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Evaluation of a Prototype Field-Portable X-Ray Fluorescence System for Hazardous Waste Screening

EVALUATION OF A PROTOTYPE FIELD-PORTABLE X-RAY
FLUORESCENCE SYSTEM FOR HAZARDOUS WASTE SCREENING

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ABSTRACT

A prototype field-portable X-ray fluorescence system developed by EPA and NASA was evaluated at a site contaminated with Pb, Zn, and Cu. The objective of the field test was to evaluate the effectiveness of the instrument as a field analytical tool for locating hot spots and as a preliminary screening device where immediate data feedback aids in decision-making in the field.

By making use of an analytical method designed specifically for the XRF system, all routine field measurements for Cu, Zn, and Pb were made on site by placing the probe on the surface of the ground ("in situ" measurements). Subsequently, confirmatory samples were collected and analyzed in the laboratory with an Inductively Coupled Plasma spectrometer (ICP) while adhering to EPA Contract Laboratory Program (CLP) protocols.

The quality assurance consisted of measuring NBS standard reference materials to verify the data measured in the field and in the laboratory in addition to duplicates, blanks, and replicate sample analysis.

The analytical results were plotted on the sampling grid. One can immediately locate the hotspots for Cu, Zn, and Pb on site. The instrument detection limits for Cu, Zn, and Pb are 250, 200, and 70 ppm, respectively. Comparison of the XRF results with the ICP results showed an overall mean percent error (MPE, which means lack of precision and bias incorporated into one term) from NBS concentrations of only a few percent for Cu, Zn, and Pb. Precision and accuracy of the in situ measurements were within plus or minus 10 percent of the true value when compared to the samples analyzed in the laboratory.

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ACKNOWLEDGEMENTS

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However, the difference in the two values should fall within the acceptance range for the overall inaccuracy of the XRF in situ measurements. For the intents and purposes of this report we will assume the in situ sample area and the collected sample containing the same area to be one and the same sample.)

- compare the XRF results with those obtained from the ICP.

The EPA has recently expressed more interest in XRF systems than in previous years because the use of microprocessors and state-of-the-art technology have made the equipment smaller and thus portable. Such field-portable XRF systems have been used to delineate hazardous waste site hotspots for priority metals in the field (Chappell et al., 1986; Mernitz and Olsen, 1985; Furst et al., 1985; and Kendal et al., 1984). With immediate data feedback from the field-portable XRF system, all samples can be collected with the knowledge of their approximate concentration. This leads to a decrease in the number of unnecessary samples which would be analyzed normally. The XRF field data allows an analyst in the laboratory to calibrate his laboratory instrument to the proper concentration on the first try; thus decreasing the number of attempts at bracketing the correct one. Another use is as a laboratory analytical instrument to screen samples of unknown concentrations quickly providing the analyst with an approximate concentration. All of these applications of the XRF systems net an overall decrease in time and in money spent.

Furst et al., 1985 described three levels of analytical requirements for establishing the extent of environmental contamination. The first or highest level of analysis is used to develop data for litigation and regulatory enforcement (see Figure 1). This level demands the most rigor in sample preparation and instrument time as well as the highest degree of precision and accuracy. The second level of analysis is used to evaluate and assess average contaminant exposures to people and animals. The data from the third level of analysis is used for screening in order to obtain a preliminary profile of sites. This data can be used for decision making while in the field. Third level data may be used also to select which samples should be sent to the laboratory for first level analysis following the Contract Laboratory Program (CLP) analytical protocols. This report discusses the results obtained by using a portable XRF system under the third level of analytical requirements.

The area that the EPA selected for the field test was the Smuggler Mountain NPL site in Aspen, Colorado, northeast of the Aspen city limits. The site was listed on the NPL June 10, 1986. The Smuggler Mountain mine produced lead, silver, and zinc ores. The site is located on one of the slopes of Smuggler Mountain; some of the mining, milling, and smelting was located here. These slopes are a mixture of native soils, mine tailings, and other mine wastes. Much of the surface has been subjected to reworking by prior and recent construction projects. Several such projects used mine tailings as fill.

Martin Marietta Aerospace people brought a prototype XRF system to field test at the Smuggler Mountain site. The first prototype system had evolved from technology used in the Martian Viking lander. This system had to be redesigned to measure metals in contaminated soils because of the changes in its intended usage. Prior to the field test, the software was not programmed

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for efficient evaluation of soil samples and field application. Reprogramming the software took place subsequent to the field test.

