SPECIAL REPORT 95-14

Rapid Screening of Metals Using Portable High-Resolution X-Ray Fluorescence Spectrometers

Alan D. Hewitt

April 1995

Abstract

Analysis of copper, zinc, arsenic, lead, chromium, cobalt, nickel, mercury, thallium, selenium, silver, antimony, cadmium, tin, and barium was performed on soils and other particle matrices using two field-portable high-resolution X-ray fluorescence spectrometers (XRF). Quantitative determinations were based on fundamental parameter analysis and a second method that relies on analyte response factors and uses the Compton K_α incoherent backscatter peak for matrix normalization. These two methods of instrumental analysis require only a few reference materials and are relatively insensitive to sample matrix composition. This study assessed the capability of these two rapid XRF analysis methods by determining metal concentrations in reference materials, field samples, and laboratory spiked soils. With the exception of nickel, cobalt, and chromium, concentrations within 50% of the expected values were consistently obtained at and below 1000 μg/g.

For conversion of SI units to non-SI units of measurement consult ASTM Standard E380-93, *Standard Practice for Use of the International System of Units,* published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

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US Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

Rapid Screening of Metals Using Portable High-Resolution X-Ray Fluorescence Spectrometers

Alan D. Hewitt

April 1995

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PREFACE

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

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Rapid Screening of Metals Using Portable High-Resolution X-Ray Fluorescence Spectrometers

ALAN D. HEWITT

INTRODUCTION

Metal pollution over the past decade has come to be of greater concern due to an increasing awareness of the pathways leading to chronic human toxicity (Spittler and Fender 1979). During this time the use of X-ray fluorescence (XRF) analysis has increased for establishing the presence of elevated levels of metals in environmental samples (e.g., Furst et al. 1985, Piorek and Rhodes 1988, Grupp et al. 1989, Watson et al. 1989, Ashe et al. 1991, Carlson and Alexander 1991, Driscoll et al. 1991, Garby 1991, Harding 1991, Puls et al. 1994, etc.). This instrumental method of analysis establishes concentration estimates for several metals over a concentration range extending from percent levels to around 100 µg/g (ppm). The method requires little or no sample pretreatment and can be performed for a small fraction of the time and cost associated with acid extraction/atomic absorption or emission analysis. Moreover, XRF analysis is nondestructive, so subsamples can be archived or analyzed by other procedures. For these reasons, XRF analysis is a very practical and economical method when screening for high concentrations of metals during a remedial investigation and feasibility study (RI/FS) at a suspected hazardous waste site.

Today several manufacturers offer energy-dispersive XRF spectrometers that have been designed to be compatible with field operations. The most transportable systems have a battery power supply option and use one or more radioactive sources as the primary incident radiation for elemental excitation. The first generation of these stand-alone systems was equipped with gas proportional detectors that had a spectral resolution on the order of 800–1000 electron volts (1000 eV = 1 keV). More recently, systems have been marketed (HNU Systems Inc., Spectrace Instruments, Inc., Metorex, Inc.) with silicon (drifted with lithium) [Si(Li)] or mercuric iodide (HgI_2) detectors capable of achieving resolutions of 170 and 300 eV, respectively. This increased spectral resolution allows for the unambiguous qualitative identification of metals in complex mixtures.

Quantitatively, however, the measurement of discrete spectral energies obtained by XRF analysis is often dependent on other metals present in the sample, due to absorption and enhancement effects. For environmental sample analysis, these matrix-specific effects are best addressed by the use of empirical coefficients (Piorek and Rhodes 1988). This method of instrumental calibration requires the acquisition or development of several well-characterized materials with a matrix composition similar to that of the samples. Moreover, the standards should contain a range of metal concentrations bracketing the desired level of quantitation. Due to these requirements, calibration standards are often both material and site specific, and their preparation and/or verification may take one or more weeks.

A more practical solution for an initial site investigation would be a calibration method that is insensitive to sample matrix so that only few standards would be needed to handle a diverse range of samples (e.g., soil composition "sand/slit/clay," sediment, sludge, dust, paint chips, etc.). Ideally, this capability would allow samples to be analyzed independent of any previous site characterization. With this concept in mind, two quantitation routines have been proposed for field-transportable high-resolution XRF systems. One routine is based on fundamental parameters (FP) analysis, which eliminates the need for several calibration standards by relying on certain physical constants to estimate metal concentration while theoretically correcting for matrix discrepancies (Figura 1987, 1993). Another approach uses response factors (RF)

and corrects for matrix discrepancies by normalizing to the Compton K_α (Comp. K_α) incoherent radiation backscatter peak.*

This study evaluates these two methods of rapid sample analysis by determining the concentrations of copper (Cu), zinc (Zn), arsenic (As), lead (Pb), chromium (Cr), cobalt (Co), nickel (Ni), mercury (Hg), thallium (Tl), selenium (Se), silver (Ag), antimony (Sb), cadmium (Cd), tin (Sn), and barium (Ba) in a variety of solid-particle matrices. All analyses are performed with transportable high-resolution XRF systems that can be configured for stand-alone operations. This combination of rapid sample analysis and instrumental transportability is well suited for screening purposes, thus a data quality objective of an accuracy of ±50% and detection limits of less than 1000 µg/g was used (Raab et al. 1987).

INSTRUMENTATION

Explanations of the principals of XRF analysis can be found elsewhere (Driscoll et al. 1991, Hewitt 1994a, b). The instruments used in this study were the X-Met 920 (Metorex, Inc.; formerly Outokumpu Electronics) and the Spectrace 9000 (Spectrace Instruments) X-ray spectrophotometers. These two field-portable systems are equipped with surface analysis probes allowing for either in situ or intrusive sample analysis and have software-supported FP analysis capabilities. The Spectrace 9000 is equipped with three primary radioactive sources, Fe-55, Cd-109, and Am-241, and has a HgI_2 solid-state detector. The X-Met 920 has two radioactive sources, Cd-109 and Am-241, and has a Si(Li) detector that requires liquid N_2 for operation. Table 1 lists some of the metals that can be determined by these XRF systems. The table also shows those metals that could be quantitated by FP software programs supplied by the respective manufacturers.

CALIBRATION

The FP software routines used in this study are proprietary to the instrument manufacturer. In general, these FP programs are a series of algorithms based on intensities measured for pure elements, sensitivity coefficients, summations of absorption-enhancement terms in appropriate matrices, and correction factors for overlapping peaks (Figura 1987). The X-Met 920 FP program also required the analysis of a fully characterized standard material, which for this study was SRM 2710, from the National Institute of Science and Technology (NIST).

