SPECIAL REPORT 97-8

Detecting Metallic Primary Explosives with a Portable X-ray Fluorescence Spectrometer

Alan D. Hewitt

April 1997

Abstract: X-ray fluorescence spectrometry (XRF) analysis is a practical means of performing in-situ screening to establish the presence of high concentrations (>0.1% or 1000 ppm) of lead (Pb) and/or mercury (Hg). These two metals are of special military interest because they are constituents in three primary explosives: lead azide [$Pb(N_3)_2$], lead styphnate ($C_6HO_6N_3Pb$), and mercury fulminate [$Hg(CNO)_2$]. The success of in-situ XRF analysis to perform this task depends on instrumental sensitivity, selectivity, effective sample volume, transportability, and user friendliness. Laboratory experiments established that the MAP-3 XRF spectrum analyzer (SCITEC Corporation) is well-suited for this application. This instrument is self-contained, portable, and equipped with a Co-57 source that allows for a simultaneous analysis of both the K and L energy lines of Pb and Hg, among other metals. Laboratory experiments established that high concentrations of Pb and Hg could be detected in an active sample area of cylindrical shape, approximately 1.0 cm in diameter and 1.5 cm in depth.

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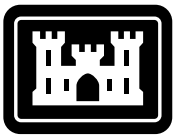
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PREFACE

This report was written by Alan D. Hewitt, Research Physical Scientist, Geological Sciences Division, Research and Engineering Directorate of the U.S. Army Cold Regions Research and Engineering Laboratory in Hanover, New Hampshire.

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Detecting Metallic Primary Explosives with a Portable X-ray Fluorescence Spectrometer

ALAN D. HEWITT

INTRODUCTION

Although the extent of environmental pollution associated with the practices of manufacturing, storage, and disposal of initiators (primary explosives) does not rival that of secondary explosives (high explosives), because of the volumes necessary for munitions production, their high reactivity warrants special attention. Unlike high explosives, initiators spontaneously detonate when subjected to mechanical shock, heat, electrical sparks, or an open flame (Yinon and Zitrin 1981). It is currently believed that within the range of 5 to 15% (w/w), a mixture of the primers lead azide, lead styphnate, or mercury fulminate with an environmental substrate (i.e., soil) would be sufficient for spontaneous detonation (Workman 1994).

The presence of lead (Pb) or mercury (Hg), which is unique to the three initiators, at or near concentrations critical for spontaneous detonation is well suited for X-ray fluorescence spectrometry (XRF) analysis. This method of chemical analysis relies on fundamental changes in the electronic configuration of atoms and causes no physical or chemical alterations to the media being analyzed. The successful use of XRF analysis for establishing the presence of elevated concentrations of metals in environmental samples has been well documented (Spittler and Fender 1979, Garby 1991, Puls et al. 1994, Schneider et al. 1995). Moreover, acceptance of XRF analysis as a screening method is scheduled for the third update of *Test Methods for Evaluation of Solid Waste* (US EPA 1986). XRF analysis is capable of providing concentration estimates over a range extending from high percent levels to below 100 mg/kg (ppm). Several manufacturers offer energy-dispersive XRF spectrometers for in-situ operations. These transportable instruments have one or more sources, a detector, and on-board or shoulder-carried spectrum analyzers, all of which can be operated by battery power for several hours.

The purpose of this study was to select and test an XRF instrument for screening sites where metallic primers may be deposited. The selection criteria used in this process included appropriate metal sensitivity and selectivity, area of effective sample analysis, portability, and user friendliness. Laboratory experiments were designed to evaluate qualitatively the performance of the selected XRF system under a variety of conditions and to provide guidelines for field operations.

INSTRUMENT SELECTION CRITERIA

Sensitivity

The concentrations of Pb and/or Hg present when a metallic primer exists at levels where spontaneous detonation could occur is some two to three orders of magnitude above the reported detection limits (10 to 100 ppm) for most XRF instruments. For example, the lead in lead styphnate, which has the lowest mole fraction of metal to primer composition, would be present at about 2.5×10^4 ppm in a 5% mixture. Therefore, at installations where these primary explosives have been manufactured, stored, or disposed of, concentrations of Pb and/or Hg near a 1% level could be used to infer that a potential explosive hazard exists.

Selectivity

Selectivity of XRF analyzers for individual metals depends on both the energy emitted by the primary source and the resolution of the detector. Portable XRF systems capable of in-situ analysis rely on one or more radioactive sources for primary incident radiation. For a metal to be detected, the incident energy emitted during the radioactive decay of a primary source must be greater than the excitation energy of the inner-shell electrons of the element (or elements) to be analyzed. Briefly, the electrons most often excited during XRF analysis are located in the K and L shells. Once excited, these inner-shell electrons are lost, and electrons from an outer shell fill the voids created. In the process of the electrons going from an outer to an inner shell, element-specific energies (photons, i.e., X-ray fluorescence) are emitted. This fluorescent energy is measured in kilo electron volts (keV; 1 keV = 1000 eV). Subscripts α, β, and γ can accompany the K and L notations, indicating which outer shell the electrons fell from, thus further specifying the discrete spectral energies measured.

