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Cold Regions Research
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Field-Portable X-Ray Fluorescence (FP-XRF) Determinations of Metals in Post-Blast Ordnance Residues

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Prepared for U.S. ARMY ENVIRONMENTAL CENTER

ABSTRACT

Field-portable X-ray fluorescence (FP-XRF) analyzers, such as the Niton 700, provide rapid, on-site analyses for a variety of elements. FP-XRF was used to determine metals in post-blast ordnance residue that was deposited on snow, which provided large collection surfaces that were free of soil particles. The ordnance items included M67 hand grenades, 40-mm grenades, 60-mm and 81-mm mortar projectiles, 105-mm howitzer projectiles, claymore mines, and C4 demo blocks with M6 blasting caps. For most of these items, the post-blast residue contained lead, iron, copper, and zinc. FP-XRF also was used to determine these elements in soils from training ranges where these ordnance items were used. When present above the FP-XRF limits of detection, the FP-XRF determinations of lead, zinc, and copper were not found to be significantly different from determinations by laboratory analyses.

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PREFACE

This report was prepared by Marianne E. Walsh, Chemical Engineer, U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire. Several people were involved in the ordnance residue and soil sample collection and preparation, including Alan D. Hewitt, Jeffrey A. Stark, Thomas F. Jenkins, Thomas A. Ranney, Charles M. Collins, Dennis J. Lambert, Nancy M. Perron, Ronald N. Bailey, Susan Taylor, Michael R. Walsh, Arthur B. Gelvin, Thomas A. Douglas, and Sherri Butters. Alan D. Hewitt and Thomas F. Jenkins provided technical reviews.

The Aberdeen Test Center emissions project samples were provided by Paul C. Klara.

Confirmation of FP-XRF determinations was provided by laboratory analyses at ERDC's Environmental Lab (EL, Vicksburg, Mississippi), CRREL, and Environmental Science and Engineering, Inc. (ESE, Gainesville, Florida). Karen E. Myers at the Environmental Lab provided the analyses for the Fort Greely samples and Alan Hewitt at CRREL analyzed the Ravenna AAP samples.

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MARIANNE E. WALSH

1 INTRODUCTION

Field-portable X-ray fluorescence (FP-XRF) analyzers have gained acceptance for on-site metal determinations in soil (U.S. EPA 1998). The majority of the published reports about FP-XRF describe investigations for lead contamination from leaded paint and gasoline (Argyraki et al. 1997, Armstrong 2002, Reames and Lance 2002, U.S. EPA 2002). Other metals that have been determined include copper and zinc from a smelter (Clark et al. 1999), mercury (Hewitt 1997), and arsenic from a cattle tick control operation (Ridings et al. 2000). High resolution instruments can provide simultaneous detection of several elements (Hewitt 1995). FP-XRF analyzers such as the NITON XL-722S Multi-Element Analyzer (Billerica, Massachusetts), the instrument we used for this study, offer the advantages of fast, nondestructive analyses. The many studies concerning lead show good agreement between determinations by FP-XRF and those by laboratory Atomic Absorption (AA) or Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

Elements for which a typical dual-source NITON 700 series analyzer is calibrated are listed in Table 1. Other elements that NITON claims have low detection limits are niobium, yttrium, gold, tungsten, and uranium. The instrument may be custom-calibrated for these elements. Cross-element interferences may occur as a result of overlap of the energy spectrum of two or more elements. NITON specifically warns that if samples contain copper and zinc, determination of the lower concentration element will be less accurate.

To perform analysis in the field, the analyzer is turned on and a self-calibration routine is run. Then the operator places the analyzer window firmly against a sample. Within 60 seconds, the analyzer screen will display the concentration, expressed as parts per million (ppm) and the precision (95% confidence interval) of elements detected. The default range of calibration is 0 to 10,000 ppm; custom calibration for matrices with concentrations higher than 10,000 ppm may be requested from NITON. The analyzer will also display the energy spectrum of the elements in the sample. The energy levels of the X-rays are plotted on the x-axis in 1,024 channels from 2 to 90 keV, and the number of X-rays is plotted on the y-axis. The number of X-rays is used to automatically calculate concentrations. The calibration of the analyzer, which is based on the Compton Normalization Method (Hewitt 1994), is verified in the field by analyzing various standard reference materials (SRM) such as National Institute of Standards and Technology (NIST) SRM 2709 (San Joaquin Soil), 2710 (Montana I Soil), and 2711 (Montana II Soil).

Because of the small size of the analyzer window (1 cm × 2 cm), the results displayed are representative of only a small area of the soil surface. Depending on the study objectives, accuracy required, and the site characteristics, the soil sample may be presented to the XRF analyzer window in one of three ways. The first two methods involve minimal sample processing and therefore provide rapid screening results. The first method is to simply place the XRF analyzer on the soil surface (in situ). The second method is to collect a discrete or multi-increment soil sample in a plastic bag and then place the analyzer against the outer surface of the bagged sample. These two methods can be used to profile an area to locate the sources of contamination and general boundaries of the contamination. However, high moisture content, large particle size, and excessive thickness of the plastic collection bag can lead to underestimates of concentrations. The third method involves processing soils samples to various degrees by drying, sieving, and/or grinding and then placing a subsample in a cup with Mylar film specifically designed for XRF analyses. This method takes time, but improves accuracy.

The purpose of this investigation was to evaluate the utility of FP-XRF to detect metals associated with post-blast ordnance residue (Table 2). We first analyzed residue from detonations of ordnance items where the residue could be collected without soil. The detonations took place in a blast chamber at Aberdeen Test Center and in the open on snow-covered ranges (Hewitt et al. 2003). Then we analyzed soils from various types of training ranges to see if the metals detected in the post-blast residues were also detected above background concentrations in soil.

Metals such as lead and mercury are found in primers, and metals such as zinc, lead, and copper are found in shell casings and various projectile components. All of these metals are natural components of soil. However, unlike organic explosives such as TNT and RDX, metals are not consumed in detonations, and multiple detonations of ordnance items on a training range may elevate the metals concentrations to sufficient levels to adversely affect human health and the environment (Table 1). FP-XRF could be a useful tool during field surveys to characterize elevated metal concentrations on training ranges. For purposes of this study, we define elevated concentrations as at least 1.5 times the geometric mean reported by the USGS for the conterminous United States and Alaska (Table 1). Judgments as to whether the concentrations are hazardous are beyond the scope of this study; soil screening levels developed by the EPA are presented in Table 1 for comparison purposes only.

Table 1. Elements for which the NITON 700-series High Resolution Instrument is factory calibrated and which are normally displayed in the screen. Also listed are the FP-XRF limits of detection, mean elemental content of soil in the conterminous United States and Alaska, and soil screening levels established by the EPA.