To perform the RF/Comp. K_α normalization analysis, a standard must be available that contains the analytes of interest in a matrix that is physically consistent (dry particles) with the samples. When possible, the RF should be established for well resolved K_α, K_β, L_α, or L_β spectral lines (Table 1). Figure 1 is an example of an XRF spectrum obtained with the X-Met 920 showing several characteristic peaks for metals along with the incoherent (Compton) and coherent (Rayleigh) sample matrix backscatter.

For this study a finely ground soil, SRM 2710 certified reference soil from NIST, was used to establish the analyte RFs for Cu, Zn, As, and Pb. Table 2 is an example of some of the daily RFs established for these four metals. For the determination of Cr, the NIST SRM 2711 was spiked with 4000 µg

Table 1. Primary sources and analyte lines for metals of environmental concern that can be detected by X-ray fluorescence spectrometry.

		Emission lines (keV)			
Source	*Metals*	K_α	K_β	L_α	L_β
FE-55	Cr†	5.41	5.95		
Cd-109	Cr†*	5.41	5.95		
Cd-109	Mn†	5.89	6.49		
Cd-109	Fe†*	6.40	7.06		
Cd-109	Co†	6.92	7.65		
Cd-109	Ni†	7.47	8.30		
Cd-109	Cu†*	8.04	8.94		
Cd-109	Zn†*	8.63	9.61		
	As†*	10.5	11.8		
Cd-109	Se†	11.2	12.6		
	Hg†			9.98	11.9
Cd-109	Tl			10.3	12.3
	Pb†*			10.5	12.6
Am-241	Ag†	22.1	25.2		
Am-241	Cd†	23.1	26.4		
Am-241	Sn†	25.2	28.8		
Am-241	Sb†	26.2	30.1		
Am-241	Ba†	32.0	36.8		

† Spectrace 9000 preprogrammed for fundamental parameter analysis of this metal.

* X-Met 920 preprogrammed for fundamental parameter analysis of this metal.

* T.M. Spittler, U.S. Environmental Protection Agency, Environmental Services Division, Region 1, Lexington, Massachusetts.

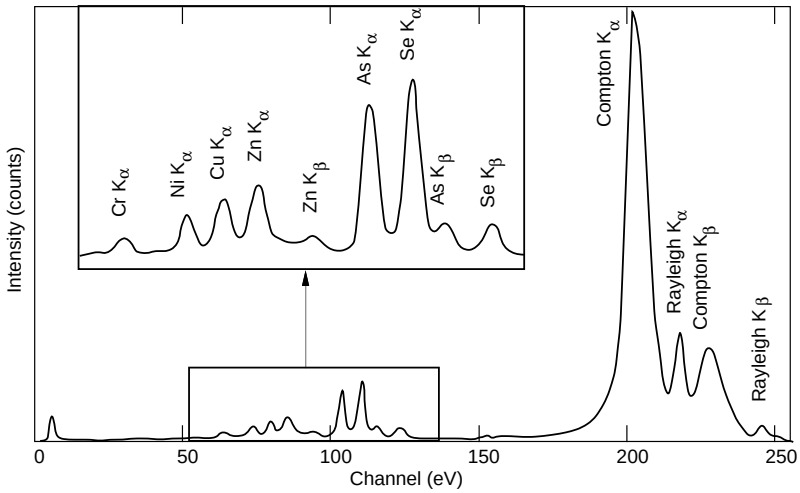

Figure 1. Spectrum of several characteristic K_α *and* K_β *peaks for metals and Compton and Rayleigh backscatter.*

Table 2. Daily response factors established for Cu, Zn, As, and Pb based on the SRM 2710 certified reference material.

	Response factor (intensity/concentration)			
	Cu	*Zn*	*As*	*Pb*
	12.0	33.9	1.09	39.5
	11.9	34.8	0.90	38.0
	12.3	34.4	1.04	39.6
Average	12.1	34.4	1.01	39.0
Std. dev.	0.21	0.45	0.098	0.90
% RSD	1.7	1.3	9.7	2.3
	SRM 2710 concentration (µg/g)			
	2950	6952	626	5532

Cr/g, to establish an RF. All of the other metals analyzed were quantified relative to RFs obtained for the Rocky Mountain Arsenal (RMA) soil matrix spiked with 1000 µg metal/g. Even with a high-resolution XRF instrument, the As K_α and Pb L_α lines (10.532 and 10.549 keV, respectively) overlap, so the As K_β and Pb L_β peaks were used. In addition, because high levels (>0.4%) of Fe were present in many of the laboratory-treated soil matrices, the Fe K_β peak (7.06 keV) had to be subtracted from the Co K_α peak (6.92 keV), due to a spectral overlap. In the case of Co, the K_β line was not used because of insufficient response (intensity).

ANALYSIS

Only intrusive sample-analysis procedures were used in this study. Samples consisted of 2- to 5-gram quantities of air-dried materials with particle sizes averaging <600 µm in diameter. All samples were placed into 31-mm-diameter cups and covered with a 0.2-mil polypropylene X-ray film window. XRF analyses were performed for a period of 300 seconds. Field operations using these two preparation steps, i.e., drying and sieving, have shown that up to a hundred samples can be processed and analyzed within a single day (Grupp et al. 1989, Garby 1991).

Fundamental parameter sample analysis was performed using both XRF instruments after the selection of the appropriate software application and assessing the instrumental tuning. For the Spectrace 9000 this involved checking the resolution and the background response with supplied reference materials and selecting the fine particle application. The FP software application supplied with the X-Met 920 system was based upon the analysis and total characterization of the finely ground NIST SRM 2710.

The RF/Comp. K_α normalization analysis method was only performed with the X-Met 920. To perform this method of analysis, the energy spectrum from each analysis was saved and transformed from a 2048- to a 256-channel spectrum for close examination. This approach was used because it was easier to measure the intensity of smoothed peaks and, once transformed, up to six spectra could be overlaid. Measurements included the intensity of elemental spectral lines and the intensity of the incoherent radiation backscatter peak (Comp. K_α). The intensity of the incoherent radiation backscatter reflects both the composition of light elements (e.g. carbon, nitrogen, silicon, etc.) in the sample matrix as well as the overall concentration of detectable analytes (Nielson and Sanders 1983). Intensities of both the baseline and peaks of interest were recorded from the computer display after selecting the appropriate spectrum channels. Concentration estimates were then manually determined by multiplying the baseline-corrected analyte signal intensity by the normalization factor, followed by the response factor. The normalization factor is the quotient of the Compton K_α peak intensity of the certified reference material, divided by that of the samples. A more complete

description of this analysis has been published elsewhere (Hewitt 1994a, 1994b).