Table 1. XRF primary sources and emission energy of metals that have fluorescent energies close to Pb and Hg.

	Primary energy	*Useful for the analysis of*	
Source	*(keV)*	*K energies*	*L energies*
Fe-55	—	Si-V (14–23)*	Nb-Ce (41–58)
Cm-244	—	Ti-Se (22–34)	La-Pb (57–82)
Cd-109	87.9 & 22.1	Ba-W (56–74)	Cu-Mo (29–42)
Am-241	59.6	Zn-Nb (30–41)	Hf-U† (72–92)
Co-57	121.9 & 136	Hg-U† (80–92)	W-U† (74–92)

	Emission energy (keV)		
Metals	*K*	*L*	*Atomic weight*
Ir	64.99	9.173	77
Pt	66.82	9.44	78
Au	68.79	9.71	79
Hg	70.82	10.27	80
Tl	72.86	10.27	81
Pb	74.96	10.55	82
Bi	77.1	10.84	83
Po	79.3	11.1	84

* Range of atomic weights.

† Useful range of emission energies includes Pb and Hg.

Portable XRF spectrometers come equipped with silicon (drifted with lithium) [Si(Li)] or mercuric iodide crystal detectors that have resolutions from 170 to 2500 eV, or gas-proportional detectors with resolution anywhere from 700 to 3000 eV. Table 1 lists common primary sources and the analytes that they can excite, along with the K and L energy lines for Pb and Hg.

Area of metal detection

The effective sample volume measured during XRF analysis is a function of the positioning of the source and detector and the energy used to excite or assess the analytes. With regard to instrumental geometry, maximum analysis depth (penetration) is achieved when the source and detector are positioned in a parallel configuration. In this orientation the angle between the incident radiation going into the sample matrix and the fluorescent energy returning to the detector is minimized. Therefore, the least amount of substrate has to be transversed.

The penetration depth with regard to the incident and fluorescent radiation is inversely proportional to wavelength and directly proportional to energy. The radiation energy necessary for exciting electrons, and the energy lost by the electrons that fill these vacancies, is greater for the K shell than the L shell for a given element.

Portability, user friendliness, cost

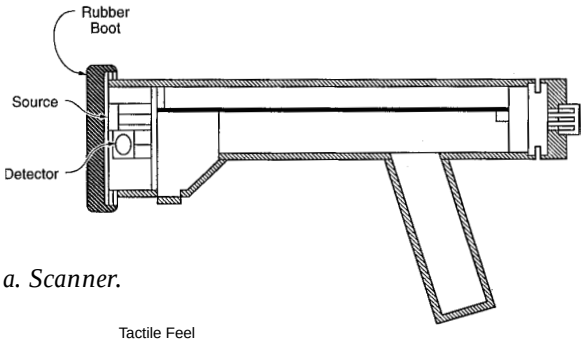
Conceptually, a small, light XRF system would be best suited for either human-portable or robotic implementation. Likewise, instrument performance verification and the number of steps to acquire measurements or view spectra should be minimal. Because these instruments contain radioactive sources that can have short half-lives (< 2 years), rental and upgrade cost should also be evaluated.

INSTRUMENT SELECTION JUSTIFICATION

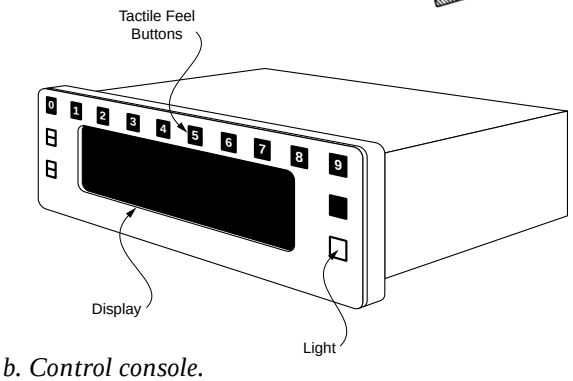
The SCITEC MAP-3, an XRF analyzer manufactured for the analysis of lead in paint, equipped with a Co-57 radioactive source, was selected for the following reasons. This XRF system allows for simultaneous analysis of both K- and L-shell lines of Pb and Hg and has an ambient-temperature Si(Li) detector with a spectral resolution of about 2.5 keV. In addition, the source and detector are positioned next to each other within the scanner, so they face in the same direction (almost parallel geometry). All other

portable XRF systems available at this time come equipped only with Fe-55, Cd-109, Cm-244, or Am-241 radioactive sources and are unable to excite the K-shell electrons of these two metals. The low resolution of the MAP-3 analyzer is probably not important since the metals with K-line energies within 3 keV of Hg and Pb are relatively scarce (gold [Au], thallium [Tl], and bismuth [Bi]; Table 1).