			Geometric mean elemental content of soil (ppm)[b]		Arithmetic mean elemental content of soil (ppm)[b]		Soil screening levels (ppm)[c]	
	Atomic number	FP-XRF limit of detection (ppm)[a]	Conterminous U.S.	Alaska	Conterminous U.S.	Alaska	Ingestion	Migration to groundwater[e]
^{109}Cadmium source								
Chromium (Cr)	24	420	37	50	54	64	390 (VI)	38 (VI)
Manganese (Mn)	25	700	330	510	550	670		
Iron (Fe)	26	560	18,000	35,000	26,000	38,000		
Cobalt (Co)	27	380	6.7	13	9.1	14		
Nickel (Ni)	28	210	13	24	19	33	1600	130
Copper (Cu)	29	100	17	24	25	29	3,100[d]	11,000[d]
Zinc (Zn)	30	70	48	70	60	79	23,000	12,000
Arsenic (As)	33	25	5.2	6.7	7.2	9.6	0.4	29
Selenium (Se)	34	25			0.39		390	5
Lead (Pb)	82	30	16	12	19	14	400	
Mercury (Hg)	80	40			0.09			
Rubidium (Rb)	37	15			67			
Strontium (Sr)	38	12	120	159	240	198		
Zirconium (Zr)	40	12			230			
Molybdenum (Mo)	42	15	0.59	0.86	0.97	1.3		
^{241}Americium source								
Cadmium (Cd)	48	50			0.35		78	8
Silver (Ag)	47	190			0.05		390	34
Barium (Ba)	56	45	440	595	580	678	5,500	1,600
Tin (Sn)	50	150	0.89	2.6	1.3	3.1		
Antimony (Sb)	51	75			0.66		31	5

[a] NITON Corporation (1999). Based on typical soils matrices represented by NIST standard reference materials and a 60-second testing time.

[b] Gough et al. (1988).

[c] USEPA (1996). Chromium soil screening levels are for oxidation state +6.

[d] EPA Region 3 risk-based concentration (http://www.epa.gov/reg3hwmd/risk/index.htm)

[e] Dilution Attenuation Factor of 20.

Table 2. Some metals found in ordnance items (U.S. Army 1977, 1981).

Metal	Source
Chromium (Cr)	Zinc chromate, cadmium chromate, chromium oxide (flash composition)
Manganese (Mn)	Projectile casings
Iron (Fe)	Projectile casings and steel components
Nickel (Ni)	Ni plating, stainless steel components, armor-piercing projectiles
Copper (Cu)	Projectile casings and bodies, liner for shaped charge in anti-armor projectiles, rotating bands, fuze components, wires
Zinc (Zn)	Zinc chromate, zinc (primer #41), projectile bodies, smoke compositions (hexachloroethane-zinc)
Barium (Ba)	Barium nitrate (primer composition), barium chromate (delay composition)
Tungsten (W)	Anti-armor cartridges, 40-mm projectile (Sgt York)
Mercury (Hg)	Mercury fulminate
Lead (Pb)	Lead styphnate, lead azide, lead thiocyanate, slugs (Pb-Sb alloy), weights in dummy projectiles, foil liner of propellant bags
Uranium (U)	Armor-piercing projectiles (depleted uranium)
Zirconium (Zr)	Flash compositions, igniter compositions
Antimony (Sb)	Antimony sulfide (primer composition), slugs (Pb-Sb alloy)
Molybdenum (Mo)	Flash compositions

2 METHODS

Post-Blast Ordnance Residue

We analyzed post-blast ordnance residues from two sources. The first set was from the Aberdeen Test Center where various types of ordnance were detonated within a chamber designed to capture the emissions for air quality studies. The ordnance items were TNT (1/4 lb) demo block, dynamite M1, M112 C4 demo block (1.25 lb), M67 hand grenade (Comp B), M72A3 rocket warhead (octol 70/30), TNT (1 lb) demo block, MK3A2 hand grenade (1/2 lb TNT), and M25 flash compound target hit simulator. The residues from these items were swept from the chamber by personnel performing the emission tests and sent to us for analysis.

The second set of post-blast residues was from detonations on snow-covered ranges (Hewitt et al. 2003). The detonations were carried out as part of Project CP1155 (Distribution and Fate of Energetics on DoD Test and Training Ranges) of the Strategic Environmental Research and Development Program. The ordnance items were M67 hand grenades, 40-mm grenades, 60-mm mortars, 81-mm mortars, 105-mm howitzers, claymore mines, and C4 demo block with M6 blasting cap. The C4 blocks were placed on top of snow over a steel plate; the steel plate was used to minimize the dispersal of the underlying soil. The ordnance detonations took place in conjunction with training exercises or by special arrangement at Camp Ethan Allen (Vermont Air National Guard), Fort Drum (10th Mountain Division, New York), and Fort Richardson (U.S. Army, Alaska). Details of the sample collection procedure are described in Hewitt et al. (2003). Briefly, the post-blast ordnance residues were visible on the snow surface as a plume of black soot (Fig. 1). Samples of the residues were collected by shoveling the top layer of snow into plastic bags. The snow was melted and then the particulate residue fraction was obtained by filtration through glass fiber filters. The filtrate and the solid residue were analyzed for explosives. Following extraction for explosives, all of the particulate residue corresponding to a particular detonation was scraped from the filters into an XRF cup. The cup was placed in the NITON soil test platform for the FP-XRF analysis (Fig. 2).

To determine which metals are associated with the above ordnance items, we used the Toxic Release Inventory (TRI) reports in the MIDAS database (restricted) (Table 3).

Figure 1. Post-blast residue plume from a 105-mm howitzer projectile. Samples of the solid residue were collected by shoveling darkened snow into bags, melting the snow, then filtering the meltwater. (Photo courtesy of Michael R. Walsh.)

Soils from Training Ranges

We analyzed soils from the following locations: Fort Lewis (Washington) Hand Grenade Range, Fort Leonard Wood (Missouri) Hand Grenade Range, Fort Wainwright (Alaska) Hand Grenade Range, Fort Greely (Alaska) Washington Range Impact Area and Firing Points, Fort Richardson (Alaska) Explosive Ordnance Disposal Pad, Fort Ord (California) Anti-Tank Range, Yakima (Washington) Anti-Tank Range, and Ravenna (Ohio) Army Ammunition Plant. These soils were collected during various studies to characterize explosives residues in soils (Jenkins et al. 1998, 2001; Walsh et al. 2001; Pennington et al. 2002).

With the exception of soils from Fort Greely, the soils were air-dried and passed through a #10 mesh. Fort Greely soils were analyzed in the field after air-drying only. All samples were analyzed using NITON XRF cups and soil test platform.

Laboratory confirmation analyses by AA or ICP were available for some of the soils. These analyses were provided by the Engineer Research and Development Center (ERDC) Environmental Lab (EL, Vicksburg, Mississippi), CRREL, and Environmental Science and Engineering, Inc. (ESE, Gainesville, Florida).