The Martin Marietta field-portable XRF system consists of three units (see Figure 2): (1) the sensor head (when filled with liquid N_2, weighs 32 pounds), (2) the Canberra main unit analyzer (16 pounds), and (3) a Gridcase 2 portable computer (12 pounds). The filtration unit shown in Figure 2 was designed for laboratory use only to preconcentrate metals in water samples. The cooled semiconductor detector has excellent energy resolution and is capable of simultaneous detection of a wide range of X-ray energies. The cooled semiconductor detector decreases the dead time response to the X-rays it senses, thus decreasing the length of time needed for analysis. A typical analysis with the system lasts between 120 and 300 seconds. The X-ray tube uses a molybdenum target operating at 30,000 volts to produce a wide enough spectrum to fluoresce the priority elements. The detector is a semiconductor made of lithium drifted silicon. The detector must be cryogenically cooled and must have a continuous supply of liquid nitrogen.

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SECTION 2

CONCLUSIONS

- The XRF system produced data of known quality from 229 in situ measurements (defined as measurements made by placing the probe on the ground surface and by analyzing the same surface without moving the probe). The XRF field results on the NBS standards compared relatively well with the certified NBS values of the same standards.

- Field personnel can greatly decrease the time spent on site by making in situ measurements. If necessary, the technician can collect a confirmatory sample after each XRF analysis.

- The detection limits are low enough for obtaining data when third level requirements are necessary for analytical work on hazardous waste site investigations.

- The NBS standards were adequate for quality control and quality assurance. These standards were SRM 1633a, coal fly ash; SRM 1645, river sediment; and SRM 1648, urban particulate.

- The instrument uses cryogenics to cool the silicon-lithium detector which requires a Dewar container filled with liquid nitrogen. Even though the Dewar container will last 8 hours before a refill is necessary, maintaining a continuous supply of liquid nitrogen in the field can be difficult in some locations.