The complete system, capable of performing measurements and displaying a spectrum, comes contained within two portable components (Fig. 1): a scanner 33.7 cm long, weighing 1.6 kg (3.5 lb), and a control console 19.3 cm long



a. Scanner.



b. Control console.

Figure 1. The SCITEC MAP-3 XRF analyzer.

× 20 cm wide × 7.6 cm high, weighing 3.2 kg (7 lb) with a battery. This instrument is available on a rental basis for under $3000/mo or it can be purchased for about $15,000. Additional important features are factory-loaded calibrations (empirical), manual control of analysis time (10 to several hundred seconds), quantitative determinations based on counts or spectral display available within a few seconds of completing an analysis, storage of up to 325 spectra and quantitative measurements, and an RS-232 serial interface port for data transfer. In addition, the instrument is considered a "low level" risk for stray radiation and operator exposure.

LABORATORY EVALUATION

Following a brief discussion of spectral interpretations and methods of instrumental measurement, some qualitative laboratory experiments will be presented that assessed effective areas of sample analysis, matrix effects, and length of analysis relative to the detection of Pb and Hg.

To perform these various tasks, three different targets and six different soil types (Table 2) were used. The targets consisted of lead shot (shotgun pellets), sealed packets (pillows) of weighed amounts of lead nitrate [$Pb(NO_3)_2$] and/or mercuric chloride ($HgCl_2$), and X-ray cells (small plastic containers) completely filled with mixtures of soil and lead nitrate. The pillows were made by heat-sealing weighed quantities of the above salts in 0.2-mil polypropylene bags (8 mm × 8 mm) so there would be 0.05, 0.10, 0.25, 0.50, or 1.00 g of the metal present. One pillow was prepared with both the Pb and Hg salts (0.50 g/each). Samples of Pb in soil were prepared by first mixing weighed amounts of lead nitrate with an air-dried soil such that the Pb content would be roughly 0.625, 1.25, 2.5, 5.0, and 10%, then completely filling a 40-mm-diameter X-ray cell.

Table 2. Soil matrix characteristics.

Matrix	*% Sand*	*% Silt and clay*	*Grain size* (mm)*
Ottawa sand	100		400
Rocky Mountain Arsenal	NA	NA	NA
Lebanon Landfill	45	55	300
CRREL soil	NA	NA	NA
Tampa Bay sediments	95	5	200
Ft. Edwards clay		100	30

* 95% cutoff.
NA = Not available.

Spectral interpretation

Illustrations of XRF spectra obtained with the MAP-3 are shown in Figure 2. The vertical scale indicates the number of counts (intensity of fluorescent energy measured), and the horizontal axis displays the 256 channels into which the X-ray energy or wavelengths are separated. When this instrument is equipped with a Co-57 source, the lowest energy that the system can detect is about 8.5 keV and the highest is 98 keV. Looking first at the spectra of a typical soil (Fig. 2a), three peaks that are common to all analyses are apparent: an electronic noise signal ranging from chan-

