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Extraction Kinetics of Energetic Compounds from Training Range and Army Ammunition Plant Soils

Platform Shaker vs. Sonic Bath Methods

Marianne E. Walsh and Dennis J. Lambert   March 2006

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ABSTRACT

Field-contaminated soils from army ammunition plants, training ranges, and an explosive ordnance disposal area were used to determine the effect of machine grinding and extraction procedure on concentration estimates of energetics. Machine grinding for one minute did not degrade the major analytes of interest (HMX, RDX, TNT, or 2,4-DNT), but did significantly reduce the subsampling error. The platform shaker extraction procedure was found to be at least as efficient as the sonic bath method specified in SW-846 Method 8330 and is therefore a suitable substitute.

Additional studies showed that extended grinding of the soil sample causes the sample to warm as a result of friction and results in analyte loss. However, grinding for five one-minute cycles, with a sufficiently long rest period between cycles to prevent soil warming, did not result in analyte loss. Repeated grind cycles were needed to reduce the subsampling error for soils contaminated with propellant residue.

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PREFACE

Extraction Kinetics of Energetic Compounds from Training Range and Army Ammunition Plant Soils

Platform Shaker vs. Sonic Bath Methods

MARIANNE E. WALSH AND DENNIS J. LAMBERT

1   INTRODUCTION

The standard analytical method to determine explosives in soils (Method 8330 [USEPA 1994]) was developed in the late 1980s to support efforts to clean up Army ammunition plants and depots where wastewater from munitions production was released onto the soil of unlined ditches and surface impoundments. This standard analytical method specifies that soil samples be manually ground with a mortar and pestle to pass through a 30-mesh sieve and that a 2-g subsample be extracted with 10 mL of acetonitrile for 18 hours in a cooled sonic bath (USEPA 1994). This method has been used successfully to determine explosives in millions of soil samples in the United States, Canada, Europe, and Australia.

By the end of the 1990s, most of the industrial sites where explosives and ammunition were manufactured were characterized and the appropriate remedial actions chosen. Then, the focus of concern shifted to training ranges where ammunition is used and the potential for off-site migration of explosives needed to be assessed. Recent research has shown that when ordnance is fired, energetic residues may be deposited on soil surfaces as particulates, both at the firing point and, in some situations, at the impact point (Jenkins et al. 2004, Taylor et al. 2004, Walsh et al. 2004, Hewitt et al. 2005, Jenkins et al. 2005, M. R. Walsh et al. 2005). Subsampling variance for soils from training ranges was unacceptably high due to these particulates, and necessitated some modifications to the soil processing procedure in Method 8330.

One of the modifications was to increase the subsample size. Our current procedure is to process the entire field sample by sieving through a 2-mm (#10 mesh) sieve, grinding the less-than-2-mm fraction on a ring mill (Walsh et al. 2002), then forming a 10-g subsample composed of at least 30 increments of the

machine-ground sample. During some recent studies of field sampling error on training ranges, discrete soil samples up to 150 g were extracted with solvent without subsampling (Jenkins et al. 2004) using a platform shaker. More samples could be extracted simultaneously using the platform shaker than in a sonic bath. The question was raised as to whether the platform shaker method is equivalent in extraction efficiency to the sonic bath.

The sonic bath extraction procedure was chosen in the 1980s in a study where four extraction methods or devices (Soxhlet, sonic bath, wrist-action shaker, and a soil-plant homogenizer) and two solvents (methanol and aceto-nitrile) were used to extract explosives from two soils from Iowa Army Am-munition Plant (AAP) (Jenkins and Leggett 1985, Jenkins and Grant 1987). Acetonitrile yielded higher concentrations for the nitramines RDX and HMX, indicating a higher extraction efficiency for these analytes, and was therefore chosen as the solvent for Method 8330. With respect to the extraction method, the sonic bath was chosen mainly because of the number of samples that could be processed simultaneously, compared to the other devices tested. Differences in extraction efficiencies were not apparent, mostly due to large subsampling uncertainty of field-contaminated soils.

2   OBJECTIVE

The primary objective of the present study was to assess whether the platform shaker is equivalent in extraction efficiency to the sonic bath. A secondary objective was to further evaluate the effect of machine grinding on estimates of analyte concentration. The data acquired could also provide an informal assessment of the stability of energetics in air-dried soils over an extended time.

3   APPROACH

For this study, we used field-contaminated soils that have been archived in our lab, one for as long as 20 years (a sample from Iowa AAP that was collected at the same time as the two soils used in the initial extraction kinetic study [Jenkins and Grant 1987] and was analyzed in a subsequent extraction kinetic study by Jenkins and Walsh [1987]). Soils were from army ammunition plants, training ranges, and an explosive ordnance demolition range, and had at least one of the following analytes: RDX, TNT, HMX, and 2,4-DNT. The soils had been air-dried prior to storage at room temperature in the dark (to prevent photodegradation). We chose soils that we expected had analyte concentrations at least 10 times greater than the method detection limit by HPLC-UV so that analytical error would be minimal. We did not use spiked soils because they do not mimic field-contaminated soils that have much slower extraction kinetics (Jenkins et al. 1989).

In the first experiment, we examined the effects of machine grinding and extraction method on concentration estimates of energetics in soils from army ammunition plants and training ranges. First, we hypothesized that one minute of machine grinding does not degrade the analytes of interest but does reduce the subsampling variance. We also hypothesized that the efficiency of the platform shaker was equal to the sonic bath for extracting the energetics from a soil matrix into the extraction solvent (acetonitrile). Because of the limited amounts of some of the soils and to reduce the number of analyses, we performed a two-stage experiment. First, we extracted replicate soil subsamples sequentially by 18 hours of shaking and an additional 18 hours of sonicating. For those soils where analyte concentrations were significantly higher following sonication, additional studies were performed to determine whether the increased concentrations were due to sonication or simply more time for equilibration with the extraction solvent.

In the final experiment, we used a soil from an explosive ordnance disposal area to examine the effect of grind time and extraction method on concentration estimates of propellant residues. Soils contaminated with propellant residues require additional processing to reduce subsampling variance and could potentially have different extraction kinetics than soils contaminated with high explosives. We have found that one minute of grinding is not adequate to reduce the subsampling variance of soils with propellant residue (M. E. Walsh et al. 2005). However, grinding for five one-minute cycles with rest time between each cycle generally results in subsampling error of less than 10% relative standard deviation (Hewitt et al. 2005).

4   METHODS

Archived soils (Table 1) were chosen to represent a variety of field conditions and the samples had sufficient mass to allow replicate subsampling. Three of the soils were from AAPs (army ammunition plants), three were from training ranges, and one was from an explosive ordnance disposal area.

The samples from Fort Lewis and Valcartier had been air-dried, but not previously analyzed. Each of these two soils was passed through a #10 sieve to remove the greater-than-2-mm fraction.

Not ground or ground soils and sequential shaking, then sonicating

Soil samples from Milan, Valcartier, Fort Lewis, and FP Mark were weighed and divided by fractional shoveling to form approximately 200-g portions. Two of the portions from each soil were randomly chosen, then one of the splits from each soil was ground for one minute on a LabTech Essa LM-2 Ring Mill equipped with a B800 bowl. The sample from Volunteer was not divided by fractional shoveling because of the small amount of this soil that was archived. Seven subsamples were formed, as described below, from the Volunteer sample, then the remaining soil was ground and subsampled again.

