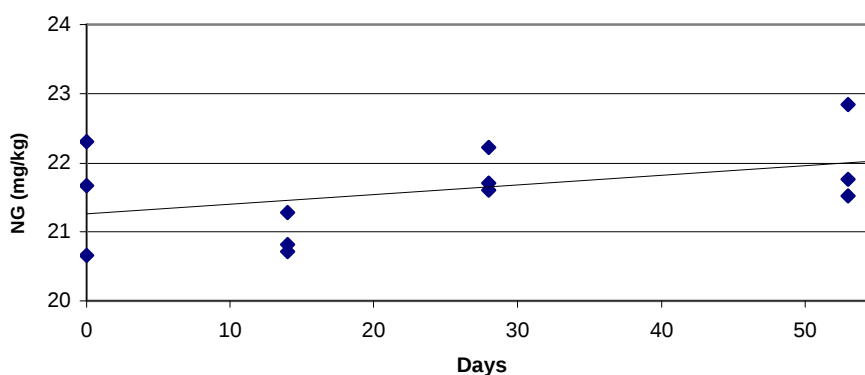


b. Sample collected at 105-mm Howitzer firing point Mark, DTA, AK.

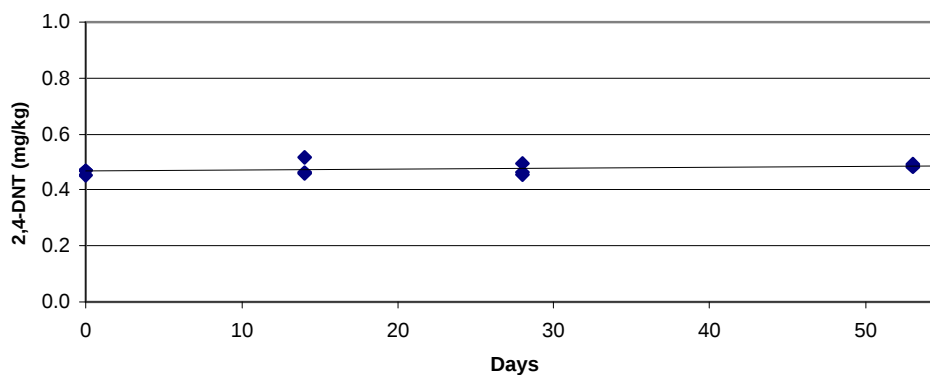
Figure 3. Holding time results.



c. Sample collected at a small arms pistol range.



d. Sample collected at mounted gun firing point.



e. Sample collected at mounted gun firing point.

Figure 3 (cont.). Holding time results.

Cross Contamination Study

A 400-g sample containing approximately 12,000 and 1,200 mg/kg of TNT and HMX, respectively, was prepared by combining two soils with high concentrations of these energetic residues. Starting with a clean bowl and puck (Appendix A), 100 g of Ottawa sand was ground for 60 s, removed, and subsampled. This step was repeated two more times (i.e., fresh Ottawa sand was ground and subsampled), and then the 400-g

residue-laden sample was ground for 60 s. After grinding, the residue-laden sample was removed from the bowl, triplicate subsamples were collected, and the bowl was cleaned following the protocol outlined in Appendix A. After cleaning, three separate 100-g quantities of Ottawa sand were ground and subsampled, as previously described. The remaining 370 g of the contaminated sand was then ground again, subsampled, and the bowl was washed following the protocol in Appendix A, except that the bowl and puck were allowed to air-dry prior to spraying with acetone. After cleaning (Appendix A), three separate 100-g Ottawa sand aliquots were ground and subsampled, as previously described.

A second trial was conducted following the same general format. In this case, however, after the heavily laden soil (360 g) was ground and the bowl was cleaned using the Appendix A procedure, the bowl, puck, lid, and gasket were placed in a sonic bath filled with a dilute detergent solution (Micro-90, Sigma-Aldrich) for 15 min. After sonic treatment, the apparatus was rinsed with water and sprayed with acetone. The residue-laden soil samples were analyzed with RP-HPLC; the blank Ottawa Sand samples were analyzed using GC-ECD. Energetic residue concentrations determined in the soils ground during these trials are listed in Table 8.

The two energetic residues most likely to present the greatest challenge for removal from equipment surfaces are HMX and TNT. This is because HMX is the least soluble in water, acetone, and acetonitrile, while TNT has a very high affinity for steel surfaces (Leggett 1977). Indeed, the first trial showed that these two compounds were not completely removed from the steel grinding bowl and/or puck, even though a fairly extensive cleaning protocol (Appendix A) had been followed. However, it should be noted that in the worst case, the energetic residue mass remaining on the grinding apparatus surface after cleaning represents more than a five order of magnitude reduction from the previous sample. Moreover, the contribution of this mass of analyte to a 300-g or larger sample would not be detectable by RP-HPLC utilizing Method 8330 or Method 8330B (USEPA 1994, 2006). The amount could only be detected by an analysis technique such as GC-ECD with detection limits equivalent or better than Method 8095 (Walsh and Ranney 1999, USEPA 1999).