EXPERIMENTAL

Several reference materials of different solid-waste matrices, along with field-contaminated and laboratory-treated soils, were analyzed to assess the performance of both the FP and RF/Comp. K_α normalization.

Reference materials

Table 3 lists the certified reference materials purchased from NIST and the Resource Technology Corporation (RTC). Those purchased from NIST have certified concentrations for the total amount of metal present, whereas the RTC materials report certified values based on the USEPA SW846, 3000-series metal acid extraction procedures (U.S. EPA 1986).

Field samples

Six river sediment subsamples from a suspected hazardous-waste site were analyzed. These field subsamples were taken from thoroughly homogenized samples that had been previously characterized by inductively coupled plasma (ICP) analysis following 3000-series metal acid extraction procedures (U.S. EPA 1986).

Treated laboratory soils

Six different soils were spiked with Cr, Cu, Zn, As, Pb, Ni, Se, Hg, Tl, Co, Ag, Cd, Sn, Sb, and Ba by using concentrated 10,000 mg/L aqueous pure element atomic absorption standards (AESAR/Alfa, Johnson Matthey). A complete description of how these soil subsamples were treated has been presented elsewhere (Hewitt 1994b). The soil characteristics and the weight of the treated subsamples are shown in Table 4.

Briefly, the soils were air dried and thoroughly mixed prior to placing subsamples into 31-mm-diameter analysis cups. Analyte spikes were made by pipetting between 0.4 and 0.025 mL quantities of the aqueous standards directly onto the individual soil subsamples, increasing the metal concentration by 1000, 500, 250, 125, or 0 µg/g. Only five analytes were applied to a set of five replicate soil subsamples in order to limit the total volume of solution added to each subsample (0.2 mL/g). Following this protocol, one set of 30 soil subsamples (5 × 6) was spiked with Cr, Cu, Zn, As, and Pb, a second with Ni, Se, Hg, Tl, and Co, and a third with Ag, Cd, Sn, Sb, and Ba. Analyte additions were performed so that a given soil subsample was not treated with the same concentration more than once (Table 5). A sixth untreated subsample of each soil type was also analyzed with each group and served as the matrix blank.

Table 3. List of certified reference materials.

National Institute of Standards and Technology
SRM 1645—River sediment
SRM 1646—Estuarine sediment
SRM 1579a—Powdered lead-based paint
SRM 2704—Buffalo River sediment
SRM 2709—San Joaquin soil
SRM 2710—Montana soil
SRM 2711—Montana soil
Resource Technology Corporation
CRM012—Incinerated sludge
CRM014—Baghouse dust
CRM013—Paint chips
CRM020—Soil (from EPA Superfund site)
CRM021—Soil (from contaminated waste site)

Table 4. Characteristics of laboratory-treated soils.

Matrix	*Sand (%)*	*Silt and clay (%)*	*Grain size* (µm)*	*Wt.† (g)*
Ottawa sand	100		400	4
Rocky Mountain Arsenal	NA	NA	NA	4
Lebanon landfill	45	55	300	4
CRREL soil	NA	NA	NA	4
Tampa Bay sediments	95	5	200	4
Ft. Edwards clay	30	70	30	2

* 95% cut off
† Weight of soil subsample spiked
NA Not analyzed

RESULTS AND DISCUSSION

Table 6 lists the estimates of detection reported by the manufacturers for FP analysis, along with some values established using the RF/Comp. K_α normalization and method detection limit (MDL) (Federal Register 1984). This table also includes the analyte intensities measured for the RMA soil treated with 1000 µg metal/g. These intensities were included to provide a means of predicting a detection limit, based on the assumption that there is a fairly constant inverse relationship between these two parameters. This table indicates that regardless of the method of analysis, all of these

Table 5. Treatment scheme for spiking soil subsamples with metals.

Sets	*Metal groups*				
1	Cr	Cu	Zn	As	Pb
2	Ni	Se	Hg	Tl	Co
3	Sb	Ag	Ba	Cd	Sn
	Treatment concentrations				
Subsample					
S1	1000*	125	0	500	250
S2	500	250	1000	0	125
S3	250	0	125	1000	500
S4	125	1000	500	250	0
S5	0	500	250	125	1000
Matrix blank	NF	NF	NF	NF	NF

* µg/g
NF Not fortified

Table 6. Detection limit estimates and intensity counts.

		Detection limits (µg/g)			
Source	*Metal*	*Spectrace 9000**	*X-Met 920†*	*RF/ Compt.***	*Peak intensity*†*
FE-55	Cr	180	—	—	—
Cd-109	Cr	525	325	270	1.18
Cd-109	Mn	410	225	—	—
Cd-109	Fe	225	200	—	—
Cd-109	Co	205	180	—	1.33
Cd-109	Ni	125	175	—	3.82
Cd-109	Cu	90	175	54	6.58
Cd-109	Zn	70	160	90	6.47
Cd-109	As	50	140	42	3.18
Cd-109	Se	35	140	—	18.0
Cd-109	Hg	60	—	—	5.33
Cd-109	Tl	—	—	—	7.83
Cd-109	Pb	30	—	48	8.34
Am-241	Ag	—	70	—	25.9
Am-241	Cd	180	100	—	24.6
Am-241	Sn	100	80	—	27.1
Am-241	Sb	65	80	—	33.5
Am-241	Ba	20	100	—	31.4

* Minimum detection limit
† Minimum determination limit
** Method detection limit
*† Matrix-corrected peak intensity for 1000-ppm spiked RMA soil

metals should be easily quantitated below 1000 µg/g by XRF analysis.