To obtain each subsample, each soil sample was spread onto a flat surface and a spatula was used to collect at least 30 soil increments, through the thickness of the sample and from random locations throughout the sample. Seven 10.00-g subsamples were formed from the unground and machine-ground samples and placed within a 60-mL (2-oz) widemouth amber jar equipped with a Teflon-lined cap. A 20.00-mL aliquot of acetonitrile was added to each subsample and the sample was capped and vortexed for 60 s. The samples were then shaken on a platform shaker (New Brunswick Scientific Innova 2100 Platform Shaker) at 150 rpm for 18 hours (Fig. 1a). The shaker was turned off and the solids allowed to settle for one hour. A 2-mL aliquot of the extract was removed from each subsample, then each subsample was vortexed for 60 s to re-suspend the solids. All the subsamples were further extracted using a sonic bath (Branson 8510 Ultra Sonic Cleaner) for 18 hours (Fig. 1b). The sonic bath water was circulated to maintain the temperature at 20°C (Neslab Endocal Refrigerated Circulating Bath). After the solids settled for one hour, a portion of each extract was removed and prepared for analysis by high-performance liquid chromatography (HPLC) as described below.

Table 1. Soils used for extraction efficiency studies.[1]				
Soil ID	**Origin and year collected**	**Previous sieving or grinding**	**Analytes (previously determined concentration [µg/g])[2]**	**Analytes detected in this study (concentration [µg/g])[2]**
Milan 75[3]	Milan AAP, TN; 1999?	10-mesh sieve	RDX (23 [44% RSD]) HMX (4 [26% RSD])	RDX (29 [0.9% RSD]) HMX (6.6 [1.2% RSD])
Iowa 1[4]	Iowa AAP, IA; 1985	Manual grinding and 30-mesh sieve	TNT (1) HMX (<mdl) RDX (<mdl)	TNT (2.2 [1.4% RSD]) HMX (0.30 [1.1% RSD]) RDX (0.46 [1.5% RSD])
Volunteer W9[5]	Volunteer AAP, TN; 1995	Manual grinding and 30-mesh sieve	TNT (10.5 [3% RSD]) 2,4-DNT (1.4 [3% RSD])	TNT (10.2 [3.4% RSD]) 2,4-DNT (2.7 [3.0% RSD])
Fort Lewis[6]	Fort Lewis hand grenade range, WA; 2001	None	Co-located sample RDX (3.8 [47% RSD]); HMX (1.0 [24% RSD]); TNT (1.4 [63% RSD])	RDX (3.8 [2.2% RSD]) HMX (0.95 [2.7% RSD]) TNT (0.96 [5.3% RSD])
Valcartier	Canadian Force Base Valcartier, anti-tank range; 1997	None	Not previously analyzed, but HMX expected.	HMX (548 [1% RSD])
FP Mark	Donnelly Training Area, AK; 1993	10-mesh sieve	Not previously analyzed, but 2,4-DNT expected.	2,4-DNT (0.14 [14% RSD])
EOD[7]	Fort Richardson, AK; 1990	Manual grinding and 30-mesh sieve	2.4-DNT (0.61 to 27) TNT (0.15 to 0.50) 2-Am-DNT (0.08 to 0.47) 4-Am-DNT (0.16 to 0.52)	2,4-DNT (1.02 [6% RSD]) TNT (0.8 [2% RSD]) 2-Am-DNT (0.2 [6% RSD]) 4-Am-DNT (0.2 [6% RSD])

[1] Soil samples were archived at room temperature.

[2] RSD (relative standard deviations) were computed if replicate analyses were done and did not deviate extremely from a normal distribution. Data ranges for the EOD sample are given because of the non-Gaussian distribution of the concentration estimates obtained in 1990.

[3] Personal communication: A. Dindal, Oak Ridge National Laboratory. Soil collected for ETV (Environmental Technology Verification) Program "Evaluation of Explosives Field Analytical Techniques." Soil was not used because of high subsampling error.

[4] Jenkins and Walsh (1987)

[5] Jenkins et al. (1996)

[6] Walsh et al. (2002)

[7] Racine et al. (1992)

a. Platform shaker.

b. Sonic bath.

Figure 1. Platform shaker and sonic bath used for extraction efficiency experiments.

We used a one-tailed paired t-test (Miller and Miller 1984) to test the hypothesis that the mean concentration of energetics after 18 hours of shaking was not significantly less than the estimate obtained after an additional 18 hours of sonication (total extraction time of 36 hours).

Follow-up studies of sequentially extracted ground soils

Based on the results of the one-tailed t-tests, soils from Milan and Volunteer, and the soil from Iowa Army Ammunition Plant, were used to determine whether increased extraction time or extraction method resulted in higher concentrations following 36 hours of extraction versus 18 hours. Twelve 10-g subsamples were formed from the remaining ground Milan soil. Six were randomly chosen for 18 hours of shaking followed by 18 hours of sonication as before, and the other six subsamples were extracted by 18 hours of sonication then 18 hours of shaking. We repeated the original extraction sequence (shaking then sonicating) so that all the extracts could be analyzed on the same day to minimize any systematic errors from slight differences in daily calibrations. The experiment was then repeated for the soil from Iowa AAP.

All of the remaining sample from Volunteer was subsampled. Enough soil remained for eleven 10-g subsamples. Five of the subsamples were extracted by a total of 36 hours of shaking or 36 hours of sonication. A 2.00-mL aliquot of acetonitrile extract was removed from each subsample after 18 hours of extraction to allow comparison of concentration estimates at the midpoint and end of extraction.

Effect of extended grinding and extraction method on a soil sample from an explosive ordnance disposal area

To determine the effect of extraction device (platform shaker or sonic bath) on concentration estimates on a soil ground for one minute and five one-minute cycles, we performed the following experiment.

We used a soil that we collected in 1990 from an EOD (explosive ordnance disposal) area at Fort Richardson, Alaska (Table 1). In July 1990 five replicate subsamples from this soil were analyzed for energetics. Each subsample had detectable 2,4-DNT, TNT, 2-Am-DNT, and 4-Am-DNT, but the concentrations were very different for each subsample (Table 1) (Racine et al. 1992). The archived soil sample (290 g) was ground for one minute using a ring mill. Twelve 10-g subsamples were collected, then the remaining soil was ground for four one-minute cycles with one minute between cycles to prevent heating of the grinder bowl and sample. Twelve more 10-g subsamples were formed. Six

subsamples from the one-minute grind and six subsamples from the five-minute grind were randomly chosen for extraction using the platform shaker, and the remainder were extracted in a sonic bath, each for 18 hours. Extracts were then analyzed by HPLC.

HPLC analysis

Prior to analysis, the acetonitrile extracts were filtered through Millex-FH (Millipore, PTFE, 0.45-µm) filter units and an aliquot combined with reagent-grade water (MilliQ) at a ratio of 1:3 v:v AcN:Water. The HPLC separations were achieved on a 15-cm $\times$ 3.9-mm (4-µm) Nova Pak C_8 (Waters Millipore) column eluted with 1.4 mL/min 15:85 isopropanol:water at 28°C. Injection volume was 100 µL. The detector was a ThermoSeparations Products Spectra System UV2000 dual wavelength. Concentration estimates were obtained at 254 nm.

5   RESULTS AND DISCUSSION

Not ground or ground soils and sequential shaking, then sonicating

Machine grinding of soils contaminated with high explosives is not an intuitively obvious method of choice to reduce subsampling variance. High explosives are shock-sensitive and thermally labile, so the process of machine grinding raises questions with respect to safety and analyte stability. Concerning safety, the soil processing and analytical methods described in this report are for soils contaminated with part-per-million concentrations of explosives, which will not detonate due to shock stimulus or flame initiation. Reactivity tests were conducted many years ago and showed that soils with concentrations of TNT and RDX below 15% (150,000 μg/g) were not reactive to shock stimuli (Kristoff et al. 1987). Heating of explosives-contaminated soils is of concern with respect to analytical accuracy. Friction between the soil, bowl, and ring or puck will generate heat and could result in loss due to thermal degradation and/or loss by sublimation for analytes with the highest vapor pressures (Appendix A: Supplemental Studies). To prevent heating, grinding cycles should be as short as possible to adequately reduce subsampling variance. Grinding for one minute does not noticeably raise the temperature of a dry soil. On the other hand, grinding could potentially enhance extraction efficiency by increasing the surface area of the solid phase exposed to the liquid solvent.