- The overall advantages of all X-ray fluorescent systems include: minimal sample preparation time, rapid turnaround time for analyses, multi-element analytical capability, nondestructive analyses, and sample size required for analysis is small or possibility of surface analysis without the need for sampling at all. These advantages make the XRF system very cost effective.
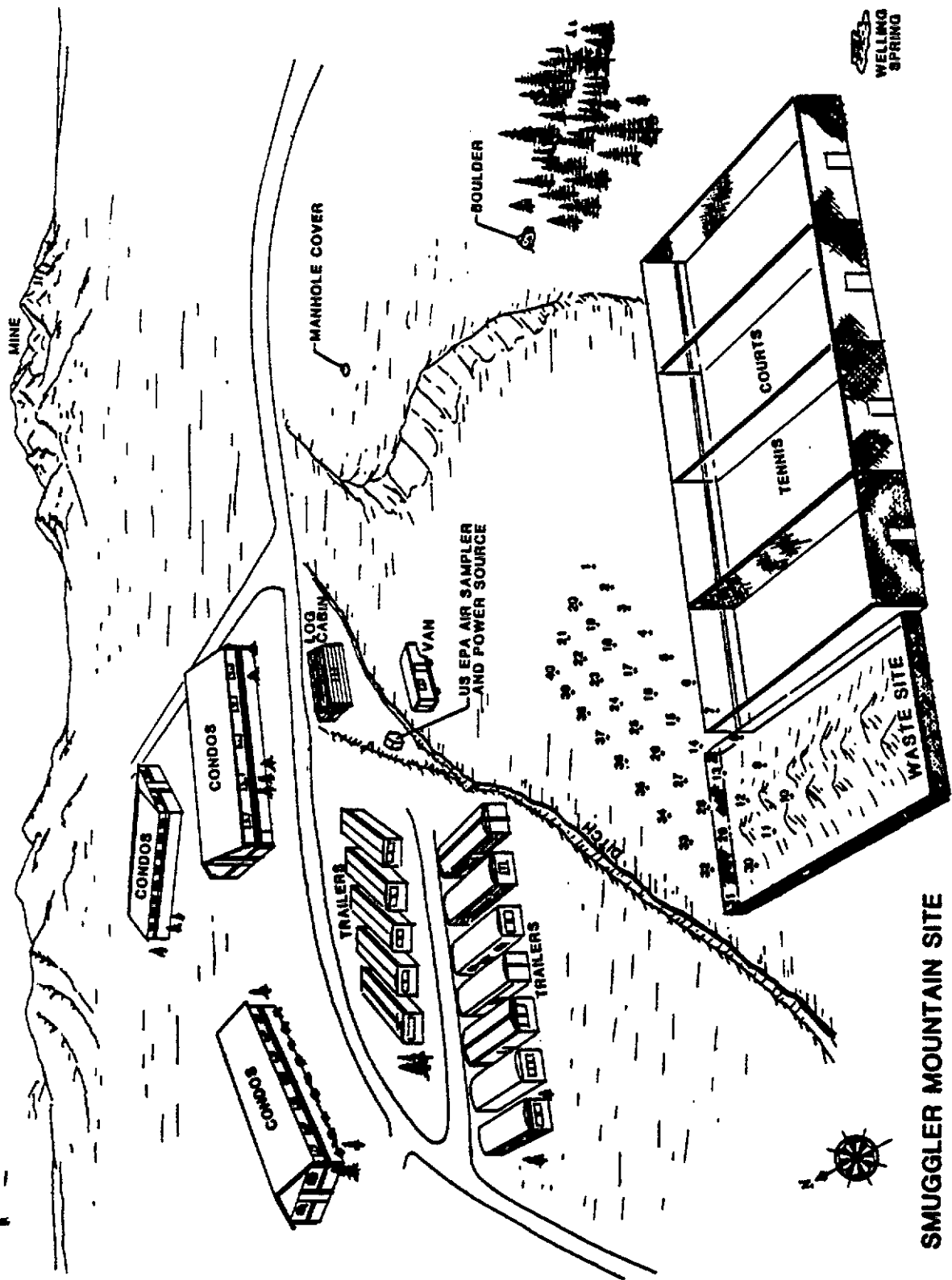
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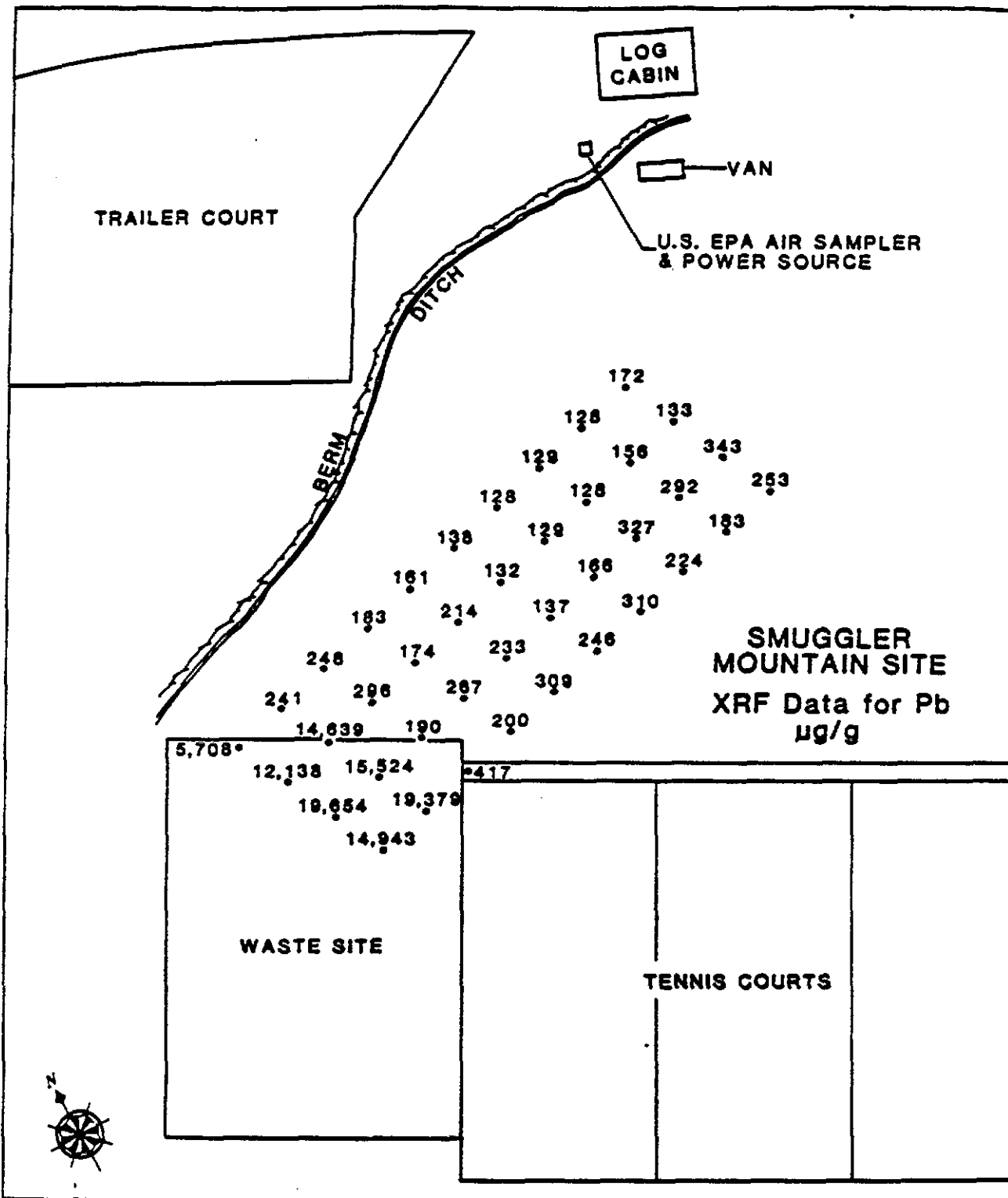
Figure 5.   Sampling grid on NPL site.