Tables 7 and 8 show the concentration estimates obtained for the commercial reference materials by these two methods of rapid sample analysis. These two tables show results for Cu, Zn, As, and Pb when the certified concentration was above one of the estimates of detection listed in Table 6. In only two cases were the values established by the RF/Comp. K_α normalization method off by more than ±50% from the certified values. An apparently high concentration was established for Cu in the CRM 021 soil, and a low one for the SRM 2704 river sediment. Fundamental parameter analysis with the Spectrace 9000 XRF failed to establish concentrations within ±50% six times, twice each for Cu, As, and Pb. No values were obtained for Cu in the SRM 2704 river sediment and SRM 2711 soil, while low determinations of As occurred for both the SRM 2710 soil and the CRM 020 soil, and high estimates were obtained for Pb in the CRM 013 paint chips and the CRM 014 baghouse dust. The FP determinations made with the X-Met 920 failed to meet this criterion in only three cases. A low value was established for As in the CRM 020 and high values for Pb in both the CRM 013 paint chips and the CRM 014 baghouse dust.

The high values obtained for the CRM reference materials by these two methods of XRF analysis are not necessarily incorrect, since the certified value is based on an acid extraction that does not necessarily represent the total amount present. However, a low determination for these standards, or one that fails to be within ±50% of the value stated for the NIST reference materials, would be aberrant. The low As concentrations determined by FP analysis had previously been identified as a problem when samples contain much larger (>10 times) quantities of Pb (Harding 1991). The false-negative Cu determinations were only for samples with certified concentrations very close to the estimates of detection. Overall, these two rapid methods of analysis showed that they were fairly insensitive to this wide variety of particulate matrices by establishing concentrations that would be appropriate for the data quality objectives stated.

Table 9 shows XRF concentration estimates obtained for Cu, Zn, and Pb along with the values obtained by acid-extraction/ICP analysis. The FP analysis was only performed with the X-Met 920 XRF analyzer. In those cases where the values obtained by acid-extraction/ICP analysis were above the appropriate estimate of detection (Table 6), only Cu in sample A and Zn in sample F had XRF estimates that were off by more than ±50%. A high Cu value was established by RF/Comp. K_α normalization analysis, and a high Zn value was established by FP analysis. Again, since these reported estimates were higher than those obtained after acid extraction and ICP analysis, which is not nec-

essarily a total concentration, the XRF values may not be incorrect.

The concentration estimates for Cu, Zn, As, Pb, Cr, Co, Ni, Hg, Tl, Se, Ag, Cd, Sn, Sb, and Ba in the laboratory-spiked soil subsamples appear in Tables 10 through 15. Tables 10–12 show the values for RF/Comp. K_α normalization analysis, and Tables 13–15 show the values for FP analysis using the Spectrace 9000 XRF analyzer. In addition to these metals that were spiked onto the soils, values for iron (Fe) determined by FP analysis are reported in Table 14. Thallium was not determined by FP analysis because this metal had not been included in the software program. All of these concentration estimates were established by using either Cd-109 or Am-241 incident radiation (Table 1).

The values in these tables were corrected for background concentrations present in the soil matrix and for spectral overlap interferences. These corrections were made when both the subsample in the treatment set (Table 5) with no spiked analyte and the subsample of the untreated matrix were determined to have concentrations that exceeded the respective estimates of detection listed in Table 6. However, in cases where there was no estimate of detection for the RF/Comp. K_α normalization method of analysis, the lowest value appearing in this table was used. Corrections for Cu, Zn, and Ba were necessary because these metals were present at detectable levels in some of the soil matrices. Corrections were required for Co because of a spectral overlap with the K_β peak of Fe and for Ag due to spectral overlap with a peak characteristic of the Am-241 primary radiation source.

Table 7. Analysis of commercial reference materials from the National Institute of Standards and Technology.

	Metal concentrations (μg/g)			
Standard	*Cu*	*Zn*	*As*	*Pb*
SRM 1645	109**	1720**		714**
river sediment	[72]	[1900]		[638]
	114*	1760*		606*
SRM 1646		138**		
estuarine sediment		[127]		
SRM 1579a				119,950**
lead-based paint				[160,000]
				144,000†
				124,000*
SRM 2704	99**	438**		161**
river sediment	[31]	[302]		[130]
	ND†	464†		133†
		527*		200*
SRM 2709 soil		106**		
		[91]		
		129†		
SRM 2710 soil	2950**	6952**	626**	5532**
	3350†	7570†	149†	6240†
SRM 2711 soil	114**	350**	105**	1162**
	[167]	[343]	[138]	[1100]
	ND†	410†	ND†	1280†
		414*		1210*

** Certified concentration
[ ] Concentration estimate based on response factor/Compton K_α peak normalization with X-Met 920
† Concentration estimate based on fundamental parameter analysis with Spectrace 9000
* Concentration estimate based on fundamental parameter analysis with X-Met 920
ND Not detected

Table 8. Analysis of commercial reference materials from the Resource Technology Corporation.

	Metal concentrations (μg/g)			
Standard	*Cu*	*Zn*	*As*	*Pb*
CRM012	3015**	635**		120**
incinerated	[2470]	[342]		[114]
sludge	3590†	744†		126†
	3340*	525*		60*
CRM 013				643**
paint chips				[460]
				2160†
				998*
CRM 014				1914**
baghouse dust				[2080]
				5360t
				4925*
CRM 020 soil	753**	3021**	397**	5195**
	[687]	[4420]	[429]	[5070]
	521†	3550†	113†	4580†
	684*	3898*	126*	4950*
CRM 021 soil	5086**	574**		
	[8720]	[549]		
	3060†	408†		

** Certified concentration
[ ] Concentration estimate based on response factor/Compton K_α peak normalization with X-Met 920
† Concentration estimate based on fundamental parameter analysis with Spectrace 9000
* Concentration estimate based on fundamental parameter analysis with X-Met 920
ND Not detected

Table 9. Concentrations (μg/g) of Cu, Zn, and Pb determined for field soil samples.

	Metal concentrations (μg/g)		
Field samples	*Cu*	*Zn*	*Pb*
A	114**	1140**	253**
	[176]	[1260]	[229]
	286*	1500*	318*
B	776**	1390**	488**
	[756]	[1310]	[473]
	984*	1810*	614*
C	1860**	261**	2060**
	[1750]	[182]	[1650]
	1600*	220*	1600*
D	3960**	735**	546**
	[3270]	[408]	[475]
	3510*	688*	494*
E	449**	1260**	350**
	[443]	[1230]	[328]
	567*	1710*	416*
F	104**	182**	87**
	[145]	[200]	[108]
	331*	391*	245*

** Concentrations based on acid-extraction/ICP analysis

[ ] Concentration estimate based on response factor/Compton K_α peak normalization with X-Met 920

* Concentration estimate based on fundamental parameter analysis with X-Met 920

This study of laboratory-spiked soils was included because commercial reference materials typically contain only a few metals (e.g., Cu, Zn, Pb) at concentrations that can be readily detected by XRF analysis. The soil spiking method used (Hewitt 1994b) appears to have resulted in fairly homogenous and accurate analyte concentrations, as shown by Figures 2 and 3. Plots of the results of Pb and Sb were chosen to show this feature because XRF analysis is particularly sensitive for these two metals (Table 6), and they are representative of metals excited by the Cd-109 and Am-241 primary sources, respectively. It is logical to assume that the other metals spiked onto the different soil matrices were likewise evenly distributed.