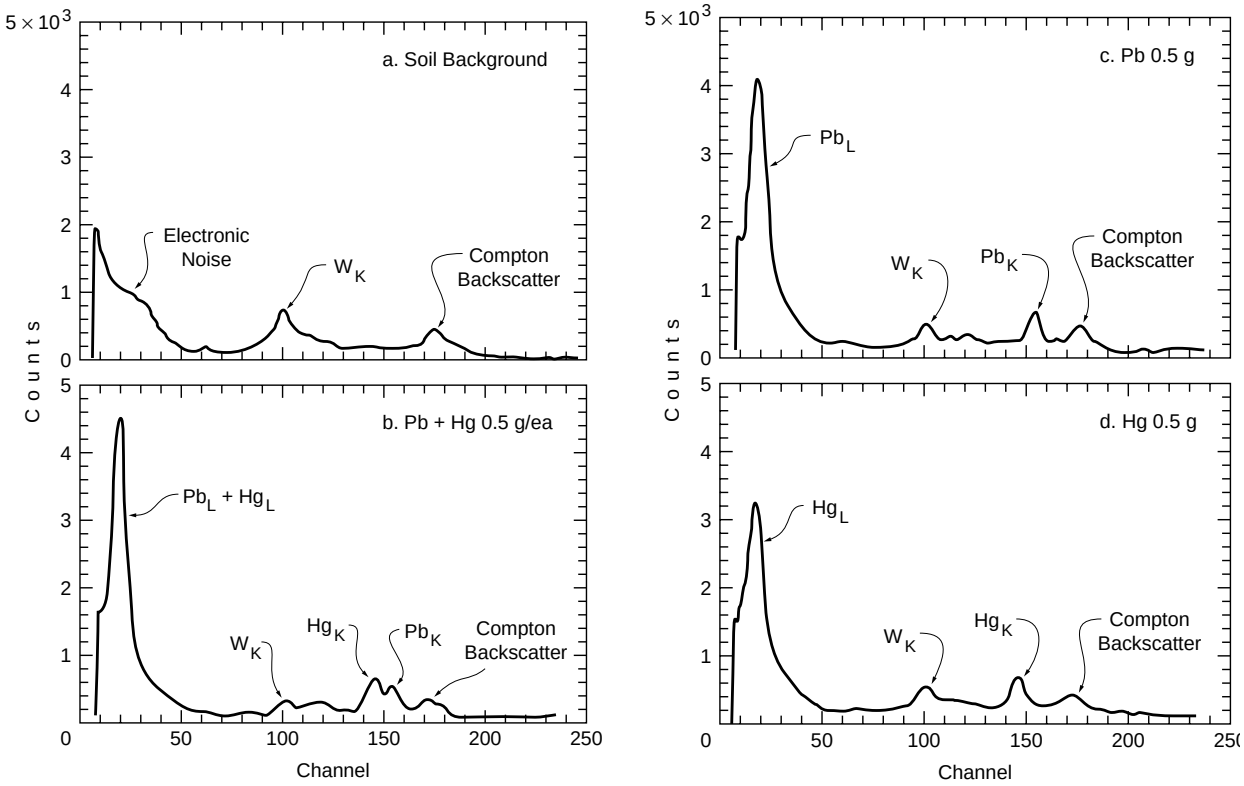


Figure 2. Spectra obtained with the MAP-3 XRF analyzer: a) a background soil, b) the 0.5-g Pb/Hg target on a soil surface, c) the Pb target on a soil surface, and d) the Hg target on a soil surface.

nel 1 to 50, a tungsten (W) K-shell peak in the channel region 101 due to the composition of the shutter for the source, and, in the region of channel 176 (85 keV), the Compton backscatter peak. In addition to these peaks, the three remaining spectra show either or both of the L- and K-shell peaks of Pb and Hg. The L-shell peaks for these two metals appear in the region of channel 26 (10.5 and 10.3 keV) superimposed over an electronic noise signal, and the K-shell peaks appear at channels 155 ±1 (75.0 keV) and 148 ±1 (70.8 keV) for Pb and Hg, respectively.

Comparing all four spectra in Figure 2 also shows how the intensity of the Compton peak changes inversely to the amount of heavy metals present in the sample. In the spectra of the background soil (no target), the Compton peak has the highest intensity (400 counts); conversely, the spectra of a sample with 0.5 g of both Pb and Hg on the soil surface has the lowest (250 counts). The Compton peak intensity changes because the incoherent radiation backscatter that comprises it is caused mainly by light elements (i.e., oxygen, silica, etc.) in the sample matrix. As the amount of heavier elements increases in the matrix analyzed, the fluorescent energy from light elements decreases. For instance, when the Pb and/or Hg K-shell peak intensities are of equal or greater magnitude than that of the Compton peak, these metals are present at extremely high concentrations (percent levels).

Instrumental analysis

The SCITEC MAP-3 came preprogrammed with calibrations for Pb in both paint and soil. The lead-in-paint calibration, which quantitively assesses both the L and K lines of Pb, was used to check the instrument's performance on a daily basis. This sensitivity check, which took less than 5 minutes to perform, involved measuring a block of wood evenly coated with leaded paint. Standards prepared for the analysis of metals in soil matrices are homogeneous (finely ground), but metallic primary explosives most likely exist as salts. As a salt or salt aggregate, large discrepancies in particle size are likely between primary explosives and soil matrices. For this reason, the analysis of the targets mentioned above, based on the factory calibration for Pb in soil (mg/kg), served only as a relative measurement of the amount of this metal. In addition, instrumental measurements of many of the spectra were manually interpreted by measuring the intensity of the respective K lines, and sometimes the L lines

and Compton peak, along with the adjacent baseline noise. Intensities of K- and L-line peaks were assessed by taking an average of the three highest intensities (counts) in the appropriate channel region, while that of the baseline noise was taken as the average intensity in the three lowest channels, in the valley either just to the right or left of the peak. This manual method of data interpretation was performed because there was no calibration for Hg, and it provides insight as to the peak intensities (spectral peak heights) relative to the background noise and that of the Compton peak.

Table 3. Measurements of 0.5 g of Pb on soil surface and through soil ranging from 0.25 mm to 2.0 mm thick.

	MAP-3				*Metorex 920*		
Target	*Co-57 source*				*Cd-109 source*		
cover	*Manual**			*Instr.*†	*Manual**		*Instr.*†
(mm)	Pb_L	Pb_K	*Comp.***	*(ppm)*	$Pb_{L\alpha}$	$Pb_{L\beta}$	*(ppm)*
None	4,300	660	260	24,000	147	150	31,000
0.25	2,600	550	280	15,000	37	57	13,000
0.5	1,000	500	280	9,500	14	30	8,200
1.0	500	510	280	6,900	2.1	9.3	2,000
1.5	250	410	290	5,900	0.18	1.0	270
2.0	ND	400	280	5,600	ND	0.54	113

* Manually measured fluorescent energies, baseline-corrected.
† Instrumental measurements based on Pb (mg/kg) in soil standards.
** Compton peak.