Results for individual subsamples of soils, both unground and ground, that were extracted sequentially by shaking then sonicating are given in Table 2 and a summary of the mean concentrations with t-statistics are given in Table 4 for HMX, RDX, TNT, and 2,4-DNT. In the soils from Milan, Fort Lewis, Valcartier, and Volunteer, the mean concentrations of HMX, RDX, TNT, and 2,4-DNT were numerically higher in almost all of the ground soils compared to the unground soils. Student's t-tests to compare the means of the unground and ground soil results were not performed due to the significantly higher variance for the unground soils. Non-parametric comparisons of the medians using the Wilcoxon-Mann-Whitney test (Natrella 1966) indicated that the medians for the ground soils were either not significantly different from or were higher than the medians for the unground soils. The highest subsampling error (% RSD) was for 2,4-DNT in the unground firing point soil (FP Mark, Table 2d); the data are not normally distributed so the mean is not a valid estimator of the central tendency of the data. The medians for the ground and unground samples were not significantly different based on the Wilcoxon-Mann-Whitney test. Based on the above, there is

no reason to conclude that machine grinding of soil samples for one minute (or five one-minute cycles) degrades HMX, RDX, TNT, or 2,4-DNT in soils.

Table 2. Concentrations found in unground and ground soil subsamples that were sequentially extracted by shaking then sonicating (subsamples are paired).

	Milan		Fort Lewis		Valcartier	
a) HMX concentration (µg/g).						
	Shaken 18 hrs	**Shaken 18 hrs then sonicated 18 hrs**	**Shaken 18 hrs**	**Shaken 18 hrs then sonicated 18 hrs**	**Shaken 18 hrs**	**Shaken 18 hrs then sonicated 18 hrs**
Not ground						
	5.86	5.86	1.21	1.21	445	456
	5.54	5.72	1.10	1.16	507	497
	7.70	7.63	1.03	1.03	446	450
	5.52	5.74	0.90	0.91	462	472
	5.84	5.87	0.84	0.82	577	571
	4.74	4.71	0.85	0.83	580	584
	8.63	8.71	0.63	0.64	423	426
Mean	6.26	6.32	0.94	0.94	491	494
s	1.38	1.36	0.19	0.20	65	61
RSD	22%	22%	20%	21%	13%	12%
Ground						
	6.27	6.58	0.95	0.97	550	545
	6.12	6.28	0.93	0.99	558	543
	6.46	6.49	0.91	0.97	544	536
	6.42	6.56	0.94	0.94	544	547
	6.18	6.25	0.94	0.91	543	534
	6.29	6.21	0.90	0.95	552	562
	6.09	6.21	0.93	0.95	546	524
Mean	**6.26***	**6.37**	0.93	0.95	548	542
s	0.14	0.17	0.018	0.026	5.5	12
RSD	2.2%	2.7%	1.9%	2.7%	1.0%	2.2%

* Means in bold print are significantly different by one-tailed paired t-test (alpha = 0.05).

Table 2 (cont'd). Concentrations found in unground and ground soil subsamples that were sequentially extracted by shaking then sonicating (subsamples are paired).				
b) RDX concentration (µg/g).				
	Milan		Fort Lewis	
	Shaken 18 hrs	Shaken 18 hrs then sonicated 18 hrs	Shaken 18 hrs	Shaken 18 hrs then sonicated 18 hrs
Not ground				
	21.2	21.3	7.31	7.26
	23.6	24.6	3.03	3.13
	28.7	28.7	2.01	1.99
	21.6	22.4	1.63	1.63
	28.8	29.5	2.51	2.43
	28.2	28.2	3.21	3.11
	31.9	32.6	1.96	1.96
Mean	26.3	26.8	3.09	3.07
s	4.13	4.10	1.95	1.93
RSD	16%	15%	63%	63%
Ground				
	31.4	32.9	3.81	3.83
	30.5	31.5	3.77	3.94
	32.0	32.6	3.69	3.88
	31.9	32.9	3.81	3.77
	30.6	31.4	3.78	3.68
	31.2	31.3	3.70	3.83
	30.6	31.3	3.76	3.79
Mean	**31.2***	**32.0**	3.76	3.82
s	0.63	0.77	0.048	0.083
RSD	2.0%	2.4%	1.3%	2.2%
* Means in bold print are significantly different by one-tailed paired t-test (alpha = 0.05).				

Table 2 (cont'd).				
c) TNT concentration (µg/g).				
	Volunteer		Fort Lewis	
	Shaken 18 hrs	Shaken 18 hrs then sonicated 18 hrs	Shaken 18 hrs	Shaken 18 hrs then sonicated 18 hrs
Not ground				
	6.14	9.38	1.22	1.13
	5.51	8.21	0.51	0.53
	6.51	8.41	0.27	0.29
	5.58	7.78	0.28	0.37
	5.87	8.03	0.75	0.64
	6.05	8.27	0.38	0.33
	5.79	8.18	0.23	0.31
Mean	**5.92***	**8.32**	0.52	0.51
s	0.35	0.51	0.36	0.30
RSD	5.9%	6.1%	69%	59%
Ground				
	7.41	10.45	1.03	1.00
	7.06	10.49	1.01	1.01
	6.67	9.90	1.00	0.99
	7.30	10.22	1.02	0.87
	6.87	10.13	1.11	0.92
	6.65	9.58	1.02	0.97
	7.27	9.69	1.00	0.93
Mean	**7.03**	**10.07**	1.03	0.96
s	0.31	0.36	0.038	0.051
RSD	4.4%	3.6%	3.7%	5.3%
* Means in bold print are significantly different by one-tailed paired t-test (alpha = 0.05).				

Table 2 (cont'd). Concentrations found in unground and ground soil subsamples that were sequentially extracted by shaking then sonicating (subsamples are paired).

	Volunteer		FP Mark*	
	Shaken 18 hrs	**Shaken 18 hrs then sonicated 18 hrs**	**Shaken 18 hrs**	**Shaken 18 hrs then sonicated 18 hrs**
Not ground				
	2.66	2.83	0.13	0.13
	1.46	1.59	0.016	0.010
	1.55	1.69	0.54	0.52
	1.59	1.71	0.39	0.39
	1.58	1.72	0.92	0.91
	1.57	1.68	0.014	0.022
	1.53	1.67	not detected	0.016
Mean	1.71	1.84	0.29	0.29
s	0.42	0.44	0.35	0.34
RSD	24.6%	23.9%	120%	117%
			median = 0.13	median = 0.13
Ground				
	2.45	2.60	0.15	0.16
	2.50	2.66	0.17	0.17
	2.21	2.48	0.13	0.17
	2.36	2.55	0.16	0.18
	2.35	2.52	0.11	0.12
	2.23	2.36	0.14	0.14
	2.29	2.45	0.12	0.13
Mean	**2.34**[†]	**2.52**	0.14	0.15
s	0.11	0.10	0.02	0.02
RSD	4.7%	4.0%	14%	13%
			median = 0.14	median = 0.16

d) 2,4-DNT concentration (µg/g).

* The FP Mark sample was ground for five one-minute cycles.

† Means in bold print are significantly different by one-tailed paired t-test (alpha = 0.05).

In soils from Milan, Fort Lewis, Valcartier, and FP Mark, the additional 18 hours of sonication following 18 hours of shaking did not produce extracts with appreciably higher concentrations of HMX, RDX, TNT, and 2,4-DNT. After 18 hours of shaking, mean concentrations were generally 97% or greater of the

mean concentrations found after the additional sonication. However, in some cases, the t-statistic indicated a significant difference at the 95% confidence level (Table 4), and the soil from Milan was used for further study.