The results in Tables 10–15 show that these two methods of rapid sample analysis consistently established concentrations for Cu, Zn, Pb, Se, Ag, Sn, Sb, and Ba that were within ±50% of the expected values from 1000 to 125 ppm. This was also the case for Hg as determined by RF/Comp. K_α normalization analysis. The few aberrant values for Hg, as established by FP analysis with the

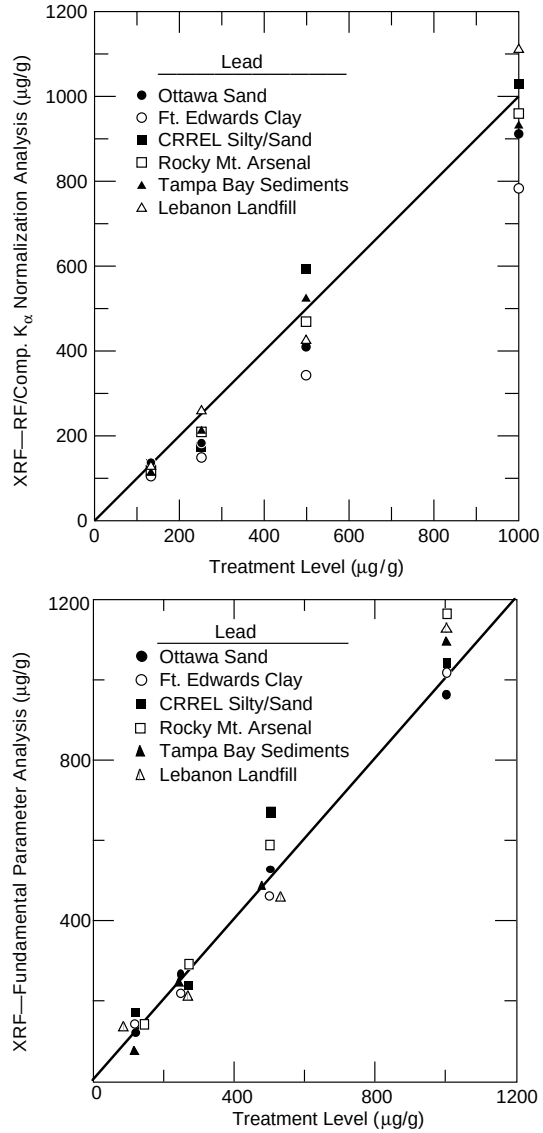

Figure 2. Lead concentrations (μg/g) established for spiked soils by both RF/Comp. K_α normalization and FP analysis.

Spectrace 9000, were most likely caused by a peak overlap with Tl. This problem occurred because Tl had not been one of the metals included in the FP software. With the exception of a few values established for the two lowest treatment levels for As and Cd (and Tl by RF/Comp. K_α) these metals were also within the ±50% concentration criterion. Clearly, the concentrations of all of these metals can be adequately estimated at 1000 μg/g and below by these two rapid methods of XRF analysis. Furthermore, since both methods established concentration trends that were consistent with the treatment levels, they would correctly define the areas of greatest concern.

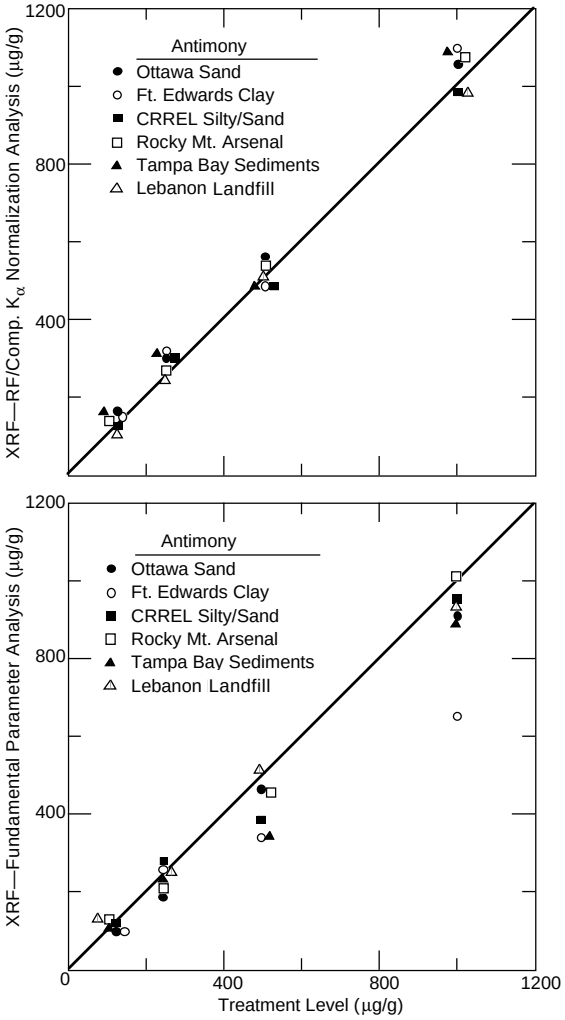

Figure 3. Antimony concentrations (µg/g) established for spiked soils by both RF/Comp. K_α normalization and FP analysis.

Table 10. Concentrations (µg/g) of Cr, Cu, Zn, As, and Pb determined for spiked soil matrices by response factor/ Compton K_α peak normalization.