Effective surface area of analysis

The effective area of analysis for a discrete object on a surface was evaluated using a Pb shot pellet and a large shallow plastic tray (100 × 60 cm) filled 5.0 cm deep with the Lebanon Landfill (LLF) soil. The Pb pellet (2-mm diameter, 62 mg) was placed on the soil surface and the scanner was positioned directly over the pellet to obtain a maximum instrumental measurement of Pb in soil, using a 24-s analysis period. When this scanner is placed on the soil, the window for the source and detector remains some 0.6 cm above the surface. The position of the scanner (i.e., the source and detector window) was fixed on the x/y plane (surface of the soil) with two rulers. The scanner was then picked up and repositioned by moving it in 0.5-cm increments on the x/y axis away from the location where the highest measurement was obtained. The maximum values obtained directly over the pellet were 4 to 5 times greater than the background (no pellet under the scanner) and were at least 2 times greater than the background after moving 0.5 cm. Positioning the scanner on the soil surface 1.0 cm away from the point where a maximum reading had been obtained often resulted in a reading similar to that of the background. This experiment indicates that the scanner excites and receives enough radiation to detect a metal aggregate lying on the surface over an effective analysis area of about 1.0 cm^2.

Depth of soil penetration

Soil disks

Soil barriers of approximately 0.25, 0.50, 1.0, 1.5, and 2.0 mm were prepared by using an appropriate amount of dry LLF soil. Using only snap rings and collars from 31-mm polyethylene X-ray cells, the soil was actually spread over a 22-mm-diam. cylindrical area and held between two sheets of 0.2-mil polypropylene. These 6-mm-high (rim) soil disks were placed between the XRF spectrometer's sensor window and a target consisting of a 0.5-g pillow of Pb. Table 3 shows the amount of Pb measured by both the MAP-3 (Co-57 source) and an X-Met 920 (Metorex, Inc.; Cd-109 source) XRF spectrometer. The results of this experiment show that while the intensity of the L lines rapidly decreases as the soil barrier increases, the intensity of the K line is not as severely affected. Indeed, the K-line intensity remains greater than the Compton peak (Fig. 3). As will be shown in subsequent tests, the energy emitted by the Co-57 source and the fluorescent energy from electrons filling the voids created in the K shell of Pb and Hg can easily penetrate this depth of soil and more.

Tube tests

Analysis of Pb and Hg through soil of various depths was also performed using a Lucite tube 3 cm high and 2 cm in diameter. The tube was covered on one end with a sheet of 0.2-mil polypropylene held in place with a rubber band. The covered end of the tube was positioned 2.8 cm below the soil surface, in a large plastic jar (11.2 cm diameter × 9.5 cm high). The level of the soil in the jar came to within 2 cm of its rim, and the mouth of the jar was just large enough to allow the sensor end of the MAP-3 scanner to fit inside and rest on the flat soil surface. The tube was positioned directly below the sensor window (source and detector window), and the jar was marked to maintain the alignment between the scanner and the target from one measurement to another. For this experiment, a pillow of 0.5 g Pb was placed in the Lucite tube at 1 or 2 cm below

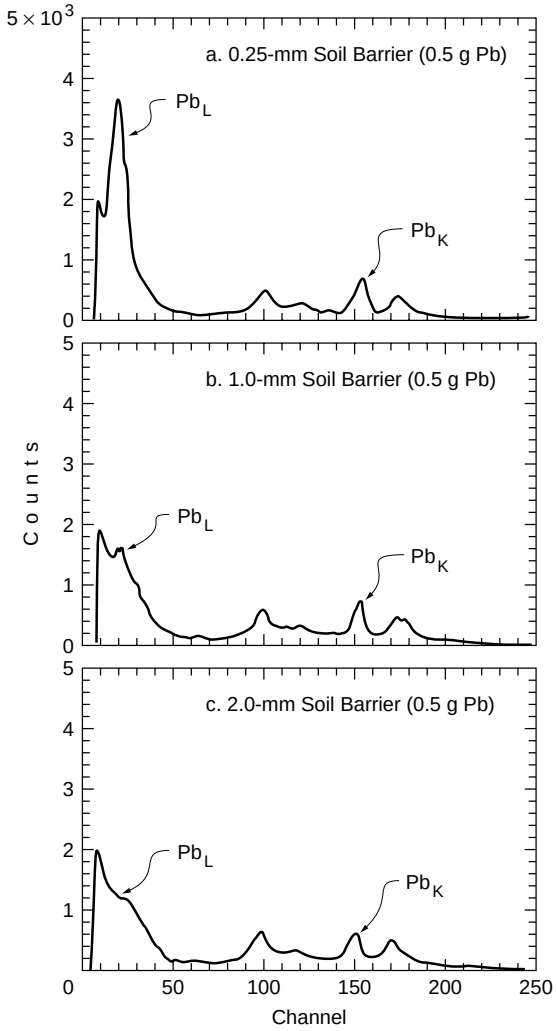


Figure 3. Illustrations of spectra obtained with the MAP-3 XRF analyzer for a Pb target beneath barriers of soil.

the rim, and then air-dried soil was transferred with a spatula to achieve various depths of coverage (the inner wall of the Lucite tube had 0.5-cm increment markings, and the same soil placed over the target was also used below it).