The soils from Volunteer had detectable concentrations of TNT, 2,4-DNT, 2,6-DNT, 2-Am-DNT, and 4-Am-DNT (Table 2 and Table B1). Concentration estimates for all of these analytes significantly increased (Table 4 and Table B3) following the additional sonication, so this soil was studied further.

Follow-up studies of sequentially extracted ground soils

The extraction sequence of shaking then sonicating was repeated with sub-samples of the ground Milan soil and, at the same time, the reverse sequence—sonicating then shaking—was used for additional subsamples of this soil. The same experiment was done with a soil from Iowa AAP. Results for individual subsamples are given in Table 3 and a summary of the means and t-statistics are given in Table 4.

For the Milan and Iowa soils, the additional extraction step did not produce appreciable increases in concentrations of the analytes, although the t-statistic was significant at the 95% confidence level for the sonic/shake extraction sequence for at least one analyte. The highest t-value (10.2) was for RDX in the Milan soil comparing the mean of 28.1 µg/g after 18 hours of sonication to the mean of 29.3 µg/g after an additional 18 hours of shaking. Estimates of RDX for the shake/sonic extraction sequence were 28.6 µg/g and 28.8 µg/g, which were not significantly different from each other. For all practical purposes, these four concentration estimates are essentially equivalent. Based on these results, the platform shaker extraction method was at least as efficient as the sonic bath for the Milan and Iowa soils.

For the follow-up study of the Volunteer soil, subsamples were either shaken or sonicated for 36 hours with aliquots of solvent removed after 18 hours. For all analytes, the additional extraction time produced significantly higher concentrations for both the platform shaker and sonic bath methods (Table 3c, Table 4, Tables B2 and B3). Extraction kinetics for this particular soil were slower (perhaps due to high clay content, mode of contamination, and/or duration of contamination) than for the other soils studied, and the platform shaker method yielded slightly higher concentration estimates. Again we can conclude that the platform shaker extraction method was at least as efficient as the sonic bath.

Table 3. Concentrations estimates found in sequentially extracted ground soil sub-samples (subsamples are paired).

		a) Milan.		
	HMX concentration (µg/g)		**RDX concentration (µg/g)**	
	Shaken 18 hrs	**Shaken 18 hrs then sonicated 18 hrs**	**Shaken 18 hrs**	**Shaken 18 hrs then sonicated 18 hrs**
	6.41	6.54	28.4	28.7
	6.52	6.45	28.7	28.4
	6.52	6.57	28.7	29.1
	6.58	6.63	28.8	29.0
	6.63	6.68	28.5	28.8
	6.52	6.59	28.7	28.9
Mean	6.53	6.58	28.6	28.8
s	0.074	0.079	0.15	0.25
RSD	1.13%	1.20%	0.52%	0.87%
	Sonicated 18 hrs	**Shaken 18 hrs then sonicated 18 hrs**	**Sonicated 18 hrs**	**Shaken 18 hrs then sonicated 18 hrs**
	6.46	6.65	27.9	29.0
	6.48	6.75	28.0	29.6
	6.45	6.60	28.0	29.2
	6.49	6.83	28.0	29.5
	6.49	6.61	28.2	29.0
	6.51	6.67	28.4	29.5
Mean*	**6.48**	**6.69**	**28.1**	**29.3**
s	0.022	0.089	0.18	0.27
RSD	0.34%	1.33%	0.64%	0.92%
* Means in bold print are significantly different by one-tailed paired t-test (alpha = 0.05).				

	HMX concentration (µg/g)		RDX concentration (µg/g)		TNT concentration (µg/g)	
Table 3 (cont'd).						
b) Iowa 1.						
	Shaken 18 hrs	**Shaken 18 hrs then sonicated 18 hrs**	**Shaken 18 hrs**	**Shaken 18 hrs then sonicated 18 hrs**	**Shaken 18 hrs**	**Shaken 18 hrs then sonicated 18 hrs**
	0.295	0.301	0.446	0.450	2.07	2.17
	0.302	0.296	0.450	0.456	2.11	2.15
	0.309	0.302	0.458	0.459	2.17	2.17
	0.295	0.300	0.442	0.457	2.03	2.15
	0.288	0.292	0.440	0.440	2.06	2.08
	0.306	0.295	0.451	0.441	2.16	2.09
Mean	0.299	0.298	0.448	0.451	2.10	2.14
s	0.00788	0.00393	0.00659	0.00831	0.0565	0.0412
RSD	2.64%	1.32%	1.5%	1.8%	2.69%	1.93%
	Sonicated 18 hrs	**Sonicated 18 hrs then shaken 18 hrs**	**Sonicated 18 hrs**	**Sonicated 18 hrs then shaken 18 hrs**	**Sonicated 18 hrs**	**Sonicated 18 hrs then shaken 18 hrs**
	0.295	0.306	0.449	0.461	2.11	2.18
	0.293	0.302	0.441	0.455	2.09	2.17
	0.302	0.300	0.452	0.450	2.16	2.14
	0.289	0.303	0.434	0.458	2.01	2.13
	0.295	0.309	0.456	0.471	2.14	2.20
	0.298	0.307	0.446	0.458	2.15	2.20
Mean	0.295	0.305	0.446	0.459	**2.11**	**2.17**
s	0.00441	0.00339	0.00792	0.00703	0.0555	0.0297
RSD	1.49%	1.11%	1.8%	1.5%	2.63%	1.37%
* Means in bold print are significantly different by one-tailed paired t-test (alpha = 0.05).						

Table 3 (cont'd). Concentrations estimates found in sequentially extracted ground soil subsamples (subsamples are paired).

	TNT concentration (µg/g)		2,4-DNT concentration (µg/g)	
	Shaken 18 hrs	**Shaken 36 hrs**	**Shaken 18 hrs**	**Shaken 36 hrs**
	8.94	10.31	2.33	2.72
	9.30	10.49	2.40	2.77
	9.04	10.43	2.33	2.73
	9.11	9.76	2.35	2.59
	8.99	9.92	2.35	2.59
Mean	**9.08**	**10.18**	**2.35**	**2.68**
s	0.14	0.32	0.03	0.08
RSD	1.54%	3.14%	1.28%	2.99%
	Sonicated 18 hrs	**Sonicated 36 hrs**	**Sonicated 18 hrs**	**Sonicated 36 hrs**
	8.38	9.20	2.09	2.30
	8.28	9.19	2.09	2.32
	8.45	9.34	2.12	2.33
	8.41	8.97	2.10	2.26
	8.21	9.61	2.06	2.40
	8.35	9.45	2.08	2.36
Mean	**8.35**	**9.29**	**2.09**	**2.33**
s	0.0882	0.224	0.0200	0.0483
RSD	1.06%	2.41%	0.96%	2.07%

c) Volunteer.

* Means in bold print are significantly different by one-tailed paired t-test (alpha = 0.05).

Table 4. Summary table of mean concentrations (µg/g) and t statistics for sequentially extracted soil subsamples.