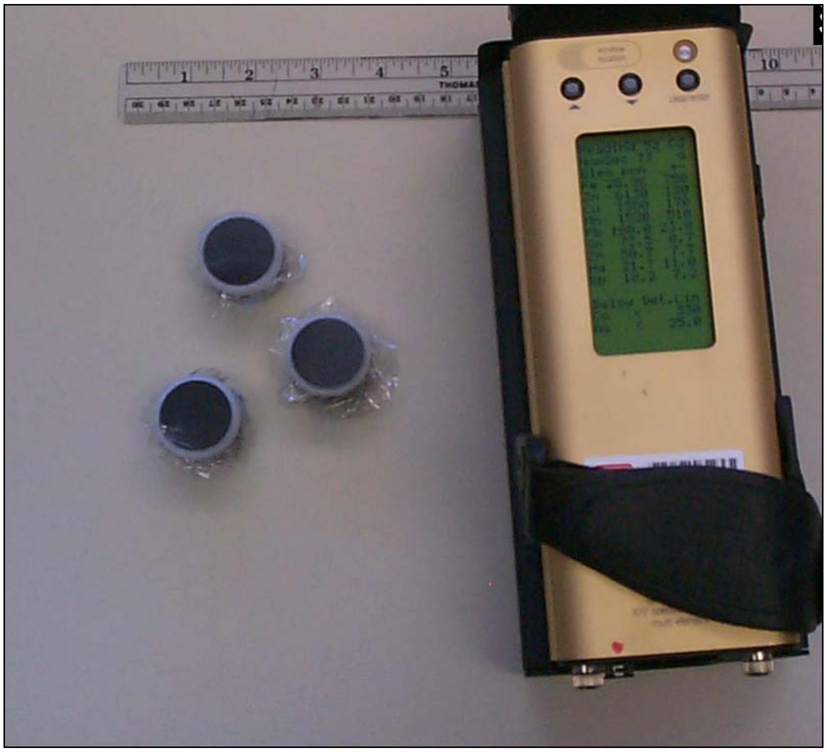


Figure 2. FP-XRF analyzer used in this study. On the left are samples of post-blast residue contained within XRF sample cups.

Table 3. Mass (g) of metals[a] in each ordnance item (DODIC number) according to the Toxic Release Inventory Report.

	Pb	Zn	Ni	Cu	Cd	Cr	Ag	Mn
M67 hand grenade (G881)	0.5[b]	45	0.2	0.3		0.1		
MK3A2 hand grenade (G911)	0.4	66	0.2	0.3	0.4	0.2		0.3
60-mm mortar (B642)	0.6	4.4	19	8	0.1	24		
81-mm mortar (C868)	0.6	40	20	17	0.1	27		
105-mm howitzer (C445)	30	150	1.6	300	0.15	6		330
40-mm grenade (B568)	0.15	20	0.1	6.4	0.1	1.5		2
Claymore mine (K143)	0.6	8.9	4.3	106	0.3	17.5		0.8
155-mm howitzer	0.3	64		550		2.7		260
C4 (M023) with M6 blasting cap (M130)	0.9							
66-mm anti-tank rocket (H557)	4.5	30	2.3	110	2.6	1.5	0.99	3.6

[a] Iron not reported. Aluminum is reported but not detectable by FP-XRF.

[b] Majority from lead azide and lead styphnate.

3 RESULTS

Post-Blast Ordnance Residue

Aberdeen Test Center Blast Chamber

The spectra from all of the samples from the Aberdeen Test Center emissions tests had large peaks at 6.4 and 7.1 keV that correspond to the X-ray emission energies from iron (Table 4, Fig. 3). There was so much iron in the sample that the NITON analyzer reported an iron concentration of greater than 2 million parts per million. The iron was likely from the wall of the blast chamber because it was the major component of not only the ordnance that contained significant masses of metal, but also the TNT demo blocks, dynamite, and C4 demo blocks. The NITON analyzer automatically corrects for cross-element interferences, and detected high concentrations of copper, zinc, and lead in the residue from the rocket warhead (Fig. 3) and zinc in the two types of hand grenades. However, the contributions of so much iron from the walls of the blast chamber made all of these samples suspect and therefore not representative of what would be deposited on a soil surface.

Table 4. X-ray emission energies (keV) of metals that could be present in ordnance residue.

	Kα	**Kβ**	**Lα**	**Lβ**	**Lγ**
Chromium (Cr)	5.4	5.9			
Manganese (Mn)	5.9	6.5			
Iron (Fe)	6.4	7.1			
Nickel (Ni)	7.5	8.3			
Copper (Cu)	8.0	8.9			
Zinc (Zn)	8.6	9.6			
Zirconium (Zr)	15.7	17.7			
Molybdenum (Mo)	17.4	19.6			
Barium (Ba)	32.1	36.6	4.5	4.8	5.5
Tungsten (W)	58.9	67.6	8.4	9.7	11.3
Mercury (Hg)	70.2	80.7	10.0	11.8	13.8
Lead (Pb)	74.2	85.4	10.5	12.6	14.8
Uranium (U)			13.6	17.2	20.2