Table 4 shows some of the measurements taken using a 24-s analysis period when a 0.5-g pillow of Pb was placed 1.0 cm below the rim of the Lucite tube and six different types of soil were used for coverings in 0.5-cm increments. Measurements taken in this fashion required that the incident and fluorescent radiation pass through a dry soil barrier or an air void of 1.4, 0.9, or 0.4 mm, depending of the amount of covering. The results of this experiment showed that the K line of Pb could easily be seen through 1.0 cm of every type of soil tested. Manual measurements

Table 4. Measurements (24 s) of 0.5-g Pb pillow on and below several air-dried soil matrices held in a Lucite tube.

	*Manual**		*Instr.†*	*Soil*	*Depth*
Soil	*Pb_K*	*Comp.***	*(ppm)*	*target*	*(cm)*
Ottawa sand					
	–20	300	210	no	0
	190	280	11000	yes	0
	150	300	2300	yes	0.5
	130	300	1300	yes	1.0
Rocky Mountain Arsenal					
	–15	300	–250	no	0
	210	260	12000	yes	0
	205	300	3500	yes	0.5
	165	300	3000	yes	1.0
Lebanon Landfill					
	–35	280	380	no	0
	190	260	10000	yes	0
	135	280	2400	yes	0.5
	125	280	2200	yes	1.0
CRREL soil					
	–35	260	–400	no	0
	175	210	12000	yes	0
	210	260	3800	yes	0.5
	155	260	4500	yes	1.0
Tampa Bay sediments					
	–30	280	–390	no	0
	220	260	11000	yes	0
	130	280	2600	yes	0.5
	120	280	1900	yes	1.0
Ft. Edwards clay					
	–10	220	89	no	0
	145	210	11000	yes	0
	130	220	2600	yes	0.5
	110	220	3300	yes	1.0

* Manually measured fluorescent energies, baseline-corrected.
† Instrumental measurements based on Pb (mg/kg) in soil standards.
** Compton peak.

of the background soil (no metal target present) resulted in negative values because the signal intensity is actually lower at the appropriate channels for Pb and Hg than the channels selected for baseline correction.

Although no results are presented, this experiment was also performed with the 0.5-g Pb pillow positioned at a depth of 2.0 cm (2.4 cm from the detector source window). Under these conditions, the K line for Pb could only be distinguished from the baseline when there was either a 0.5-cm soil barrier or none at all. The results of these experiments indicate that the scanner does not have to be in direct contact with the surface in order to measure these metals on or below the surface.

Modified X-ray cell test

A third experiment used several polyethylene 31-mm X-ray cells, modified so that they were only 0.5, 1.0, and 1.5 cm high. Each was covered on the bottom with a single sheet of 0.2-mil polypropylene. After packing the modifed cells with soil, they were buried in the large soil-filled jar so that the top rim was flush with the surface. The cells were buried with and without the packets of metal salts positioned beneath. With these cells the mass (density) of soil between the source and the metal target could be established, and soil moisture experiments could be performed.

Table 5 shows the manually measured peak intensities for the K lines of Pb and Hg on and beneath an air-dried soil and for Pb beneath a soil of 20 and 40% moisture content. All measurements used a 24-s analysis period, and only the CRREL soil was used. As indicated by the previous experiment, the K lines of these metals were detected above the baseline through barriers up to 1 cm in thickness, even when the moisture content was increased.

In Table 5, the measured intensities of Pb buried beneath the air-dried CRREL soil were lower than established in the previous experiment (Table 4). An explanation for this decrease in signal intensity between experiments is that greater soil densities most likely were present in the modified cell experiment. In addition, measurements through the moistened soil barriers appeared to decrease the Pb-line intensity, and the measurement of this line became inconclusive when the barrier was increased to 1.5 cm.

Table 6 shows values for both Pb and Hg based on manually measured intensities and for instrumental measurement of Pb using a 96-s analysis period. The targets for this experiment consisted of pillows containing 0.5 g of both of these metals, or just Pb. While the findings of this experiment again indicate that both of these metals could be detected if present as a 0.5-g aggregate or larger on or near the surface, to achieve detection at depths greater than 1.0 cm beneath the soil surface, the measurement time had to be increased.

Table 5. Measurements (24 s) of 0.5-g pillows of Hg and Pb uncovered and below disks of air-dried and moist CRREL soil.