Analyte	Soil	Processing	n	Extraction sequence	Concentration (µg/g) 18 hrs	Concentration (µg/g) 36 hrs	t
HMX	Milan	not ground	7	shake/sonic	6.26	6.32	1.43
		ground	7	shake/sonic	6.26	6.37	**2.35***
		ground	6	shake/sonic	6.53	6.58	1.76
		ground	6	sonic/shake	6.48	6.69	**6.01**
	Iowa AAP	ground	6	shake/sonic	0.299	0.298	0.50
		ground	6	sonic/shake	0.295	0.305	**3.80**
	Fort Lewis	not ground	7	shake/sonic	0.937	0.942	0.65
		ground	7	shake/sonic	0.93	0.95	**2.02**
	Valcartier	not ground	7	shake/sonic	491	494	0.93
		ground	7	shake/sonic	548	542	1.63
RDX	Milan	not ground	7	shake/sonic	26.3	26.8	**2.95**
		ground	7	shake/sonic	31.2	32	**5.01**
		ground	6	shake/sonic	28.6	28.8	1.81
		ground	6	sonic/shake	28.1	29.3	**10.2**
	Iowa AAP	ground	6	shake/sonic	0.448	0.451	0.80
		ground	6	sonic/shake	0.446	0.459	**3.65**
	Fort Lewis	not ground	7	shake/sonic	3.09	3.07	0.86
		ground	7	shake/sonic	3.76	3.82	1.38
TNT	Volunteer	not ground	7	shake/sonic	5.92	8.32	**14.4**
		ground	7	shake/sonic	7.03	10.07	**24.4**
		ground	5	shake/shake	9.08	10.18	**7.86**
		ground	6	sonic/sonic	8.35	9.29	**8.21**
	Iowa	ground	6	shake/sonic	2.10	2.14	1.24
		ground	6	sonic/shake	2.11	2.17	**3.15**
	Fort Lewis	not ground	7	shake/sonic	0.52	0.51	0.19
		ground	7	shake/sonic	1.03	0.96	**2.62**
2,4-DNT	Volunteer	not ground	7	shake/sonic	1.71	1.84	**18.9**
		ground	7	shake/sonic	2.34	2.52	**10.2**
		ground	5	shake/shake	2.35	2.68	**9.05**
		ground	6	sonic/sonic	2.09	2.33	**9.26**
	FP Mark	not ground	7	shake/sonic	0.29	0.29	0.38
		ground	7	shake/sonic	0.14	0.15	**2.46**

* Bold print indicates that the t-statistic exceeds the critical value for a one-tailed paired t-test (alpha = 0.05). Critical values are 2.13, 2.02, and 1.94 for 4, 5, and 6 degrees of freedom (n – 1), respectively.

Effect of extended grinding and extraction method on a soil sample from an explosive ordnance disposal area

The soil from an EOD area was ground for one minute, subsampled, then ground for four additional one-minute cycles and subsampled again. Subsamples were randomly chosen for platform shaker or sonic bath extraction.

Means for concentration estimates of TNT, 2,4-DNT, and 2,6-DNT by shaking or sonicating were compared using a Student t-test and were not significantly different at the 95% confidence level (Table 5). Means for the one-minute and five-minute grinds were not statistically compared due to the much larger variance for the shorter grind time, but the means for each analyte were numerically similar, indicating no obvious loss of analyte by the additional grind cycles.

The biotransformation products of TNT yielded different analytical results. For 2-Am-DNT, the sonic bath extraction produced statistically higher concentrations, although again the differences were small. For 4-Am-DNT, the sonic bath yielded statistically higher concentrations for the one-minute grind while the platform shaker yielded higher concentrations for the five-minute grind subsamples. Perhaps of more importance, the similarity in variance of the one-minute and five-minute grind results permitted the use of analysis of variance (ANOVA), which showed that the means for the five-minute grind were significantly higher than for the one-minute grind. The mono-amino-dinitrotoluenes are formed in soils in the early stages of TNT biotransformation that eventually forms non-solvent-extractable conjugation products. Thorne and Leggett (1999) found that additional amino-dinitrotoluenes were released by hydrolysis of solvent-extracted biotreatment soils; the hydrolysis was thought to disrupt the humic polymers. Similarly, machine grinding could physically break apart organic polymers and facilitate solvent extraction of the amino-DNTs.

Comparison with previous extraction studies

There are some differences that should be noted between extraction conditions used in this study and the previous study by Jenkins and Grant (1987) and with Method 8330.

In the previous study, a wrist-action shaker, not a platform shaker, was used to agitate 2-g subsamples with 50 mL of acetonitrile in 25- × 200-mm culture tubes. Unlike the platform shaker that was used in the present study, wrist-action shakers simply rock or oscillate each sample and were adequate to suspend the 2 g of soil in the 50 mL of solvent. To reduce subsampling variance, we have increased the subsample size to 10 g, and to minimize solvent consumption, we

have reduced the solvent volume to 20 mL. With this soil-to-solvent ratio, the rocking motion of the wrist action shaker results in the formation of a soil layer on the bottom of the culture tube that appears to be unmixed with the solvent oscillating above it. Although we did not re-evaluate the wrist-action shaker, we suspect that the increased soil-to-solvent ratio may decrease the extraction efficiency of this technique.

The change to a larger soil-to-solvent ratio may also affect the efficiency of the sonic bath. Jenkins and Grant (1987) pointed out that "the extent of particle disruption varies inversely with solid/solution ratio." The ultrasonic waves in a sonic bath produce cavitation (the formation and collapse of microbubbles) in the liquid phase. Collapse of the bubbles releases energy and agitates the soil particles within the extraction solvent. In the original study by Jenkins and Grant (1987), 2-g subsamples were extracted with 50 mL of acetonitrile in a sonic bath. In subsequent studies, Jenkins et al. (1988) compared concentrations estimated from 50-, 25-, and 10-mL extracts of 2-g soil subsamples; concentration estimates were similar for the three soil/solvent ratios and the 10-mL/2-g ratio was found to be advantageous in terms of enhanced detection capability for analytes at low part-per-million concentrations. As a result, Method 8330 specifies a solvent volume of 10 mL for each 2-g subsample. The change in soil-to-solvent ratio to 10 g and 20 mL may lessen the extraction efficiency of the sonic bath by dampening the ultrasonic waves. A slight decrease in efficiency was observed for 50-g subsamples extracted with 50 mL acetonitrile compared to 2-g/10-mL subsamples of the same soil (Walsh et al. 2002).

The platform shaker produces a rotary or orbital motion in a horizontal plane. Each 10-g/20-mL sample is contained in a widemouth 60-mL jar with a 4-cm base. We set the rotations per minute (150 rpm) such that the solids are suspended in the solvent during extraction. Following 18 hours of shaking, the solvent is turbid, and the solids are sludge-like, which is an indication of good mixing between the liquid and solid phases. Based on the data for the soils extracted in the present study, the platform shaker is a suitable substitute for a sonic bath for the extraction of energetics from soil. Extraction efficiencies are at least as good as the sonic bath and there are some advantages to the platform shaker. In addition to larger batch sizes, samples do not require external cooling, and the platform shaker is relatively quiet.

Table 5. Analyte concentrations (µg/g) found in subsamples of a soil from an EOD area.*					
	Concentration (µg/g) with 1-min grind			Concentration (µg/g) with 5-min grind		
	Shaken 18 hrs	Sonicated 18 hrs	t-statistic	Shaken 18 hrs	Sonicated 18 hrs	t-statistic
TNT	0.594	0.793		0.750	0.801	
	0.784	0.948		0.722	0.824	
	0.708	0.790		0.719	0.806	
	0.916	0.666		0.751	0.786	
	0.833	0.631		0.737	0.780	
	0.728	0.913		0.874	0.796	
Mean	0.761	0.790	0.43	0.759	0.799	1.63
s	0.111	0.127		0.058	0.016	
RSD	14.6%	16.1%		7.64%	2.00%	
2,4-DNT	1.25	0.923		1.00	0.967	
	0.929	1.40		0.974	0.959	
	1.64	0.695		0.962	0.994	
	0.609	1.27		0.981	1.01	
	0.862	0.882		0.975	0.954	
	1.62	1.15		1.16	1.01	
Mean	1.15	1.05	0.48	1.01	0.982	0.83
s	0.423	0.265		0.074	0.025	
RSD	36.8%	25.2%		7.33%	2.55%	
2,6-DNT	0.100	0.068		0.095	0.089	
	0.108	0.118		0.093	0.092	
	0.145	0.077		0.096	0.082	
	0.060	0.089		0.091	0.094	
	0.061	0.098		0.089	0.101	
	0.116	0.096		0.101	0.097	
Mean	0.098	0.091	0.48	0.094	0.093	0.52
s	0.033	0.018		0.0042	0.0066	
RSD	33.7%	19.8%		4.26%	7.53%	

* The soil was ground for one minute and subsampled, then ground for four one-minute cycles and subsampled again. Subsamples were either shaken or sonicated in acetonitrile for 18 hours. (Subsamples are not paired).