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Figure 6. XRF values for Cu plotted on sampling grid.

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Figure 8. XRF values for Pb plotted on sampling grid.

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SECTION 5

PROCEDURES

X-RAY FLUORESCENCE PRINCIPLES

The X-ray fluorescence (XRF) system used in this study is energy dispersive by design. All XRF depends on either an electron or X-ray beam bombarding the sample. The X-rays produced by an X-ray tube impinge on the electron clouds or orbitals in the atoms within the sample. When the X-ray displaces an electron from an inner orbital of an atom, such as the k-shell, a vacancy is created. This causes an instability below the electrons in outer shells. As the outer electrons seek stability by filling the inner shell vacancies, a cascade of electrons spontaneously follows. Energy is released or emitted for each shell vacancy that is filled. This emitted energy is characteristic of the atom from which it was produced. This emission is called fluorescence. All elements excited by the X-rays fluoresce simultaneously to produce a spectrum of characteristic and backscattered radiation. It is this spectrum that the detector senses and counts. The whole spectrum data is transferred to the analyzer where the software deconvolutes the peaks for the desired elements.

THE PROBLEM OF RESOLUTION WITH VARYING PARTICLE SIZE

The bulk density of the sample and the particle size distribution affect the characteristic X-ray intensity. When dealing with varied distribution of particle sizes, an accurate analysis of these particles is difficult if there is no attempt to make all the particles the same size, either by segregation or reduction.

The varied particle sizes have an effect on X-ray absorption and enhancement especially during in situ emission analysis. Collecting and grinding the sample to <0.075-mm (200 M) will generally solve the problem, but this is not always a practical solution in the field. It also defeats the purpose of using the field-portable XRF system with an in situ technique, i.e., a fast turn-around time. We can address this problem in a sample preparation step by using a mortar and pestel to break up the soil samples and by grinding the sample to approximately sand size assuming the sample is dry. Even though this approach does not entirely solve the problem, it does reduce the effect to an acceptable constant error while keeping sample preparation time to a minimum.

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- Clean the trowel by wiping the blade with a paper towel and then rinsing with distilled water.

h. Take samples with contamination levels ranging from approximately five times the IDL for Cu, Zn, and Pb up to the maximum values found on site.

i. Use NBS standards for the reference calibration.

j. Use silica sand for the blank sample. The grains of silica sand will closely approximate the grain geometry of the soils.

The sample preparation for the ICP analyses was done by both the standard CLP method and the Parr bomb method which is described below. The CLP method and QA/QC protocol for analysis may be found in Exhibit D of the Invitation for Bid for the Contract Laboratory Program (U.S. EPA, 1984).

ICP Analysis

Digestion of soil by a generic Parr bomb method (adapted from Bernas, 1968, Buckley and Cranston, 1971; and Dolezal et al., 1969):

a. Dry at 60°C and homogenize the sample.

b. Weigh 0.5 g of soil and place it in the Parr bomb.

c. Add 5 mL of concentrated nitric acid (HNO_3) and 2 mL of concentrated hydrochloric acid (HCl).