Hg

	*Manual**		*Soil depth*
Soil	*Hg_K*	*Comp.†*	*(cm)*
CRREL air dried			
	395	180	0.0
	75	240	0.5
	45	250	1.0
	5	295	1.5

Pb

	*Manual**		*Soil depth*
Soil	*Pb_K*	*Comp.†*	*(cm)*
CRREL air dried			
	500	250	0.0
	120	280	0.5
	65	280	1.0
	15	280	1.5
CRREL 20% moisture			
	80	290	0.5
	15	290	1.0
	0	290	1.5
CRREL 40% moisture			
	100	290	0.5
	40	290	1.0
	0	290	1.5

* Manually measured fluorescent energies, baseline-corrected.
† Compton peak.

Table 6. Measurements (96 s) of Hg and Pb below disks of air-dried and moist soil matrices.

	*Manual**		*Instr.†*	
Pb_K	*Hg_K*	*Comp.***	*(ppm)*	*Moisture/depth (cm)*
Lebanon Landfill (mean density 1.5 g/cm^3)				
240	400	750	5000	AD†† / 0.5
110	170	860	2500	AD†† / 1.0
10	80	890	1400	AD†† / 1.5
410	—	920	2230	20% / 0.5
170	—	890	1200	20% / 1.0
70	—	870	1050	20% / 1.5
440	—	910	3000	40% / 0.5
180	—	890	1400	40% / 1.0
70	—	830	820	40% / 1.5
Ft. Edwards clay (mean density 1.3 g/cm^3)				
280	400	760	5200	AD†† / 0.5
120	190	840	2700	AD†† / 1.0
20	70	860	1200	AD†† / 1.5
500	—	950	2800	20% / 0.5
200	—	910	1900	20% / 1.01
50	—	890	610	20% / 1.5
380	—	960	1800	40% / 0.5
210	—	940	1200	40% / 1.0
30	—	910	690	40% / 1.5

* Manually measured fluorescent energies, baseline-corrected.
† Instrumental measurements based on Pb (mg/kg) in soil standards.
** Compton peak.
†† Air dried.

Table 7. Measurements of Pb in soil mixtures using different analysis periods.

Sample (%)	Analysis period (s)	Manual* Pb_K	Manual* Comp.**	Instr.† (ppm)
Background	96	–50	1400	354
0.625	96	185	835	3000
0.625	10	15	85	3400
1.25	96	315	790	5000
1.25	10	25	85	5100
2.5	96	700	830	6400
2.5	10	60	90	6300
5.0	96	980	740	7100
5.0	10	115	65	7100
10	96	1500	825	8500
10	10	170	80	8400

* Manually measured fluorescent energies, baseline-corrected.
† Instrumental measurements based on Pb (mg/kg) in soil standards.
** Compton peak.

Table 8. Measurements of Hg and Pb on and below disks of Lebanon Landfill soil using different periods of analysis.

Hg

Manual* Hg_K	Manual* Comp**	Target (g)	Moisture	Depth (cm)	Analysis period (s)
–50	920	none	AD††	0.5	96
–15	105	none	AD††	0.5	10
210	840	0.25	AD††	0.5	96
30	100	0.25	AD††	0.5	10
115	869	0.5	AD††	1.0	96
5	90	0.5	AD††	1.0	10

Pb

Manual* Pb	Manual* Comp.**	Instr.† (ppm)	Target (g)	Moisture	Depth (cm)	Analysis period (s)
–40	920	380	none	AD††	0.5	96
–5	105	–930	none	AD††	0.5	10
265	930	1900	0.25	20%	0.5	96
25	85	2600	0.25	20%	0.5	10
490	800	3100	0.5	20%	0.5	96
45	75	5100	0.5	20%	0.5	10
135	880	1400	0.5	AD††	1.0	96
10	95	1200	0.5	AD††	1.0	10

* Manually measured fluorescent energies, baseline-corrected.
† Instrumental measurements based on Pb (mg/kg) in soil standards.
** Compton peak.
†† Air dried.

Detection level of rapid analysis

The sensitivity of elemental detection in environmental matrices performed by XRF depends upon several factors, including the length of analysis time. The sensitivity for rapid analyses with the MAP-3 scanner was assessed by analyzing mixtures of the LLF soil and $Pb(NO_3)_2$ held in XRF cups and pillows of both the Pb and Hg salts beneath the modified XRF cups (Tables 7 and 8) for either 10 or 96 seconds. The 10-s measurement period is the fastest analysis time for this instrument. The objective of this experiment was not to establish the smallest amount of Pb or Hg that could be measured, but to determine if percent levels could be quickly detected.

The results in Table 7 show that Pb was easily detectable using a 10-s analysis period when mixed with soil so that ≥0.625% was present. Likewise, it appears that 0.5-g quantities of these two metals could be rapidly detected even when covered with 0.5 cm of soil (Table 8).