Table 5 (cont'd).*					
	Concentration (µg/g) with 1-min grind			Concentration (µg/g) with 5-min grind		
	Shaken 18 hrs	Sonicated 18 hrs	t-statistic	Shaken 18 hrs	Sonicated 18 hrs	t-statistic
2-Am-DNT	0.145	0.172		0.200	0.216	
	0.145	0.173		0.194	0.233	
	0.146	0.142		0.192	0.215	
	0.148	0.167		0.200	0.216	
	0.137	0.158		0.198	0.245	
	0.123	0.170		0.226	0.207	
Mean	*0.141*[†]	*0.164*	*3.70*	*0.202*	*0.222*	*2.65*
s	*0.0094*	*0.012*		*0.012*	*0.014*	
RSD	*6.38%*	*7.32%*		*5.94%*	*6.31%*	
4-Am-DNT	0.145	0.181		0.228	0.199	
	0.174	0.189		0.234	0.215	
	0.158	0.171		0.220	0.196	
	0.177	0.177		0.229	0.187	
	0.139	0.161		0.220	0.226	
	0.160	0.173		0.257	0.191	
Mean	**0.159**	**0.175**	**2.26**	**0.231**	**0.202**	**3.49**
s	0.015	0.010		0.014	0.015	
RSD	9.43%	5.71%		6.06%	7.43%	

* The soil was ground for one minute and subsampled, then ground for four one-minute cycles and subsampled again. Subsamples were either shaken or sonicated in acetonitrile for 18 hours. (Subsamples are not paired.)

[†] Bold print indicates the means are significantly different by a two-tailed t-test (alpha = 0.05). The critical value for t (10 degrees of freedom [$n_1 + n_2 - 2$]) is 2.23.

Effects of grinding and storage time

A secondary objective of this study was to gather more data on the effect of machine grinding on concentration estimates of energetics. Statistical comparisons were not done because of the much higher variance of the means for unground field samples. However, in the machine-ground portions of soils from Milan, Fort Lewis, Valcartier, and Volunteer, the mean concentrations of HMX, RDX, TNT, and 2,4-DNT were in general numerically higher in the machine-ground (one minute) soils than for the unground soils. For the soil from the explosive ordnance disposal area, means for TNT, 2,4-DNT, and 2,6-DNT were numerically similar for subsamples of soil ground for one minute and for five one-minute cycles. Concentration estimates of the amino transformation products

of TNT were higher in the ground soils. Based on the above, grinding for one minute does not degrade energetics in soil.

Lastly, this study provided the unique ability to obtain concentration estimates of energetics in archived soils from which replicate analyses were done years ago. Prior to the use of machine grinding, subsampling variance was generally much higher, so only a qualitative comparison can be made (Table 1) in most cases. For the Milan, Iowa, Volunteer, and Fort Lewis soils, concentration estimates obtained in this study were either numerically higher or very similar to those obtained previously. For the EOD soil, previous concentration estimates varied considerably between subsamples; estimates obtained in the present study were within the range or higher (e.g., TNT) than the previous analyses. Based on these data, the energetics were stable under the storage conditions for these soils (air-dried and stored at room temperature in a cabinet).

6   CONCLUSIONS

Concentration estimates were obtained for energetics (HMX, RDX, TNT, and 2,4-DNT) in field-contaminated soils from army ammunition plants and training ranges using both platform shaker and sonic bath methods, and a platform shaker was found to be a suitable substitute for a sonic bath for the extraction of energetics from soil. Energetics in air-dried soils were not degraded after years of storage at room temperature, nor by machine grinding for one minute (or five one-minute grind cycles) to reduce subsampling variance.

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APPENDIX A. SUPPLEMENTAL STUDIES OF THE EFFECT OF MACHINE GRINDING ON ESTIMATES OF ENERGETIC CONCENTRATIONS IN SOIL

Part I. The effect of machine grinding for one minute on concentration estimates of RDX and TNT in performance evaluation samples.

Objective

Experiments to determine whether machine grinding for one minute affects the accuracy of concentration estimates of energetics in soil have resulted in qualitative comparisons of means as a result of the high subsampling variance for unground field-contaminated soils. The objective of this experiment was to compare the means of RDX and TNT obtained before and after grinding of a spiked soil sample, which should have low subsampling variance prior to grinding.

Methods

Soils

Performance evaluation soil samples were obtained in 2002 from the Oak Ridge National Laboratory, courtesy of Amy Dindal. These soils had been used for an evaluation of explosives detection technologies in 1999 (Dindal et al. 2001) and contained TNT and/or RDX. The soils were prepared by Environmental Resource Associates (Arvada, Colorado) for the technology demonstration. The soils had been analyzed by a reference laboratory (Specialized Assays, Inc. [SAI] of Nashville, Tennessee). We chose the two soils (labeled Mix 3 and Mix 4) with the lowest concentrations of TNT and RDX for a grinding study.

Mix 3. In 1999, the reference laboratory reported concentrations for four replicate subsamples (Dindal et al. 2001). For RDX, the mean of the four replicates was 52 µg/g and the relative standard deviation was 15%. For TNT, the mean was 8.6 µg/g and the relative standard deviation was 12%.

Mix 4. In 1999, the reference laboratory estimate for RDX in Mix 4 was 8.8 µg/g with a relative standard deviation of 4.1%. For TNT the mean was 47.9 µg/g and the relative standard deviation was 1.6%.

The grinding experiment described here took place in May 2004, so the spiked soils had been stored for at least five years. In our lab, the soils were stored at room temperature.

Subsampling, Processing, Extraction

Each soil sample was spread onto a clean, flat surface and six 10.00-g subsamples were obtained by combining at least 30 increments of soil in individual 40-mL vials. The remainder of each soil was ground for one minute on a LabTech Essa LM-2 Ring Mill equipped with a B800 bowl, then subsampled using the same method as for the unground soil. A 20.00-mL aliquot of acetonitrile was added to each vial and the vials were capped, vortexed for 60 s, and placed in a sonic bath overnight (20°C for 18 hours).

HPLC Analysis

Prior to analysis, the acetonitrile extracts were filtered through Millex-FH (Millipore, PTFE, 0.45-μm) filter units and an aliquot combined with reagent-grade water (MilliQ) at a ratio of 1:3 v:v AcN:Water. The HPLC separations were achieved on a 25-cm $\times$ 4.6-mm (5-μ) Supelcosil LC-CN column eluted with 1.2 mL/min 65:12:23 water:methanol:acetonitrile. Injection volume was 100 μL. The detector was a dual-wavelength ThermoSeparations Products Spectra System UV2000. Concentration estimates were obtained at 254 nm.

Results

RDX. Mean concentration estimates (Table A1) for RDX in Mix 3 were 39.7 and 40.4 μg/g for the unground and ground soils, respectively. For Mix 4, the mean concentrations were 7.84 and 8.40 μg/g for the unground and ground soils, respectively. The variances of each pair of means were compared using an F-test at the 95% confidence level. The critical value of $F_{5,5}$ is 5.05, which was exceeded for each pair of variances, indicating that we cannot perform a Student's t-test that assumes equal variances. For both soils, mean RDX concentrations were numerically higher and the subsampling variances were significantly smaller after the soil samples were machine-ground for one minute.