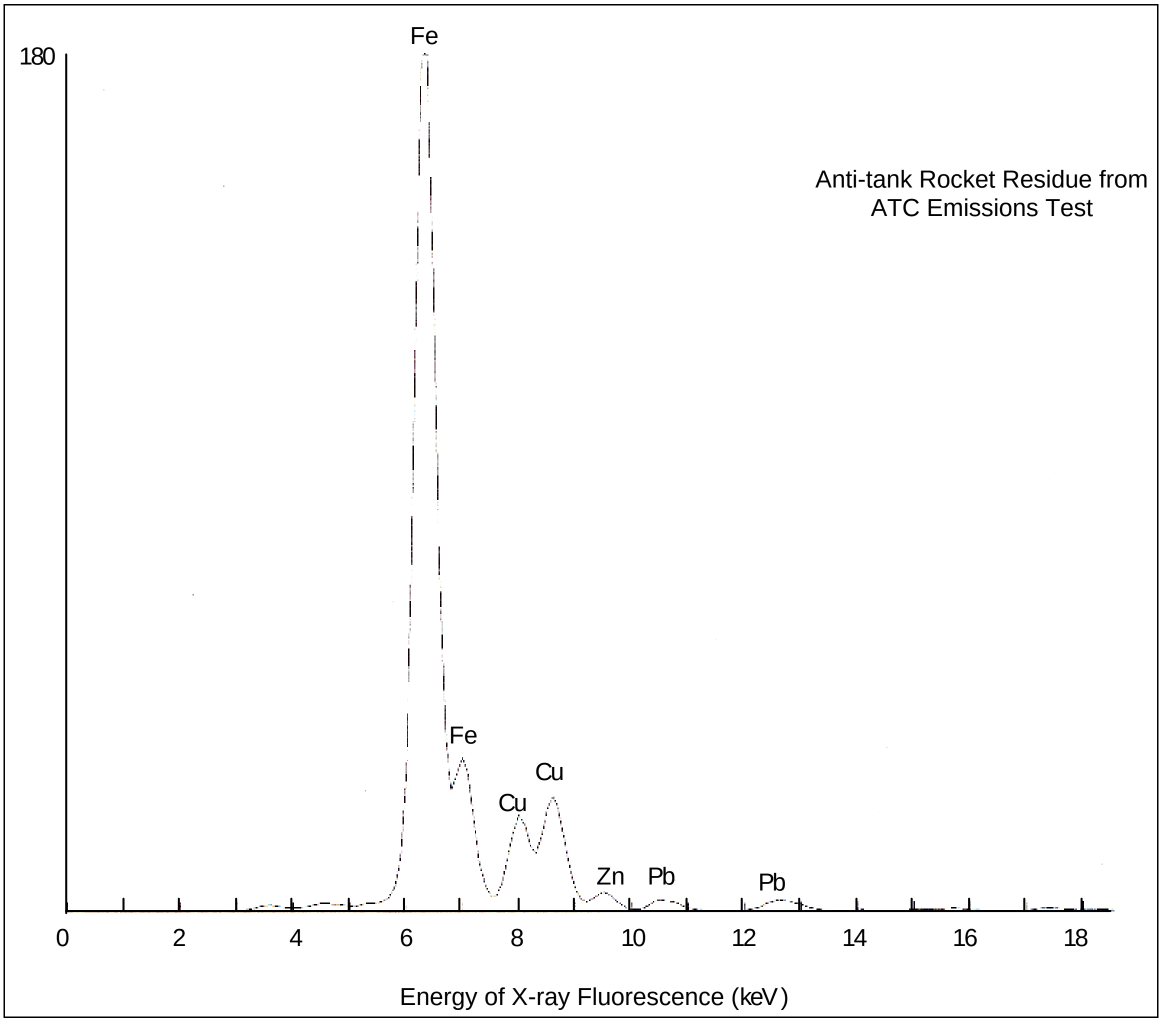
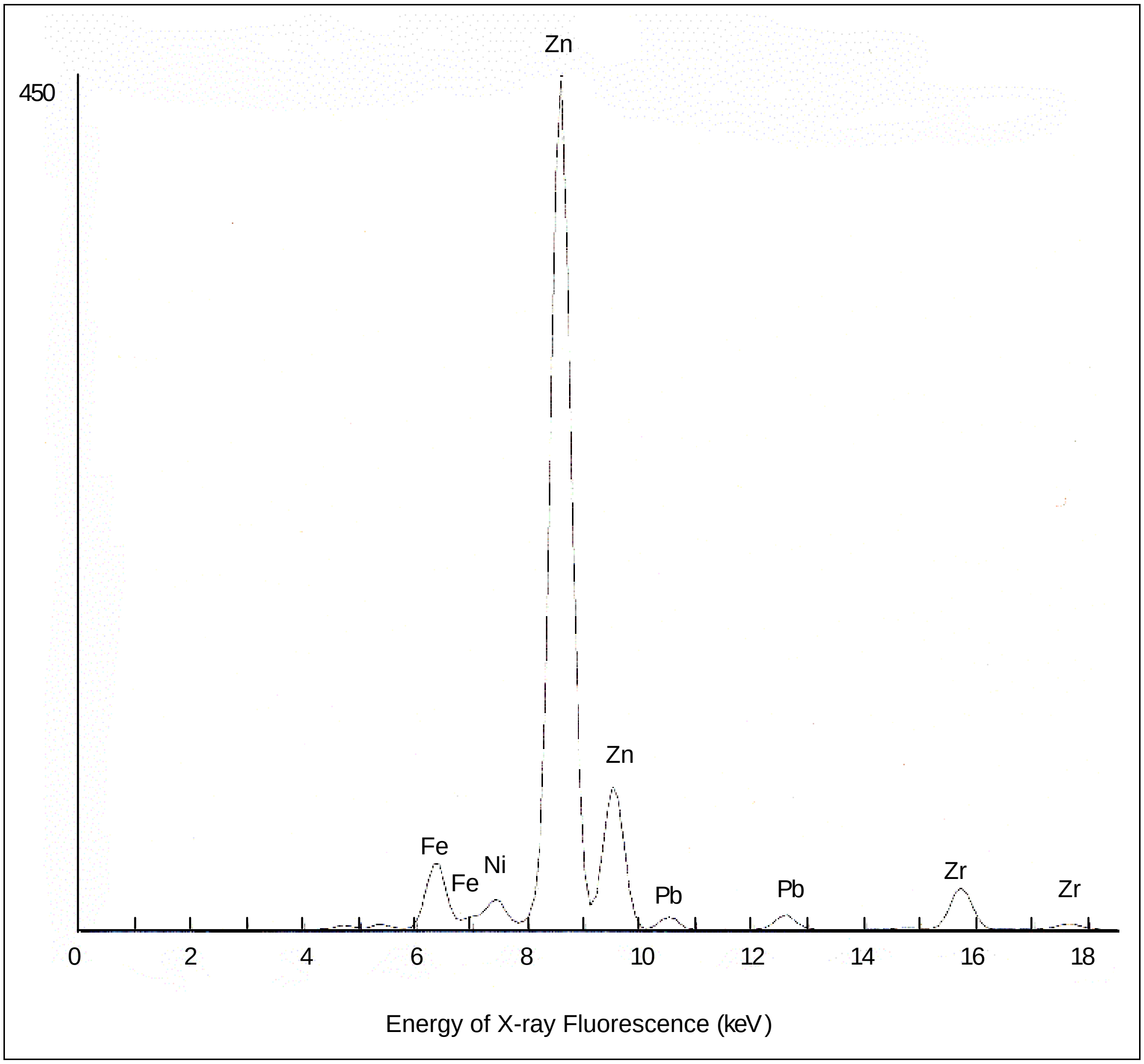


Figure 3. FP-XRF spectra of samples of post-blast ordnance residue from the Aberdeen Test Center Blast Chamber.