	Metal concentrations (µg/g)				
Material & spike	*Cu*	*Zn*	*As*	*Pb*	*Cr*
Ottawa sand					
1000 ppm	1010*	1020	1420	911	1770
500 ppm	534*	458	381	411	856
250 ppm	264*	224	324	182	312
125 ppm	132*	127	72	139	84
0 ppm	69	ND	ND	ND	ND
Matrix	64	18	ND	10	ND
Ft. Edwards clay					
1000 ppm	711*	751*	906	785	979
500 ppm	289*	374*	491	344	638
250 ppm	144*	252*	229	150	175
125 ppm	142*	91*	104	108	304
0 ppm	199	81	ND	19	46
Matrix	218	80	ND	4	ND
CRREL soil					
1000 ppm	787*	870	782	1030	1100
500 ppm	461*	541	635	597	439
250 ppm	250*	247	320	178	220
125 ppm	69*	152	26	130	250
0 ppm	86	48	48	ND	93
Matrix	62	59	ND	18	257
Rocky Mountain Arsenal					
1000 ppm	897*	1050	1450	960	1160
500 ppm	483*	459	608	470	493
250 ppm	209*	245	304	211	349
125 ppm	93*	153	105	125	229
0 ppm	76	ND	37	ND	205
Matrix	62	2	41	23	ND
Tampa Bay sediments					
1000 ppm	842*	939	1350*	936	1570
500 ppm	513*	486	560*	526	653
250 ppm	250*	218	200*	219	639
125 ppm	103*	159	73*	124	219
0 ppm	60	11	220	7	120
Matrix	71	ND	249	ND	99
Lebanon landfill soil					
1000 ppm	859*	872	988	1192	1500
500 ppm	373*	469	536	423	495
250 ppm	195*	224	305	264	407
125 ppm	94*	140	78	135	326
0 ppm	99	2	ND	ND	ND
Matrix	70	8	ND	24	ND

* Average of 0 ppm and matrix subsamples subtracted

The remaining metals in this study, Ni, Co, and Cr, required additional qualifications because their estimates of detection precluded some of the lower laboratory treatment levels. For instance, Ni and Co could only be assessed for spiked concentrations that were >205 ppm (µg/g), likewise Cr for concentrations >525 ppm and >270 ppm for FP and the RF/Comp. K_α analysis, respectively. Values for all three of these metals were established by both methods of analysis that failed to meet the ±50% concentration criterion. High concentration estimates tended to be established for both Ni and Co by FP analysis in soils with low Fe content (Table 14). In contrast, low concentrations of these two metals were established by RF/Comp. K_α normalization analysis when high levels of Fe were present. Both methods of analysis tended to establish high estimates for Cr for soil matrices with low Fe content. Even though this apparent matrix effect was not adequately handled by either of these two methods of analysis to meet the ±50% criterion consistently, the appropriate concentration trends were established.

Table 11. Concentrations (μg/g) of Co, Ni, Hg, Tl, and Se determined for spiked soil matrices by response factor/ Compton K_α peak normalization.

	Metal concentrations (μg/g)				
Material & spike	*Co*	*Ni*	*Hg*	*Tl*	*Se*
Ottawa sand					
1000 ppm	1250	1230	758	909	977
500 ppm	539	609	471	532	502
250 ppm	267	290	149	421	231
125 ppm	199	90	132	225	89
0 ppm	ND	ND	13	52	ND
Matrix	ND	ND	ND	13	ND
Ft. Edwards clay					
1000 ppm	200*	496	623	813	675
500 ppm	50*	260	268	482	449
250 ppm	ND*	187	145	347	136
125 ppm	ND*	90	120	199	73
0 ppm	6500	45	ND	63	ND
Matrix	6300	16	ND	ND	ND
CRREL soil					
1000 ppm	390*	761	823	993	882
500 ppm	ND*	356	323	553	519
250 ppm	180*	93	141	330	238
125 ppm	ND*	15	110	225	128
0 ppm	4050	ND	43	66	8
Matrix	4070	ND	ND	ND	ND
Rocky Mountain Arsenal					
1000 ppm	560*	947	933	1030	977
500 ppm	270*	481	395	545	483
250 ppm	60*	298	179	449	211
125 ppm	50*	86	161	216	111
0 ppm	1580	12	21	33	ND
Matrix	1680	ND	ND	12	ND
Tampa Bay sediments					
1000 ppm	846*	962	933	997	1010
500 ppm	482*	457	395	519	460
250 ppm	178*	315	179	425	221
125 ppm	103*	129	161	199	124
0 ppm	193	22	21	73	ND
Matrix	135	ND	ND	7	11
Lebanon landfill soil					
1000 ppm	435*	838	550	996	968
500 ppm	395*	470	472	460	511
250 ppm	135*	179	207	435	192
125 ppm	85*	88	148	253	123
0 ppm	2260	ND	21	45	ND
Matrix	2170	ND	ND	14	ND

* Average of 0 ppm and matrix subsamples subtracted

Table 12. Concentrations (μg/g) of Ag, Cd, Sn, Sb, and Ba determined for spiked soil matrices by response factor/Compton K_α peak normalization.

	Metal concentrations (μg/g)				
Material & spike	*Ag*	*Cd*	*Sn*	*Sb*	*Ba*
Ottawa sand					
1000 ppm	1170	1000	986	1060	1160
500 ppm	646	499	398	557	527
250 ppm	269	176	226	302	262
125 ppm	109	48	145	160	121
0 ppm	19	ND	97	ND	ND
Matrix	25	ND	25	12	ND
Ft. Edwards clay					
1000 ppm	1032*	936	899	1080	996*
500 ppm	604*	334	447	495	496*
250 ppm	297*	162	248	317	288*
125 ppm	166*	42	146	152	163*
0 ppm	312	ND	92	ND	703
Matrix	263	ND	26	20	665
CRREL soil					
1000 ppm	896*	1040	918	996	1030*
500 ppm	363*	531	459	493	489*
250 ppm	179*	253	286	295	273*
125 ppm	82*	153	142	142	118*
0 ppm	169	ND	81	ND	392
Matrix	159	ND	36	14	410
Rocky Mountain Arsenal					
1000 ppm	992*	984	745	1070	1060*
500 ppm	410*	416	418	538	530*
250 ppm	297*	142	246	274	220*
125 ppm	140*	42	155	143	130*
0 ppm	246	ND	95	ND	914
Matrix	230	ND	37	11	967
Tampa Bay sediments					
1000 ppm	1210*	1060	899	1080	1050
500 ppm	567*	488	447	495	596
250 ppm	368*	203	348	317	287
125 ppm	153*	94	146	152	152
0 ppm	167	ND	92	ND	28
Matrix	160	ND	26	20	29
Lebanon landfill soil					
1000 ppm	1040	1070	902	1060	990*
500 ppm	535	436	454	496	498*
250 ppm	314	297	248	304	247*
125 ppm	180	182	150	144	118*
0 ppm	49	36	90	ND	360
Matrix	55	72	31	15	439

* Average of 0 ppm and matrix subsamples subtracted

Several factors that control the sensitivity of elemental analysis by XRF analysis are independent of matrix composition. First of all, elements with low atomic numbers have low fluorescence yields (Fig. 4). The fluorescence yield is the ratio of number of vacancies created within an atom by the incident radiation to the number of vacancies that actually result in the production of characteristic X-ray photons (Jenkins 1986). In addition, since only a few isotopes are available for field-portable XRF systems, there can be a large separation between incident and excitation energies. The greater this separation, the lower the analyte response, because fewer atoms become excited. A third factor

Table 13. Concentrations (μg/g) of Cr, Cu, Zn, As, and Pb determined by fundamental parameter analysis using the Spectrace 9000.