Table 8. Energetic residue concentrations (mg/kg) carried over in grinding equipment following the processing of a sample containing high concentrations of HMX and TNT.

Sample*	Weight (g)	HMX	TNB	RDX	TNT	NG	2,4-DNT	2&4 AmDNT
First Trial								
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	0.014 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	<0.002 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	<0.002 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Soil #2	400	1170±22	28**	<40	14700±254	<100	<40	<80
Ottawa	100	0.046	<0.003 [†]	<0.006 [†]	0.120 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	0.022 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	0.014 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Soil #2	370	1140	34**	<40	14400	<100	<40	<80
Ottawa	100	0.022**	<0.003 [†]	<0.006 [†]	0.082 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	0.034 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	0.026 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Second Trial								
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	0.0025 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	<0.002 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	<0.002 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Soil #2	360	1130	42	<40	14100	<100	<40	<80
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	<0.002 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	<0.002 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]
Ottawa	100	<0.04	<0.003 [†]	<0.006 [†]	0.0025 [†]	<0.01 [†]	<0.002 [†]	<0.002 [†]

* Samples ground sequentially

[†] GC-ECD analysis

** value below estimated detection limit

The addition of a 15-min sonic bath treatment prevented any detectable levels of carryover energetic residues, with the possible exception of spurious trace quantities of TNT. As a consequence, laboratories may want to add this step to their cleaning protocol, or at least implement this step after processing a single or set of samples that are anticipated to contain very high energetic residue concentrations. Guidance in the Method 8330B Appendix recommends that laboratory staff be informed of those samples collected in areas where energetic residues were sighted (USEPA 2006).

4 Summary

No losses of energetic compounds were detected when archived soil samples were ground for a second time following the currently recommended protocols (Method 8330B). As Walsh et al. (2004) previously reported, some small losses of energetic residues may follow a prolonged period of grinding in a ring puck mill. In some circumstances, however, repeated grinding or prolonged grinding periods may increase the amount of energetic residues available for extraction. Compounds that increased the most with additional grinding were two transformation products of TNT: 2ADNT and 4ADNT. The sample that contained these two analytes was from a hand grenade range that had been inactive for more than 30 years.

With respect to reducing energetic residues subsampling variances, acetone dissolution appears to be as effective as mechanical pulverization with a ring puck mill. However, because of small losses of both NG and 2,4-DNT in laboratory-spiked soils, this technique needs further investigation or optimization. These two energetic compounds have the highest vapor pressure and therefore are likely to be more susceptible to volatilization during the period when the excess solvent is allowed to evaporate. Subsequent to our findings, experiments were performed at RDDC Valcartier, where aluminum foil punctured with several small holes was used to cover the pans during the acetone-drying step. Partially covering the wetted soil slowed the evaporation process and increased the recovery of NG to >94%.

Although not reported here, there have been some preliminary studies performed using two different ball mills, a commercial coffee grinder, and an automated mortar and pestle to pulverize soils collected from two firing points at CFB Petawawa. The subsample variances obtained for NG and 2,4-DNT associated with propellant residues at these two firing positions following pulverization with these other mechanical devices were much greater than either the ring puck mill or acetone dissolution.

An air-dried and sieved (<2 mm) sample of >1 kg mass could not be evenly divided with respect to energetic residues when containing concentrations below 40 mg/kg, even when using the most precise laboratory method currently available. Moreover, this source of indeterminate error would

likely increase with a reduction in the size of the split sample relative to the entire sample (removal of less than half the sample) and with less sample preparation (air-drying and removal of debris and particles >2 mm). Therefore, with the exception of sampling locations with very high energetic residue concentrations, splitting samples in the field most likely will introduce a large amount of uncertainty.

In this study, the most frequently detected energetic residues in soil samples from military training ranges showed no apparent losses after being air-dried and stored at room temperature in the dark for periods up to 53 days. Indeed, it appears that air-dried samples can be stored in the dark at room temperature for months, and perhaps years, without showing appreciable changes in the concentration of HMX, RDX, TNT, NG, and 2,4-DNT. Additional studies should be performed to assess if the common breakdown products of these compounds are also stable under these conditions.

Concerns have been expressed regarding the ability to prevent cross-contamination between samples processed by mechanical pulverization. An assessment of the cleaning procedure described in Appendix A indicated it would be prudent to sonicate the bowl, puck, lid, and gasket in soapy solution after processing a sample with high levels (>100 mg/kg) of energetic residues to further reduce the possibility of any detectable cross-contamination. It should be noted that the slight cross-contamination observed in this study when following the Appendix A protocol was detected because the samples were analyzed using gas chromatography following Method 8095A, which has very low detection limits (Table 1). This amount most likely would not have been detectable by Method 8330 or Method 8330B using liquid chromatography. Further precautions regarding the collection, transportation, and processing of samples taken in areas where energetic residues were observed on the surface are cited in the Appendix to Method 8330B (USEPA 2006). Most importantly, these samples should be screened in the field to establish that energetic residues do not exceed a level of 10% (100,000 mg/kg) prior to shipment. In addition, samples from locations where residues are observed should be transported in separate shipping containers and should be processed and analyzed as a separate batch in the laboratory. Therefore, the laboratory must be informed of those samples suspected to contain high levels of energetic residues to prevent cross-contamination during all aspects of the sample storage, processing, and analysis.