TNT. Results for TNT (Table A1) followed the same pattern as those for RDX. Mean concentration estimates for TNT in Mix 3 were 9.28 and 9.31 μg/g for the unground and ground soils, respectively. For Mix 4, the mean concentrations were 46.0 and 47.8 μg/g for the unground and ground soils, respectively. The variances were not homogeneous. For both soils, mean TNT concentrations

were numerically higher and the subsampling variances were significantly smaller after the soil samples were machine-ground for one minute.

Table A1. RDX and TNT concentration estimates in six replicate subsamples of a spiked soil taken before and after machine grinding for one minute.

	RDX (µg/g)		TNT (µg/g)	
a) Mix 3.				
	Unground	Ground (1 min)	Unground	Ground (1 min)
	40.7	40.4	9.52	9.29
	40.6	40.2	9.53	9.33
	37.4	40.1	8.82	9.18
	40.5	40.8	9.34	9.42
	40.3	40.8	9.32	9.39
	38.6	40.2	9.15	9.28
Mean	39.7	40.4	9.28	9.31
Std dev	1.36	0.293	0.26	0.085
RSD	3.4%	0.73%	2.8%	0.91%
Variance	1.86	0.0977	0.0708	0.00739
Ratio of variances	19		9.6	

	RDX (µg/g)		TNT (µg/g)	
b) Mix 4.				
	Unground	Ground (1 min)	Unground	Ground (1 min)
	8.00	8.45	48.6	48.9
	7.96	8.30	47.4	46.9
	7.94	8.47	46.2	48.2
	7.89	8.39	45.5	47.4
	7.66	8.47	45.2	47.4
	7.59	8.35	43.2	47.8
Mean	7.84	8.40	46.0	47.8
Std dev	0.17	0.070	1.87	0.71
RSD	2.2%	0.83%	4.1%	1.49%
Variance	0.0295	0.00495	3.50	0.499
Ratio of variances	5.9		7.0	

Conclusions

For each pair of means, the estimates for the ground samples were numerically greater than for the unground soil. Therefore, there is no reason to conclude that grinding for one minute reduces accuracy by degrading the analytes of interest. In each case, grinding significantly reduced the subsampling variance.

Part II. The effect of machine grinding for one minute and four continuous minutes on the precision and accuracy of concentration estimates of RDX, HMX, and TNT in sand containing particulates of energetics.

Objectives

Machine grinding of field-contaminated soil for one minute significantly reduces the subsampling variance for concentration estimates of high explosives. However, grinding of soils on a ring mill will generate heat and prolonged grinding will raise the temperature of a soil sample. The objective of this study was to assess the effect of one minute of prolonged grinding (sufficient to heat a soil sample) on the precision and accuracy of concentration estimates for a soil containing particulates of high explosives.

Methods

Crystals of SARM (Standard Analytical Reference Material) were weighed on a Sartorius Analytical (A200S) balance. The masses obtained were 3.3 mg of HMX, 3.9 mg of RDX, and 1.2 mg of TNT. The crystals were then added to 400 g of Ottawa sand that was contained in a grinding bowl. The nominal concentrations were HMX, 8.3 µg/g; RDX, 9.8 µg/g; and TNT, 3.0 µg/g.

Similarly, a particle of Composition B was weighed and added to 400 g of Ottawa sand. The mass of the particle was 1.4 mg. Assuming a 60/40 RDX/TNT ratio (U. S. Army 1984), the nominal concentrations in soil were RDX, 2.1 µg/g and TNT, 1.4 µg/g.

Each sand sample was ground for one minute, then spread on a clean surface for subsampling. Twelve replicate 10.00-g subsamples were formed as described previously (Appendix A, Part I). Each sand sample was then ground for four continuous minutes. After the four-minute grind cycle, each sample was warm. A second set of twelve 10-g subsamples was collected from each ground sample.

Concentration estimates of HMX, RDX, and TNT were obtained as described in Appendix A, Part I. Means for the one-minute and extended-grind times were

compared using a Student's t-test (subsamples are not paired). The critical t value for a two-tailed t-test with 22 degrees of freedom is 2.07.

Results

Crystals of HMX, RDX, and TNT

One minute of grinding was adequate to reduce subsampling error to less than 2% RSD for HMX, RDX, and TNT in the sand spiked with SARM crystals (Table A2). Mean concentration estimates were very close to nominal values.

Grinding continuously for four additional minutes resulted in significant analyte loss. Loss was greatest (29%) for TNT, the analyte with the highest vapor pressure, implying that sublimation was responsible for greater loss than was thermal degradation. HMX and RDX have very low vapor pressure, but are thermally labile. Losses for these two analytes due to continuous grinding were 7% and 9%, respectively.

Particle of Composition B

For the sand spiked with a particle of Composition B, one minute of grinding was adequate to reduce the subsampling error to less than 2% RSD for RDX and TNT, and the mean concentrations were close to the nominal values based on the mass of the Composition B particle (Table A2). HMX, which is present as an impurity in RDX, was also detected. The subsampling error for this analyte was around 5% RSD. The variance for HMX was less than that for RDX and TNT, but the mean concentration was also lower and resulted in a higher relative standard deviation.

Grinding continuously for four additional minutes yielded results similar to those for the crystals. Loss was greatest for TNT (30%) and was around 10% for HMX and RDX.

Table A2. Concentration estimates in 12 subsamples of Ottawa sand spiked with milligram quantities of solid explosives.*

	a) Spiked with crystals of HMX, RDX, and TNT.[†]					
	HMX (µg/g)		RDX (µg/g)		TNT (µg/g)	
	1 minute	1 minute plus 4 minutes	1 minute	1 minute plus 4 minutes	1 minute	1 minute plus 4 minutes
	8.69	7.96	10.09	9.04	3.43	2.41
	8.23	8.04	9.86	9.12	3.35	2.53
	8.44	7.95	9.82	9.16	3.38	2.52
	8.60	8.07	10.10	9.24	3.50	2.58
	8.54	7.95	10.04	8.98	3.42	2.50
	8.57	7.93	10.08	9.09	3.47	2.53
	8.50	8.00	9.96	9.12	3.45	2.42
	8.63	8.01	10.01	9.19	3.50	2.55
	8.72	7.94	10.06	9.00	3.53	2.27
	8.56	7.70	9.99	8.72	3.46	2.32
	8.61	7.95	10.03	9.04	3.39	2.37
	8.62	7.87	9.90	8.97	3.44	2.32
Mean	8.56	7.95	10.00	9.06	3.44	2.44
s	0.129	0.0944	0.0925	0.135	0.0533	0.105
RSD	1.51%	1.19%	0.93%	1.49%	1.55%	4.30%
t	13.3		19.8		29.0	

*   Each 400-g sand sample was ground for one minute, subsampled, and then ground for four continuous minutes, which was sufficient to heat the samples.

[†]   Nominal concentrations based on the mass of the crystals and soil were HMX, 8.3 µg/g; RDX, 9.8 µg/g; and TNT, 3.0 µg/g.