	Metal concentrations (μg/g)				
Material & spike	*Cu*	*Zn*	*As*	*Pb*	*Cr*
Ottawa sand					
1000 ppm	1430	1320	1380	976	3010
500 ppm	731	652	389	531	1120
250 ppm	270	287	335	274	580
125 ppm	102	152	51	131	310
0 ppm	ND	ND	ND	ND	ND
Matrix	ND	ND	10	ND	ND
Ft. Edwards clay					
1000 ppm	1340	1140*	1020	1020	850
500 ppm	532	524*	660	467	300
250 ppm	334	192*	343	225	ND
125 ppm	227	147*	13	138	ND
0 ppm	131	99	ND	ND	ND
Matrix	67	99	66	ND	ND
CRREL soil					
1000 ppm	1130	1270*	1280	1040	940
500 ppm	489	550*	656	657	57
250 ppm	253	221*	311	232	53
125 ppm	77	120*	60	172	ND
0 ppm	ND	74	ND	ND	ND
Matrix	ND	95	56	ND	ND
Rocky Mountain Arsenal					
1000 ppm	1280	1240	1350	1170	1480
500 ppm	678	675	636	589	440
250 ppm	236	333	375	281	280
125 ppm	74	125	19	141	120
0 ppm	ND	ND	22	ND	ND
Matrix	ND	36	28	ND	ND
Tampa Bay sediments					
1000 ppm	1210	1250	1230	1100	1490
500 ppm	662	545	651	477	700
250 ppm	312	289	278	256	120
125 ppm	70	118	63	83	ND
0 ppm	ND	ND	12	ND	66
Matrix	ND	ND	23	ND	ND
Lebanon landfill soil					
1000 ppm	1130	1130	1110	1130	1350
500 ppm	584	613	567	460	450
250 ppm	316	327	332	218	150
125 ppm	71	133	59	130	ND
0 ppm	ND	13	11	ND	ND
Matrix	ND	22	43	ND	ND

* Average of 0 ppm and matrix subsamples subtracted

Table 14. Concentrations (μg/g) of Co, Ni, Hg, Se, and Fe determined by fundamental parameter analysis using the Spectrace 9000.

	Metal concentrations (μg/g)				
Material & spike	*Co*	*Ni*	*Hg*	*Se*	*Fe*
Ottawa sand					
1000 ppm	1830	1538	1010	1240	ND
500 ppm	994	846	781	637	79
250 ppm	442	427	228	307	67
125 ppm	109	183	380	143	120
0 ppm	ND	ND	111	ND	118
Matrix	ND	ND	ND	ND	1420
Ft. Edwards clay					
1000 ppm	727*	999	791	1100	55,400
500 ppm	277*	495	458	503	54,600
250 ppm	67*	207	200	265	56,700
125 ppm	ND*	12	360	120	57,000
0 ppm	560	ND	80	ND	55,600
Matrix	406	ND	ND	ND	56,900
CRREL soil					
1000 ppm	965*	1210	1321	1350	40,000
500 ppm	295*	624	665	611	40,900
250 ppm	235*	216	259	332	41,100
125 ppm	315*	148	155	146	41,100
0 ppm	190	11	95	ND	41,300
Matrix	280	ND	16	ND	40,900
Rocky Mountain Arsenal					
1000 ppm	1490	1480	1170	1390	18,600
500 ppm	900	786	736	689	19,600
250 ppm	479	324	301	304	22,500
125 ppm	224	141	579	140	21,700
0 ppm	ND	ND	121	ND	21,100
Matrix	ND	ND	ND	ND	20,100
Tampa Bay sediments					
1000 ppm	1710	1720	1350	1310	4410
500 ppm	738	687	728	758	4240
250 ppm	423	308	356	350	3930
125 ppm	198	152	529	185	3470
0 ppm	122	32	151	ND	3500
Matrix	24	ND	ND	ND	4190
Lebanon landfill soil					
1000 ppm	1330	1280	1040	1260	24,900
500 ppm	660	578	744	705	25,900
250 ppm	208	294	227	346	25,500
125 ppm	160	119	336	134	27,200
0 ppm	ND	ND	151	ND	25,600
Matrix	109	14	ND	ND	25,700

* Average of 0 ppm and matrix subsamples subtracted

is the depth of penetration achieved by the incident radiation, i.e., how much of the sample is actually analyzed. The penetration depth of incident radiation is inversely proportional to its wavelength and directly proportional to its energy. For the sources used in this study, the depth of penetration (99% attenuation) for a quartz matrix ranges from 40 mm for Am-241 to 4.8 mm for Cd-109. The combination of these factors controls the intensity that will be measured for a given element. For example, Table 6 shows the range of analyte intensities obtained for the same concentration in the RMA soil.

To illustrate the combination of these two ef-

Table 15. Concentrations (µg/g) of Ag, Cd, Sn, Sb, and Ba determined by fundamental parameter analysis using the Spectrace 9000.