Snow-Covered Ranges and Training Range Soils

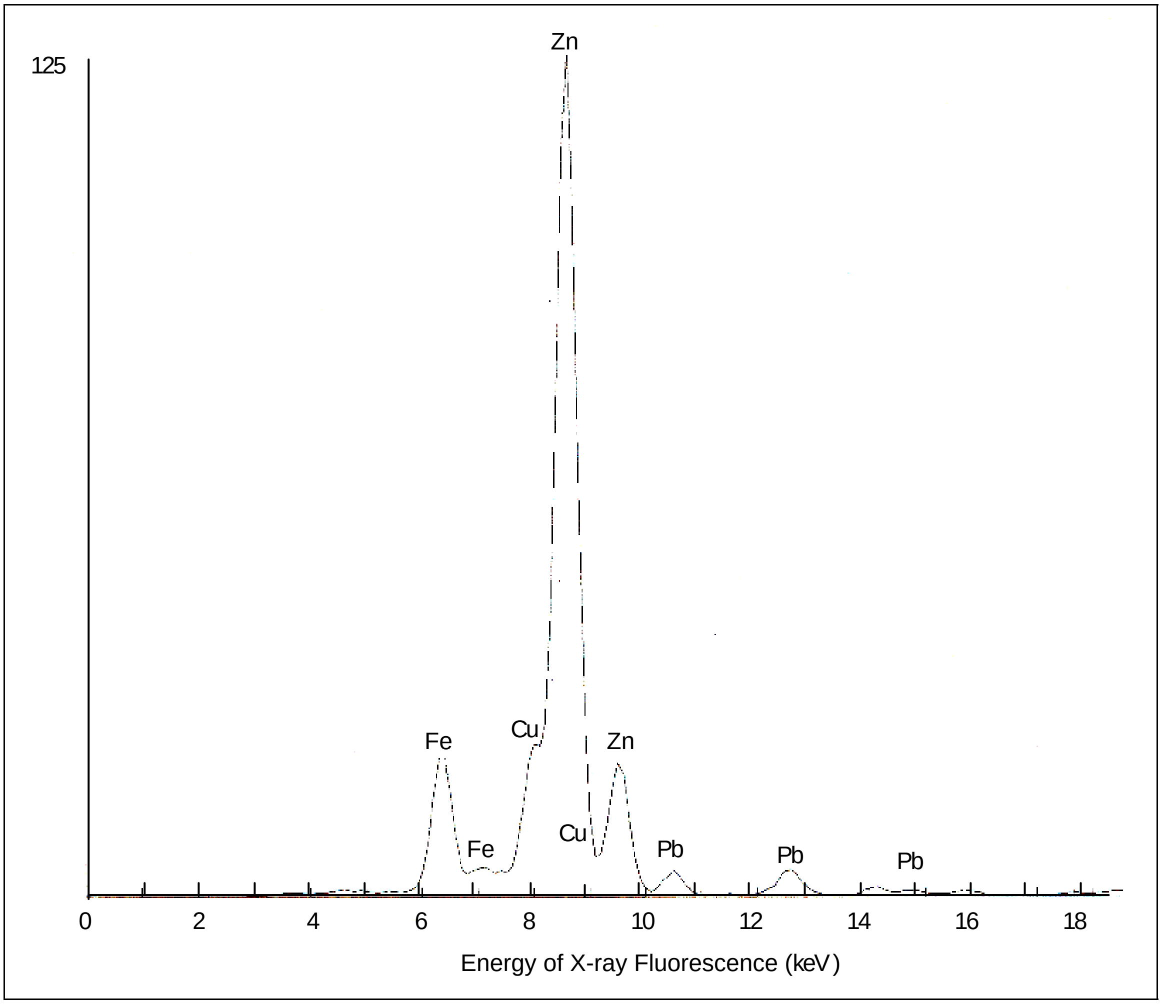
The detonations on snow provided residue that was not contaminated with extraneous particulate matter and was therefore more like the residue that would be deposited on soil during normal training exercises. The results from the snow-covered range detonation residues are presented below with data from corresponding training ranges, where available.

M67 Hand Grenades. The spectra for the M67 hand grenade were dominated by a peak for zinc (Fig. 4a); the body of the hand grenade is a zinc alloy. The hand grenade also contains various components made of steel and the spectrum of the residue shows peaks corresponding to iron. Nickel was also detected by the analyzer, but at concentrations much greater than what would be expected based on the TRI report (Tables 3 and 5a). Peaks for lead were evident in each of the spectra. The source of the lead is mostly from the primers lead azide and lead styphnate.



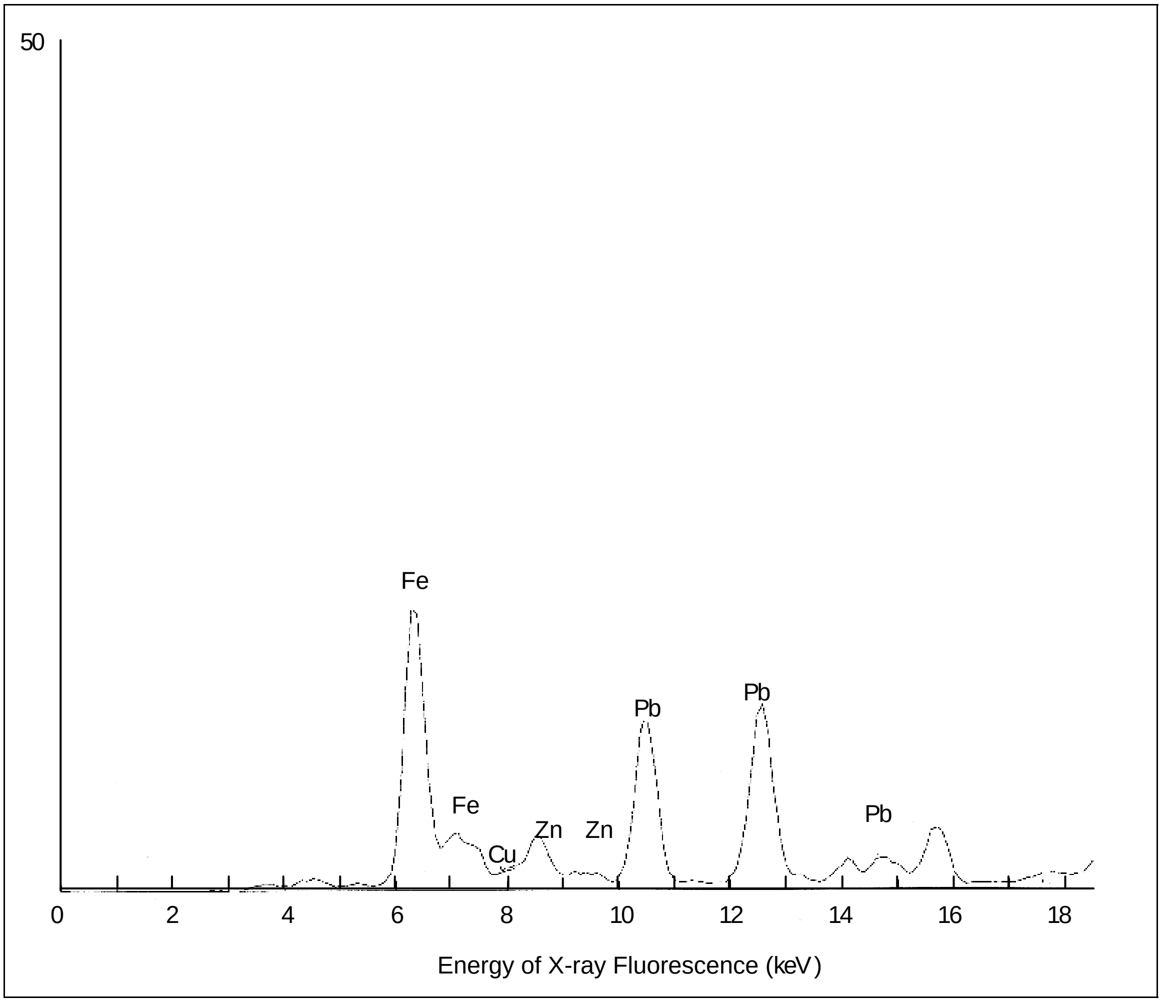
a. Hand grenade residue.