NOTE: • Do not add more than the 2 mL HCl prescribed. Too much can generate enough chlorine gas to cause the Parr bomb to explode.

• Do not add any soil with carbonates; the evolution of CO_2 could cause the Parr bomb to explode.

• Do not add the filter paper if it is a cellulose base. This could cause the formation of nitrocellulose which is explosive.

d. Seal the Parr bomb and place it in an oven at 120°C for 2 hours.

e. Remove the bomb from the oven and allow it to cool to room temperature.

f. Open and rinse the contents into a filter funnel feeding into a 100-mL volumetric flask. Bring the flask up to volume with DI water. The digest is ready for analysis.

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TABLE 1. COMPARISON OF XRF AND ICP RESULTS FROM NBS STANDARDS

Analysis Number		Fe	Cu	Zn	Pb
			Elements		
			(all units are in ug/g)		
			Coal Fly Ash		
SRM	1	94,000	118	220	72.4
1633a	2	91,555	178	261	152.4
	3	33,780	75.6	103	34.4
	4	17,944	54.0	84	n.a.
			River Sediment		
SRM	1	113,000	109	1720	714
1645	2	313,686	183	1551	735
	3	84,410	109	1632	688
	4	n.a.	n.a.	n.a.	n.a.
			Urban Particulate		
SRM	1	39,100	609	4760	6550
1648	2	41,252	584	2212	6247
	3	21,746	550	4486	5986
	4	20,857	432	3443	4192

No. 1 Certified by National Bureau of Standards.
No. 2 Martin-Marietta XRF unit. The Martin Marietta values for the SRM 1633a and 1648 are the averages of 7 replicates; for the SRM 1645, the values are the averages of 14 replicates.
No. 3 Perkin Elmer ICP II, Parr Bomb Method. The values are the averages of 3 replicates.
No. 4 Perkin Elmer ICP II, CLP Methods. The values are the averages of 3 replicates.
n.d. = not detected.
n.a. = not analyzed.

standards. When the individual Pb values for the different standards from Table 1 are plotted, the XRF results of the NBS standards show excellent concurrence with the ICP, especially for Pb (Figure 9).

The detection limits for the XRF system were determined by Martin Marietta. Three 300-second spectra were collected for each element, and the ratios of the net Kα and Lα peaks to net backscatter calculated. The instrumental detection limit was calculated from the formula:

$$IDL = 3S \sqrt{C_b/C_s}$$

where S is the quantity (in micrograms) of metal present in the sample, C_b is the background counts under the peak, and C_s the net sample counts. The peak

TABLE 2.   COMPARISON OF THE MARTIN MARIETTA XRF SYSTEM AND THE ICP
INSTRUMENT DETECTION LIMITS AGAINST CLP CONTRACT REQUIRED
DETECTION LIMITS (CRDL)

Element	Martin Marietta XRF System[1] (ppm)	Perkin Elmer ICP[2] (ppb)	ICP CRDL (ppb)
Cu	250	8	25
Pb	70	35	(5)*
Zn	200	17	20
Cr	1000	5	10
Ni	300	30	40
As	150	80	(10)*
Se	140	170	(5)*
Ag	>1000	5	10
Cd	ND	4.8	5
Sb	ND	50	60
Ba	>1000	20	200
Hg	80	50	(0.2)*
Tl	75	160	(10)*

[1] Data provided by Martin Marietta.
[2] IDL's qualified for CLP.
* These metals are not required for analysis on the ICP under CLP
   protocols. The values in the parentheses are the measured IDL's for
   the atomic absorption spectrometer to show its capability.
ND = not detected.

background is calculated, and the net sample counts are calculated by subtrac-
ting the background level from the total number of counts in the peak. The
detection limits for the XRF (the IDL for iron was not included) and ICP instru-
mental detection limit (IDL's) are listed in Table 2 and are compared in the
CLP contract required detection limits (CRDL). The CRDL's represent a level
one requirement regime for analytical work. The XRF IDL's might represent a
proposed level three requirement regime for hazardous waste site investigations
with field-portable XRF systems.