Material & spike	*Metal concentrations (µg/g)*				
	Ag	*Cd*	*Sn*	*Sb*	*Ba*
Ottawa sand					
1000 ppm	937	1110	1000	915	772
500 ppm	504	581	429	474	353
250 ppm	274	394	269	196	174
125 ppm	193	229	174	109	75
0 ppm	77	111	43	ND	ND
Matrix	25	74	41	ND	ND
Ft. Edwards clay					
1000 ppm	820	976	857	654	601*
500 ppm	377	542	452	345	300*
250 ppm	197	361	226	261	215*
125 ppm	86	172	154	108	148*
0 ppm	ND	127	74	ND	379
Matrix	ND	100	81	17	436
CRREL soil					
1000 ppm	998	1060	1050	955	715*
500 ppm	508	584	527	490	381*
250 ppm	268	302	301	276	201*
125 ppm	191	225	153	122	92*
0 ppm	67	51	37	16	288
Matrix	40	99	28	ND	329
Rocky Mountain Arsenal					
1000 ppm	1060	1200	1040	1010	850*
500 ppm	535	613	486	562	472*
250 ppm	296	406	336	221	250*
125 ppm	190	253	194	133	105*
0 ppm	77	143	33	22	716
Matrix	37	80	58	14	734
Tampa Bay sediments					
1000 ppm	989	1141	1030	897	706
500 ppm	486	557	485	445	365
250 ppm	268	299	205	235	215
125 ppm	181	189	114	115	92
0 ppm	56	42	51	ND	ND
Matrix	56	84	55	12	ND
Lebanon landfill soil					
1000 ppm	914	1190	1020	930	832*
500 ppm	525	608	538	515	343*
250 ppm	301	337	287	259	232*
125 ppm	205	223	165	133	111*
0 ppm	39	66	41	ND	278
Matrix	ND	18	71	18	300

* Average of 0 ppm and matrix subsamples subtracted

fects, matrix composition and characteristic analyte response, Figure 5 shows the average concentration and standard deviations for the 1000 µg metal/g spiked soil matrices. Overall, both the precision and accuracy of analysis improves with atomic number. However, for Cr, Co, and Ni, the degree of bias and range of uncertainty shows that values

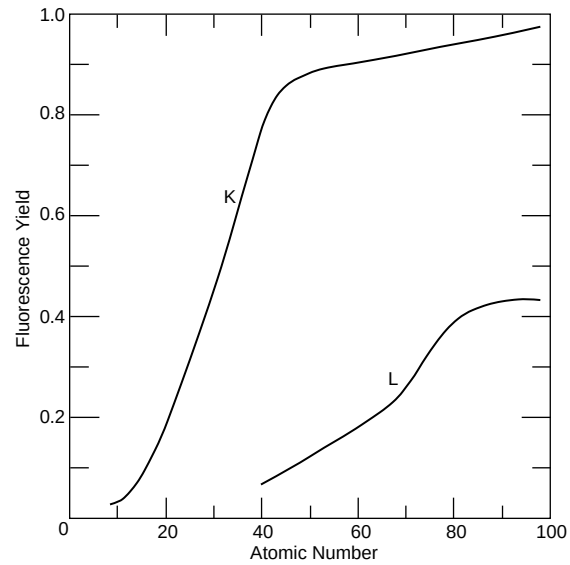

Figure 4. Fluorescence yield vs. atomic number for K *and* L *lines.*

even at this level can be greater than ±50% from the true concentration when analyzing a variety of soils. Most likely, the bias in the determined concentrations is the result of a matrix effect, while the extent of uncertainty is a function of both the matrix effect and the characteristic analyte response.

In summary, these two methods of rapid sample analysis with field-portable XRF systems often achieved the data requirement for screening of ±50% accuracy at and below a concentration of 1000 µg/g. This goal was accomplished for a variety of soil matrices, and the results in Tables 7–9 show that this approach is also promising for several other particulate matrices (e.g., sediment, dust, paint chips, and sludge). The determination of Ni, Co, and Cr, however, was not found to accomplish this goal consistently, even though reported estimates of detection for XRF analysis are well below 1000 µg/g. It appears that for analytes with poor XRF sensitivity, matrix effects are more problematic, and matrix-specific standards would be necessary to achieve a ±50% accuracy.

CONCLUSIONS

With the exception of Ni, Co, and Cr, the determination of Cu, Zn, As, Pb, Hg, Tl, Se, Ag, Cd, Sn, Sb, and Ba at and below 1000 µg/g in a variety of solid particulate materials was often within ±50% of the expected values when using either funda-

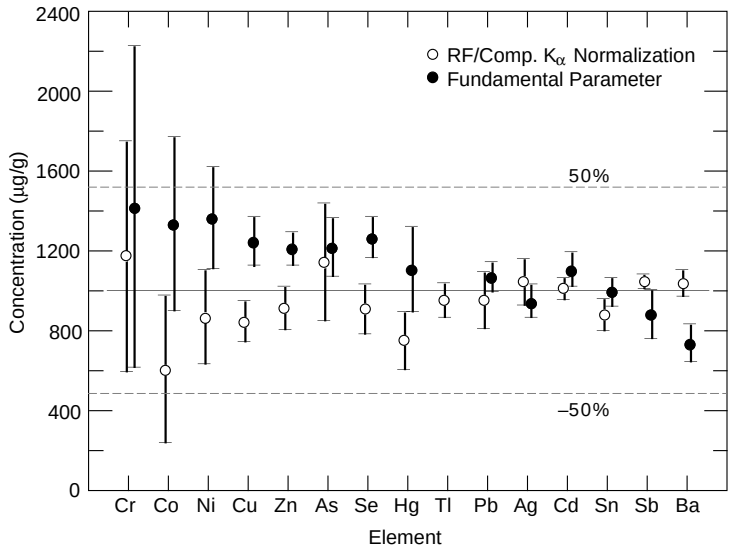

Figure 5. Average and standard deviation of concentrations established for soils spiked with 1000 µg metal/g, as determined by RF/Comp. K_α normalization and FP analysis.

mental parameter or response factor/Compton K_α peak-normalization methods of analysis. These alternative approaches to XRF analysis are very useful for screening a variety of matrices during RI/FS activities when it is impractical to produce matrix-matched standards.

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Analysis of copper, zinc, arsenic, lead, chromium, cobalt, nickel, mercury, thallium, selenium, silver, antimony, cadmium, tin, and barium was performed on soils and other particle matrices using two field-portable high-resolution X-ray fluorescence spectrometers (XRF). Quantitative determinations were based on fundamental parameter analysis and a second method that relies on analyte response factors and uses the Compton K_α incoherent backscatter peak for matrix normalization. These two methods of instrumental analysis require only a few reference materials and are relatively insensitive to sample matrix composition. This study assessed the capability of these two rapid XRF analysis methods by determining metal concentrations in reference materials, field samples, and laboratory spiked soils. With the exception of nickel, cobalt, and chromium, concentrations within 50% of the expected values were consistently obtained at and below 1000 µg/g.

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