Figure 4. FP-XRF spectra of samples of post-blast ordnance residue collected from snow-covered ranges.



b. 105-mm howitzer projectile residue.

Figure 4 (cont'd). FP-XRF spectra of samples of post-blast ordnance residue collected from snow-covered ranges.



c. 105-mm howitzer firing point residue.

Figure 4 (cont'd).

Soils from hand grenade ranges from three different installations were analyzed. On all three ranges, zinc (1,100 to 3,400 ppm) and lead (35 to 70 ppm) were above mean elemental concentrations for soil (Tables 1 and 6a). Laboratory analyses (ICP) were available for three Fort Wainwright hand grenade range samples collected from the same general location as those analyzed by FP-XRF. Lead by FP-XRF was 35 ppm; the three lab results were 32, 39, and 40 ppm. Similarly for zinc, the FP-XRF estimated 1,100 ppm and laboratory analyses estimated 1,160, 1,260, and 1,540 ppm. Nickel was not detected by FP-XRF nor ICP for the Fort Wainwright soils. However, FP-XRF did detect nickel in the soils from Fort Lewis and Fort Leonard Wood. Corresponding laboratory analyses were not available for these soils.

60-mm and 81-mm Mortar Projectiles. Metals detected by FP-XRF in post-blast residues from 60-mm and 81-mm mortar projectiles were iron, copper, zinc, and lead (Table 5b and c). Nickel was also detected in the residue from the 60-mm mortars.

Soils from an 81-mm and 60-mm mortars impact site (Table 6b) at Fort Greely were analyzed by FP-XRF in a field laboratory with minimal sample processing. The only metals corresponding to those found in the post-blast residues were zinc and iron, neither of which was elevated above background concentrations. Confirmation by AA on two samples (Table 6a) showed generally good agreement between the field and laboratory analyses even though zinc concentrations were around the FP-XRF detection limit of 70 ppm.

40-mm Grenades. Metals detected by FP-XRF in 40-mm grenade post-blast residue were iron, zinc, copper, and lead (Table 5d). For these rounds to detonate, they needed to impact a hard surface and were fired at metal targets (a car and a metal chimney). Therefore some of the metal, especially the iron, may be from the targets.

In soil from a gravel berm that served as a target for 1,800 40-mm grenades at Fort Greely (Walsh et al. 2001), we detected the same suite of metals as those found in the post-blast residue (Table 6b). The FP-XRF analyses were done in a field laboratory with air-dried soils. Copper was the only metal that was clearly above background concentrations in all of the samples. The maximum copper concentration detected by FP-XRF was 1,100 ppm, which was confirmed by AA. The ogive of the grenade is an aluminum alloy that is 4% copper. The highest copper concentration (1,100 ppm) corresponded to the highest RDX concentration (1.7 ppm) detected in the berm samples (Walsh et al. 2001). Zinc and lead were confirmed in a few samples (Table 6b); the lead concentration was elevated above background in one sample.

105-mm Howitzer Projectiles. Metals detected by FP-XRF in 105-mm howitzer post-blast residue were iron, zinc, copper, and lead (Table 5e, Fig. 4b). We also had one sample of residue from the 105-mm howitzer firing point (Fig. 5). This sample, which was the combined particulate residue from five guns, had a significant amount of lead (Table 5e, Fig. 4c), probably from the lead foil that is present in one of the propellant bags that is in each cartridge case for this projectile.

Table 5. Metals detected by FP-XRF in post-blast residue collected from snow-covered ranges. Numbers reported are concentrations in parts-per-million (ppm) as reported by the NITON 722S analyzer.

a. M67 hand grenades.

Replicate	Pb	Zn	Ni	Fe	Zr
1	6,700	520,000	36,000	150,000	3,500
2	6,000	330,000	17,000	150,000	2,000
3	6,000	410,000	25,000	150,000	2,800
4	6,500	280,000	15,000	120,000	1,600
5	6,100	350,000	37,000	130,000	2,600
6	6,300	470,000	30,000	150,000	3,100
7	6,900	360,000	24,000	150,000	4,800

b. 60-mm mortar projectiles.

Replicate	Pb	Cu	Ni	Fe
1	900	11,000	2,800	20,000
2	1,700	4,100	3,600	56,000
3	2,500	10,000	7,100	56,000
4	700	5,700	2,500	16,000
5	1,900	7,500	4,700	64,000
6	400	4,300	3,000	28,000

c. 81-mm mortar projectiles.

Replicate	Pb	Cu	Zn	Fe
1	310	1,000	900	73,000
2	960	2,300	1,500	78,000
3	410	1,500	1,300	89,000

d. 40-mm grenades.

Replicate	Pb	Zn	Cu	Fe
1	3,000	81,000	12,000	800,000
2	2,100	420,000	48,000	59,000
3	2,300	380,000	68,000	48,000

e. 105-mm howitzer projectiles.

Sample	Pb	Cu	Zn	Fe
Crater	930	9,600	34,000	38,000
Plume 1	210	910	3,900	30,000
Plume 2	170	1,500	6,500	26,000
Plume 3	1,000	12,000	46,000	30,000
Plume 4	380	3,500	12,000	28,000
Plume 5	600	8,000	27,000	35,000
Firing point	26,000	7,800	2,300	45,000

Table 5 (cont'd). Metals detected by FP-XRF in post-blast residue collected from snow-covered ranges. Numbers reported are concentrations in parts-per-million (ppm) as reported by the NITON 722S analyzer.

f. Claymore mines.

Replicate	Pb	Cu	Zn	Sr	Fe
1	380	3,700	2,000	155	180,000
2	280	<d	840	150	140,000
3	540	9,100	3,100	130	50,000

g. C4 block with M6 blasting cap.

Replicate	Pb	Zn	Cu	Fe
1	4,000	810	760	6,700
2	1,900	720	<d	15,000
3	1,700	530	<d	14,000

We did not have soil from an impact area that was specifically used for 105-mm howitzer projectiles that we could use for comparison of FP-XRF and laboratory analyses. However, we did have laboratory analytical results for soils from several training ranges that were impacted by large caliber projectiles. For the most part, concentrations of zinc, copper, and lead were below the FP-XRF detection limit.

We did have several soil samples from 105-mm firing points at Fort Greely. We analyzed 42 soils by FP-XRF to see if lead concentrations were elevated. In all samples, lead was either undetectable or near the FP-XRF detection limit for lead (30 ppm) (Table 6c).

Claymore Mines. The three samples of claymore mine post-blast residue had detectable concentrations of iron, zinc, and lead; two of the samples had detectable copper concentrations (Table 5f). The TRI reports that 106 g copper are present in each claymore mine, most of it as copper wire used for firing the mine.

We analyzed 16 Yakima Training Center soil samples that were collected where a Claymore mine had been recently detonated (Pennington et al. 2002). Lead, copper, and zinc were not detectable in the soils by FP-XRF.