Table A2 (cont'd). Concentration estimates in 12 subsamples of Ottawa sand spiked with milligram quantities of solid explosives.*

	b) Spiked with a particle of Composition B.[†]					
	HMX (µg/g)		RDX (µg/g)		TNT(µg/g)	
	1 minute	1 minute plus 4 minutes	1 minute	1 minute plus 4 minutes	1 minute	1 minute plus 4 minutes
	0.22	0.18	2.05	1.77	1.35	0.98
	0.22	0.18	2.00	1.75	1.35	0.95
	0.21	0.19	2.03	1.77	1.41	0.96
	0.20	0.18	2.01	1.75	1.39	0.95
	0.22	0.19	2.06	1.77	1.39	0.95
	0.23	0.18	2.09	1.78	1.36	0.95
	0.20	0.19	2.05	1.80	1.39	1.00
	0.20	0.20	2.02	1.82	1.39	1.01
	0.21	0.19	2.00	1.82	1.37	1.00
	0.20	0.17	2.02	1.76	1.39	0.95
	0.20	0.20	2.02	1.81	1.36	0.94
	0.21	0.19	2.04	1.79	1.39	0.94
mean	0.21	0.19	2.03	1.78	1.38	0.97
s	0.010	0.0089	0.0267	0.0253	0.0195	0.0254
RSD	4.8%	4.7%	1.32%	1.42%	1.41%	2.6%
t	5.9		23.6		45	

* Each 400-g sand sample was ground for one minute, subsampled, and then ground for four continuous minutes, which was sufficient to heat the samples.

[†] Assuming a 60/40 RDX/TNT ratio, the nominal concentrations in soil were RDX, 2.1 µg/g and TNT, 1.4 µg/g.

Conclusions

Grinding soils on a ring mill for one minute does not degrade HMX, RDX, or TNT. However, the sample must not be ground continuously for times long enough for the sample to warm. Warming of the sample will result in loss of accuracy of concentration estimates, most likely as a result of sublimation of the analytes with the highest vapor pressure and thermal degradation.

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APPENDIX B. CONCENTRATIONS OF 2,6-DNT, 2-Am-DNT, AND 4-Am-DNT IN THE VOLUNTEER SOIL

Table B1. Concentrations found for 2,6-DNT, 2-Am-DNT, and 4-Am-DNT in sequentially extracted subsamples (subsamples are paired) of the Volunteer soil.*						
	2,6-DNT (µg/g)		2-Am-DNT (µg/g)		4-Am-DNT (µg/g)	
	Shaken 18 hrs	Shaken 18 hrs then sonicated 18 hrs	Shaken 18 hrs	Shaken 18 hrs then sonicated 18 hrs	Shaken 18 hrs	Shaken 18 hrs then sonicated 18 hrs
Not ground						
	2.40	2.44	1.73	1.94	2.08	2.39
	1.87	1.95	1.73	1.91	2.07	2.35
	2.05	2.14	1.79	1.94	2.12	2.34
	1.86	1.97	1.64	1.79	2.05	2.15
	1.93	1.98	1.71	1.88	2.07	2.32
	1.94	2.04	1.76	1.91	2.13	2.33
	1.94	2.03	1.76	1.98	2.14	2.44
Mean	2.00	2.08	1.73	1.91	2.09	2.33
s	0.19	0.17	0.05	0.06	0.035	0.090
RSD	9.5%	8.2%	2.9%	3.1%	1.7%	3.9%
Ground						
	2.43	2.57	2.36	2.50	2.84	3.01
	2.51	2.61	2.36	2.54	2.83	3.05
	2.26	2.44	2.12	2.36	2.53	2.85
	2.39	2.54	2.26	2.43	2.70	2.94
	2.34	2.57	2.24	2.35	2.68	2.76
	2.29	2.33	2.14	2.28	2.51	2.76
	2.36	2.48	2.13	2.26	2.50	2.67
Mean	2.37	2.51	2.23	2.39	2.66	2.86
s	0.08	0.10	0.10	0.11	0.15	0.14
RSD	3.4%	4.0%	4.5%	4.6%	5.6%	4.9%
* Means for all of the analytes were greater following extraction for an additional 18 hours.						

Table B2. Concentrations estimates found for 2,6-DNT, 2-Am-DNT, and 4-Am-DNT in sequentially extracted ground soil subsamples (subsamples are paired) of the Volunteer soil.*

	2,6-DNT (µg/g)		2-Am-DNT (µg/g)		4-Am-DNT (µg/g)	
	Shaken 18 hrs	**Shaken 36 hrs**	**Shaken 18 hrs**	**Shaken 36 hrs**	**Shaken 18 hrs**	**Shaken 36 hrs**
	2.35	2.77	2.04	2.40	2.38	2.83
	2.41	2.79	2.08	2.37	2.47	2.92
	2.34	2.78	2.01	2.39	2.40	2.84
	2.36	2.68	2.02	2.27	2.38	2.66
	2.37	2.69	2.01	2.26	2.36	2.65
Mean	2.37	2.74	2.03	2.34	2.40	2.78
s	0.0270	0.0526	0.0295	0.0676	0.0427	0.1194
RSD	1.14%	1.92%	1.45%	2.89%	1.78%	4.29%
	Sonicated 18 hrs	**Sonicated 36 hrs**	**Sonicated 18 hrs**	**Sonicated 36 hrs**	**Sonicated 18 hrs**	**Sonicated 36 hrs**
	2.13	2.31	1.82	2.02	2.10	2.37
	2.13	2.34	1.78	2.04	2.08	2.37
	2.17	2.35	1.77	2.04	2.10	2.40
	2.15	2.26	1.80	2.01	2.10	2.36
	2.12	2.34	1.76	2.11	2.03	2.55
	2.14	2.32	1.78	2.10	2.06	2.54
Mean	2.14	2.32	1.79	2.05	2.08	2.43
s	0.0179	0.0329	0.0217	0.0418	0.0286	0.0889
RSD	0.84%	1.42%	1.21%	2.04%	1.38%	3.66%

* Means for all of the analytes were greater following extraction for an additional 18 hours.

Table B3. Summary table of means and t statistics for sequentially extracted soil sub-samples of the Volunteer soil.

Analyte	Processing	n	Extraction sequence	Concentration (µg/g) 18 hrs	36 hrs	t
2,6-DNT	not ground	7	shake/sonic	2.00	2.08	**8.20***
	ground	7	shake/sonic	2.37	2.51	**6.03**
	ground	5	shake/shake	2.37	2.74	**15.1**
	ground	6	sonic/sonic	2.14	2.32	**11.5**
2-Am-DNT	not ground	7	shake/sonic	1.73	1.91	**15.8**
	ground	7	shake/sonic	2.23	2.39	**9.76**
	ground	5	shake/shake	2.03	2.34	**11.2**
	ground	6	sonic/sonic	1.79	2.05	**11.1**
4-Am-DNT	not ground	7	shake/sonic	2.09	2.33	**8.63**
	ground	7	shake/sonic	2.66	2.86	**7.20**
	ground	5	shake/shake	2.40	2.78	**9.63**
	ground	6	sonic/sonic	2.08	2.43	**7.51**

* Bold print indicates that the t-statistic exceeds the critical value for a one-tailed paired t-test (alpha = 0.05). Critical values are 2.13, 2.02, and 1.94 for 4, 5, and 6 degrees of freedom ($n - 1$), respectively.

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14. ABSTRACT

Field-contaminated soils from army ammunition plants, training ranges, and an explosive ordnance disposal area were used to determine the effect of machine grinding and extraction procedure on concentration estimates of energetics. Machine grinding for one minute did not degrade the major analytes of interest (HMX, RDX, TNT, or 2,4-DNT), but did significantly reduce the subsampling error. The platform shaker extraction procedure was found to be at least as efficient as the sonic bath method specified in SW-846 Method 8330 and is therefore a suitable substitute.

Additional studies showed that extended grinding of the soil sample causes the sample to warm as a result of friction and results in analyte loss. However, grinding for five one-minute cycles, with a sufficiently long rest period between cycles to prevent soil warming, did not result in analyte loss. Repeated grind cycles were needed to reduce the subsampling error for soils contaminated with propellant residue.

15. SUBJECT TERMS

Explosives	TNT
RDX	2,4-DNT

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