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Appendix A. Sample Processing and Subsampling Protocol

Sample Processing

1. All soil samples are returned to CRREL by overnight carrier and stored on ice until they are processed.
2. Soil samples are spread out on aluminum-foil-lined trays (multi-increment) or aluminum dishes (discrete) and allowed to air-dry (1–3 days, typically). The sample bag or bottle should also be air-dried.
3. Inside a laboratory exhaust hood the entire sample is then passed through a 10-mesh (2-mm) sieve to remove oversized material. This includes any additional sample from the sides of the shipping container (bag or bottle). Vegetation (clumps of moss, plant roots, grasses, etc.) are broken apart on top of the sieve with a large stainless steel spoon to release entrapped particles of energetic materials. The oversized fraction should be weighed and stored in a plastic bag.
4. The entire <2-mm air-dried fraction is weighed, and then the entire sample is either extracted (e.g. discrete) with twice the volume of acetonitrile as sample weight or ground (e.g. multi-increment) in a Lab TechEssa LM2 (LabTech Essa Pty. Ltd., Bassendean, WA, Australia) puck-mill grinder equipped with an 800-cm³ bowl.

Soils containing only crystalline energetic residues are ground for 60 s. Soils containing propellant residues (i.e., those from firing point, demolition areas, rocket impact ranges, etc.) are ground for 5 minutes (in five 60-s periods with a one-minute cooling time between grinds). Both grinding protocols reduce the particle size of the material to the consistency of flour (<75 µm). No grains should be felt if a portion of the ground soil is pinched between the fingers.

Note: No more than 500 g and no less than 200 g of material should be ground in an 800-cm³ bowl. Preferably each portion ground in the 800-cm³ bowls would weigh between 300 and 500 g.

5. After grinding, the sample (sample portions) is returned to the exhaust hood, mixed thoroughly on a sheet of aluminum foil, and spread thinly (1–2 cm), and subsamples are obtained by collecting 30 increments randomly through the entire thickness of the layer of ground material to obtain a subsample mass of 10.0 g.
6. The 10.0-g subsamples are extracted with 20 mL of acetonitrile while being agitated for 18 hours on a shaker table or in a cooled sonic bath. At the end of this extraction period the sample should be vigorously shaken, then allowed to settle for about 1 hour.
7. Each extract is filtered through a Millex-FH PTFE 0.45 syringe filter (Millipore Corp.). For GC-ECD analysis, this extract is injected without further dilution. For RP-HPLC-UV analysis, this extract is often diluted either 1/1 v/v or 1/3 v/v with de-ionized water, depending on the solvent strength of the HPLC eluent.

Cleaning

All trapped particles are pushed out of the sieve with the stainless steel spoon. The 800-cm³ bowl, puck, lid, sieve, spoon, and any other items that come in contact with the sample are placed into the sink and filled with hot soapy water. The rubber lid gasket is removed, and, using a scrub pad (3M), the cover, puck, bowl, sieve, spoon, and any other items are washed in the soapy water. The items are rinsed with hot water followed by de-ionized water and placed on a clean surface in an exhaust hood. The surface of each item is sprayed with acetone in the hood and dried with clean paper wipes. The rubber gasket in the bowl lid is replaced.

The exhaust hood is cleaned between each sample by vacuuming (HEPA vacuum cleaner) visible soil, wiping the bench surface with hot water, and then spraying this surface with acetone and wiping it dry.

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14. ABSTRACT Large soil samples are often necessary to represent areas where analytes are distributed as particulates. Proper processing of these large samples impose additional time, space, and equipment requirements on the laboratory community servicing environmental programs to investigate military training ranges. Part of this study evaluated the robustness of two methods used to process large soil samples for the determination of energetic munitions residues—whole sample mechanical grinding (comminution) and solvent dissolution. Both methods have been used successfully to reduce subsampling variance for samples collected on training ranges where particles of energetic residues have accumulated. However, two energetic compounds frequently detected in such samples—nitroglycerin (NG) and 2,4-dinitrotoluene (2,4-DNT)—may be susceptible to evaporative losses during solvent dissolution. Robustness experiments involved both lab-spiked and field-collected soils with various concentrations of energetic residue. An experiment utilizing field-collected soils involved the use of a rotary splitter. Even with this highly regarded equipment, the samples could not be split consistently, preventing a direct comparison of the two techniques in soils with residue concentrations less than 40 mg/kg. Two other investigations evaluated sample holding times and cross-contamination resulting from grinding processes. The results indicated that energetic compounds typically found on military training ranges were stable in air-dried soils for periods in excess of 53 days when stored in the dark at room temperature. A slight amount of cross-contamination from grinding was detectable using gas chromatography. The concentrations were below detectable levels when using liquid chromatography and were eliminated by adding a step of soaking the grinding bowl in a sonic bath filled with dilute cleaning detergent to the cleaning protocol.					
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