C4 Block with M6 Blasting Cap. The only metals detectable by FP-XRF and expected to be released from detonations of C4 blocks with M6 blasting caps are copper (from wire), lead from lead azide, and minute amounts of zinc and iron from an aluminum alloy cup. The FP-XRF detected each of these metals in the post-blast residue (Table 5g). The higher-than-expected concentration of iron was probably from the steel plate that was placed under the snow to minimize disturbance of the underlying soil (Fig. 6). We did not have soils from a training range for comparison.

Table 6. Metals detected by FP-XRF in soils. Numbers are concentrations in parts-per-million (ppm). The FP-XRF concentrations are as reported by the NITON 722S analyzer.

a. M67 hand grenade range soils.

Installation	Pb	Zn	Ni	Fe
Fort Lewis	50	2,100	780	29,000
Fort Lewis	50	1,400	2,440	30,000
Fort Wainwright[a]	35	1,100	<d	15,500
Fort Wainwright[a]	35	1,100	<d	15,000
Fort Leonard Wood	50	2,200	5,800	13,000
Fort Leonard Wood	70	3,400	700	18,000

[a] Lab (ICP) analyses for three samples in the same area: 39, 32, and 40 ppm for Pb; 1260, 1160, and 1540 ppm for Zn; and 14,700, 14,500, and 14,600 for Fe. Nickel was less than 30 ppm.[*]

b. Metals detected in Fort Greely soils by FP-XRF with confirmation by AA.

	Zn		Cu		Pb		Sb	
Ordnance	**FP-XRF**	**AA**	**FP-XRF**	**AA**	**FP-XRF**	**AA**	**FP-XRF**	**AA**
60-mm and 81-mm mortar projectiles	54	56	<d	32	<d	8.2	<d	<4
	<d	48	<d	24	<d	6.6	<d	<4
	60	98	<d	55	<d	12	<d	<4
	<d	60	<d	28	<d	7.7	<d	<4
40-mm grenades	120	67	680	350	34	14	<d	<4
	81	71	1100	1100	<d	27	<d	<4
	<d	46	195	160	<d	8.2	<d	<4
	<d	48	340	510	240	140	<d	<4
TOW missile targets	214	200	113	370	82	140	<d	3.3
	290	300	311	260	90	60	<d	2.7
	70	90	<d	70	80	50	<d	<4
	200	230	330	410	100	70	88	30
	<d	110	<d	89	<d	19	<d	<4
	<d	49	<d	22	<d	7	<d	<4

c. Mean concentrations (ppm) by FP-XRF from 105-mm howitzer firing points at Fort Greely.

Firing point	Pb	Sr	Fe	Zr
A (6 samples)	<d	140	28,000	170
M (20 samples)	<d	112	23,000	140
S (16 samples)	<d	130	19,000	120

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[*] Personal communication, Thomas F. Jenkins, ERDC-CRREL, 2001.

Table 6 (cont'd). Metals detected by FP-XRF in soils. Numbers are concentrations in parts-per-million (ppm). The FP-XRF concentrations are as reported by the NITON 722S analyzer.

d. Anti-tank range soils.

Distance from target	Pb	Cu	Zn	Sr	Fe	HMX[a]
Fort Ord						
1 (within 5 m)	170	840	<d	180	5,500	270
2 (within 5 m)	330	1,400	700	180	13,000	300
3 (within 5 m)	500	2,500	1000	170	21,000	480
4 (within 5 m)	240	990	<d	180	9,500	140
5 (5 to 10 m)	370	1,500	<d	150	10,000	590
6 (5 to 10 m)	350	1,300	<d	170	9,600	270
7 (5 to 10 m)	210	1,100	300	170	6,800	340
8 (5 to 10 m)	210	1,100	<d	200	10,000	80
9 (10 to 15 m)	50	600	<d	180	5,200	20
10 (10 to 15 m)	100	1,300	<d	160	5,000	36
11 (10 to 15 m)	140	800	800	160	5,300	200
12 (10 to 15 m)	60	300	2100	170	3,800	74
13 (15 to 20 m)	60	<d	<d	190	5,300	0.45
14 (15 to 20 m)	80	<d	<d	180	5,000	4.3
15 (15 to 20 m)	70	<d	<d	170	3,200	0.48
16 (15 to 20 m)	<d	<d	<d	180	4,100	0.27
Yakima						
YC3 (2 to 5 m)[b]	64	212	380	124	34,000	12

[a] Lab (ICP) analyses for three samples in the same area: 170, 180, and 49 ppm for Pb; 315, 440, and 190 ppm for Cu; 310, 530, and 170 ppm for Zn.[*]

[b] HMX concentrations were determined by HPLC (Jenkins et al. 1998).

e. Ravenna Army Ammunition Plant.

	Pb		Zn	Fe
Sample ID	**FP-XRF**	**AA**	**FP-XRF**	**FP-XRF**
67 Comp. 1–4	210	200	349	19,891
67 Comp. 9–12	96	86	303	19,699
67 Comp. 13–16	160	130	238	18,893
W11-1	190	150	424	18,893
W11-2	130	250	440	15,693
W11-4	200	150	457	16,192
W11-5	190	170	365	16,192
W11-6	180	140	415	16,794
W11-Comp	200	190	402	16,896

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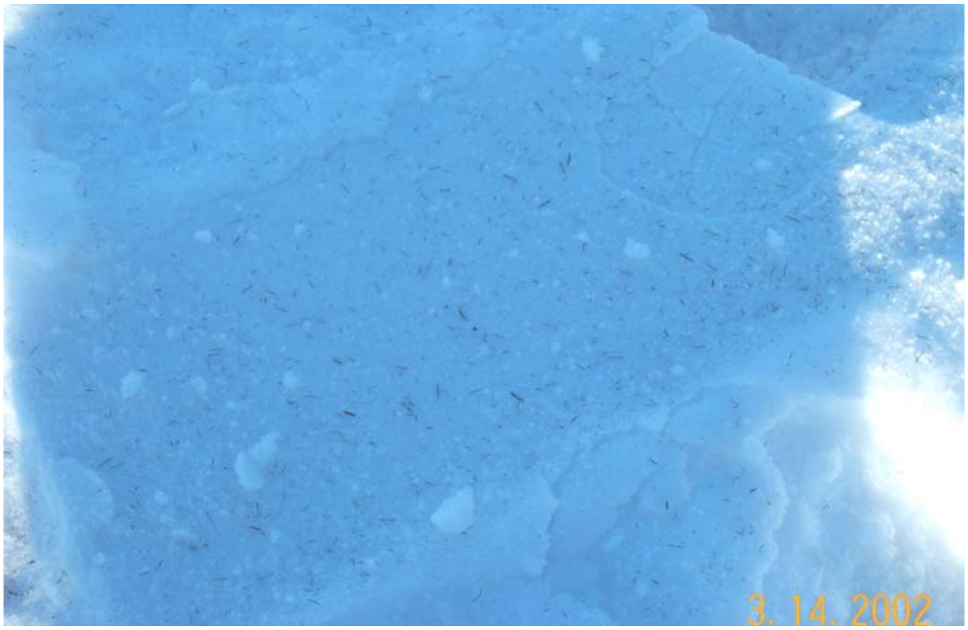
[*] Personal communication, Thomas F. Jenkins, ERDC-CRREL, 2002.

a. Firing of 105-mm howitzer projectiles.



b. Pieces of propellant residues visible on the snow surface.