A comparison between the changes in response relative to metal concentration as seen by the manual and instrumental measurement methods is also shown in Table 7. For a 16-fold increase in Pb, the manual method established an 8.1- to 11-fold increase in Pb_K peak intensity, but the Pb concentrations (mg Pb/kg) determined by the calibrated instrument method only showed a 2.8- to 2.5-fold increase. The large discrepancy in range of relative response between the two methods of analysis indicates that a different approach to instrumental calibration would be necessary before quantitative measurements could be performed. Ideally, correction factors could be also be applied so that measured metal concentrations could be converted readily to estimations of primer concentration [i.e., 1.4 times for $Pb(N_3)_2$ and $Hg(CNO)_2$ or 2 times for $C_6HO_6N_3Pb$].

SUMMARY

This study shows that the MAP-3 XRF analyzer is well suited for rapidly determining if either lead or mercury exists on or near the surface in high concentrations (percent levels). This system has several features that are not currently matched by other commercially available portable XRF spectrometers, most importantly the use of a Co-57 source. This source, coupled with the instrument's capability for rapid analyses and a complete spectral display of both the K and L lines of energy for these two metals, not only provides immediate information as to the concentrations present, but their location within the first 1.5 cm of the surface as well. In addition, the manufacturer can provide calibrations for Hg in soil upon request.

The design of this instrument is well suited for in-situ manual operations and could also be adapted for robotic implementation. Two likely adaptations are increasing the distance between the scanner and analyzer console by acquiring a longer connecting cable and changing the software to allow for rapid quantification of both the K and L lines for both of Pb and Hg in soil matrices, as currently performed for the analysis of Pb in paint.

Sensitivity of XRF analysis increases with length of analysis up to a period of several minutes. Unique to this system (Co-57 source) is that not only does the ability to detect lower concentrations at the immediate surface increase with analysis time, but the ability to detect aggregates within the first 1.5 cm also increases. If site plan objectives call for detection of percent levels on the surface, then a 10-s analysis period is sufficient. However, if the first 1.5 cm is of concern, then measurement periods of 1.5 minutes or longer are necessary. The use of portable XRF systems that cannot be equipped with a Co-57 source for screening sites for primary explosives is not recommended.

LITERATURE CITED

Garby, J.C. (1991) Comparison of mobile laboratory XRF and CLP split sample lead results from a superfund site remediation in New Jersey. In *Proceedings of the 2nd International Symposium Field Screening for Hazardous Waste and Toxic Chemicals, 12–14 February, Las Vegas, Nevada*. ICAIR, Life Systems, Inc., p. 671–672.

Puls, R., D.A. Clark, C. Carlson, and J. Vardy (1994) Characterization of chromium-contaminated soils using field-portable X-ray fluorescence. *Ground Water Monitoring and Remediation*, Summer, p. 111–115.

Schneider, J.F., J.D. Taylor, D.A. Bass, S.D. Zellmer, and M. Rieck (1995) Evaluation of a field-portable X-ray fluorescence spectrometer for the determination of lead contamination in soil. *American Environmental Laboratory*, **6**(10): 35–36.

Spittler, T.M., and W.A. Fender (1979) A study of soil contamination and plant lead uptake in Boston urban gardens. *Communications in Soil Science and Plant Analysis*, **10**(9): 1195–1210.

US EPA (1986) *Test Methods for Evaluating Solid Waste*. U.S. Environmental Protection Agency, vol. 1B, SW-846.

Workman, W.R. (1994) Reactivity testing of primary explosives in soil, final report. Global Environmental Solutions, Inc., Roy F. Weston, Inc., U.S. Army Environmental Center Report No. SFIM-AEC-TS-CR-94057.

Yinon, J., and S. Zitrin (1981) *The Analysis of Explosives*. New York: Pergamon Press, Inc., Maxwell House.

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U.S. Army Cold Regions Research and Engineering Laboratory
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13. ABSTRACT (*Maximum 200 words*)

X-ray fluorescence spectrometry (XRF) analysis is a practical means of performing in-situ screening to establish the presence of high concentrations (>0.1% or 1000 ppm) of lead (Pb) and/or mercury (Hg). These two metals are of special military interest because they are constituents in three primary explosives; lead azide [$Pb(N_3)_2$], lead styphnate ($C_6HO_6N_3Pb$), and mercury fulminate [$Hg(CNO)_2$]. The success of in-situ XRF analysis to perform this task depends on instrumental sensitivity, selectivity, effective sample volume, transportability, and user friendliness. Laboratory experiments established that the MAP-3 XRF spectrum analyzer (SCITEC Corporation) is well-suited for this application. This instrument is self-contained, portable, and equipped with a Co-57 source that allows for a simultaneous analysis of both the K and L energy lines of Pb and Hg, among other metals. Laboratory experiments established that high concentrations of Pb and Hg could be detected in an active sample area of cylindrical shape, approximately 1.0 cm in diameter and 1.5 cm in depth.

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