Figure 5. Photographs taken at Fort Richardson, Alaska. (Photos courtesy of Michael R. Walsh.)

Figure 6. Post-blast residue of a C4 block with M6 blasting cap at Camp Ethan Allen, Vermont. A metal plate was placed under the snow to minimize disturbance of the underlying soil.

Other Training Range Soils

Fort Ord and Yakima Training Center Anti-Tank Ranges. We had several soils archived that were collected from the Fort Ord Anti-Tank Range (Jenkins et al. 1998). Sixteen samples were collected within grids located within 5 m behind the target, 5 to 10 m beside the target, 10 to 15 m in front of the target, and 15 to 20 m beside the target for 66-mm M72 anti-tank rockets. All of the samples had detectable concentrations of HMX by prior analyses by HPLC. Of the metals listed on the TRI report, copper, mostly from the copper liner of the shaped charge within the rocket, should be deposited in the soils around the targets. Also, copper, zinc, and lead were detectable in the Aberdeen Test Chamber emission test residue from these rockets.

The FP-XRF results (Table 6d) show elevated concentrations of copper and lead near the tank targets. HMX concentrations are shown in Table 6d as well, and there is a significant correlation between lead and HMX concentrations (R = 0.85) and copper and HMX concentrations (R = 0.79). These relationships could be useful when performing site characterization on anti-tank ranges simply because of the speed of the FP-XRF analyses and the persistence of HMX in surface soils. Although we did not have laboratory analyses to confirm the lead and copper concentrations for the Fort Ord samples, we did have FP-XRF and ICP results for a few soils collected at the Yakima Training Center Anti-Tank Range (Pennington et al. 2002) where the same types of rockets were fired. Similar to Fort Ord, the concentrations of copper, lead, and zinc, as determined by ICP, were highest near the targets. The one sample available for FP-XRF analysis yielded concentrations similar to that found by ICP (Table 6d) for the same sample area.

Fort Greely Washington Range TOW Missile Target. At Fort Greely, we collected a series of soil samples surrounding two tank targets used for testing of Tube-Launched Optically Tracked Wire-Guided (TOW) missiles (Walsh et al. 2001). We collected six discrete samples adjacent to two targets and a series of composite samples from 5-m to 50-m distance from one of the targets.

By FP-XRF, we detected zinc, copper, and lead in most of the discrete samples adjacent to the tank targets, and antimony in one sample. These elements were below the FP-XRF detection limit in the composite samples collected farther away from the target. Laboratory confirmation by Atomic Absorption (AA) showed generally good agreement between the two methods of analyses (Table 6b).

Fort Richardson Explosive Ordnance Disposal Pad. We had one sample from an explosive ordnance disposal site on Fort Richardson. The FP-XRF detected lead (80 ppm), zinc (500 ppm), and copper (260 ppm). Concentrations determined by ICP were lead (77 ppm), zinc (720 ppm), and copper (350 ppm).

Ravenna Army Ammunition Plant. The last set of samples was from Ravenna Army Ammunition Plant. These samples were collected to assess the spatial distribution of lead, arsenic, cadmium, and beryllium[*] on grounds where explosives were burned. These samples had been analyzed by AA. Of these metals, only lead was detectable by FP-XRF (Table 6e), and the results for the two methods of analysis were similar.

Correlation of FP-XRF and Laboratory Determinations

We used a paired t-test to compare the FP-XRF and laboratory determinations of lead, zinc, and copper in soils from training ranges. We did not compare determinations of metals that are not ordnance-related or that have high natural soil concentrations (strontium, zirconium, iron).

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[*] Personal communication, Alan D. Hewitt, ERDC-CRREL, 2000.

The paired t-tests showed that the concentration estimates provided by FP-XRF were not significantly different from those provided by laboratory analyses for lead, zinc, and copper (Table 7). Correlation of two methods of analyses not only depends on the accuracy of each analytical method, but also on the degree of heterogeneity of the analyte of interest in the soil. Considering that the variability due to sampling frequently exceeds the variability due to analysis, the FP-XRF has the advantage of rapid, nondestructive determinations so that many more samples can be analyzed to assess the distribution of a contaminant.

Table 7. Results of paired t-test for FP-XRF and laboratory (AA or ICP) determinations of lead, zinc, and copper in training range soils.

Element	Number of paired samples	t value	$t_{0.95}$	Correlation
Pb	18	0.36	2.1	0.78
Zn	11	0.64	2.2	0.97
Cu	9	0.32	2.3	0.85

4 CONCLUSIONS

The advantages of FP-XRF are that it is designed for on-site analysis and is very portable. It provides rapid determination of several elements and does not destroy the sample. For the metals expected to be deposited on soils following detonation of ordnance items, the FP-XRF provided reasonably accurate determinations for lead, zinc, and copper. Thiboutot et al. (2003) recently reported that these three metals and cadmium were the most common metals that exceeded the Canadian Council of Ministers of Environment agricultural soil quality guidelines in soils on training ranges at Canadian Force Base Gagetown, New Brunswick.

For site remediation of lead and zinc, the FP-XRF limits of detection for lead and zinc are much lower than current USEPA soils screening levels (Table 1). Copper concentrations may be of more interest to analytical chemists because high copper concentrations can interfere with determinations of other ordnance-related contaminants such as white phosphorus and 2,4-DNT (Jenkins and Walsh 1992). High concentrations of copper may also affect how soil is treated for other contaminants. Chromium and nickel are also potential contaminants from ordnance detonations, but the FP-XRF limit of detection for these elements is relatively high (420 ppm for chromium and 210 ppm for nickel).

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14. ABSTRACT

Field-portable X-ray fluorescence (FP-XRF) analyzers, such as the Niton 700, provide rapid, on-site analyses for a variety of elements. FP-XRF was used to determine metals in post-blast ordnance residue that was deposited on snow, which provided large collection surfaces that were free of soil particles. The ordnance items included M67 hand grenades, 40-mm grenades, 60-mm and 81-mm mortar projectiles, 105-mm howitzer projectiles, claymore mines, and C4 demo blocks with M6 blasting caps. For most of these items, the post-blast residue contained lead, iron, copper, and zinc. FP-XRF also was used to determine these elements in soils from training ranges where these ordnance items were used. When present above the FP-XRF limits of detection, the FP-XRF determinations of lead, zinc, and copper were not found to be significantly different from determinations by laboratory analyses.

15. SUBJECT TERMS

Copper	Soils	Zinc
Lead	Training range	

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