In comparison of the IDL's for Cu, Zn, and Pb against the values for the
soil samples in Table 3, what immediately becomes apparent is that 29 of the
values for Cu measured by the Martin Marietta XRF system are less than or
equal to the instrumental detection limit. Any values below five times the IDL
should not be used. The variation of precision in this range is, as a rule of
thumb, plus or minus the IDL. Between 5 and 10 times the IDL, the variation in
precision ranges from 10 percent to 20 percent of the amount present. Above 10
times the IDL, the variation in precision is less than 10 percent of the amount
present.

TABLE 3. (Continued).

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Sample No.	Analysis No.	Fe	Cu	Zn	Pb
			Elements (all units are in ug/g)		
G-11	1	82,978	1,660	5,240	19,654
	2	23,422	42.4	5,265.9	11,615
	3	36,969	80.7	9,383.5	15,294
G-12	1	52,830	912	3,711	15,524
	2	27,606	77.8	6643.4	11,619
	3	26,673	102.7	6347.0	4,135.1
G-13	1	30,009	174	269	190
	2	11,405	13.0	241.9	165.1
	3	12,413	14.2	263.5	176.1
G-14	1	39,972	313	421	267
	2	n.a.	n.a.	n.a.	n.a.
	3	15,099	17.1	344.1	226.8
G-15	1	38,180	208	354	233
	2	n.a.	n.a.	n.a.	n.a.
	3	14,157	15.9	293.6	176.9
G-16	1	35,277	163	168	137
	2	n.a.	n.a.	n.a.	n.a.
	3	21,159.3	23.2	102.7	19.1
G-17	1	35,331	151	153	166
	2	n.a.	n.a.	n.a.	n.a.
	3	25,141	27.2	243.6	137.6
G-18	1	31,529	158	343	327
	2	n.a.	n.a.	n.a.	n.a.
	3	17,234	22.3	422.5	327.6
G-19	1	39,512	373	536	292
	2	n.a.	n.a.	n.a.	n.a.
	3	15,069	21.8	451.3	812.7
G-20	1	38,321	373	449	343
	dup	33,990	304.3	417.0	281.9
	2	n.a.	n.a.	n.a.	n.a.
	3	14,003	21.4	459.3	396.2

Footnotes at end of table.

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TABLE 3. (Continued)

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Sample No.	Analysis No.	Fe	Cu	Zn	Pb
			Elements (all units are in ug/g)		
G-31	1	47,989	550	1,332.5	5,707.9
	2	25,092	68.0	5,347.1	7,090.8
	3	27,010	79.9	6,164.1	1,016.3
G-32	1	34,662	b.d.l.	424	241
	2	9,521	11.4	234.5	240.6
	3	9,897	11.2	253.4	269.4
G-33	1	29,650	485	629	248
	2	7,902	8.4	175.3	159.6
	3	12,007	13.9	282.6	255.4
G-34	1	20,454	b.d.l.	b.d.l.	183
	2	46,904	41.3	209.8	178.5
	3	9,916	11.2	244.2	164.3
G-35	1	21,212	n.d.	b.d.l.	161
	2	n.a.	n.a.	n.a.	n.a.
	3	14,970	17.2	366.1	286.4
G-36	1	37,457	n.d.	b.d.l.	138
	2	n.a.	n.a.	n.a.	n.a.
	3	25,310	37.5	143.5	47.8
G-37	1	40,321	b.d.l.	b.d.l.	128
	2	n.a.	n.a.	n.a.	n.a.
	3	20,846	19.4	119.0	43.9
G-38	1	35,042	n.d.	b.d.l.	129
	2	n.a.	n.a.	n.a.	n.a.
	3	21,700	20.8	180.2	100.2
G-39	1	36,218	b.d.l.	b.d.l.	128
	2	n.a.	n.a.	n.a.	n.a.
	3	24,390	21.5	108.5	28.7

Footnotes at end of table.

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concentrations but they are still closer to the NBS certified concentrations than the CLP recovered concentrations.

COMPARISON OF TWO FIELD-PORTABLE XRF SYSTEMS

We sent 13 soil samples to the Kevex Corporation for analysis with their field-portable XRF system, X-site 9900 and Analyst 6700. Kevex agreed to analyze the samples at no cost. Because Kevex analyzed these samples without contractual requirements the analyses were not verifiable. Therefore, the data must be accepted only as approximate values. In spite of this deficiency, we gain enough insight from the data to warrant its inclusion here (Table 4). The samples were shipped as loose soils sealed in petri dishes. Kevex analyzed the samples by placing the probe of their x-site 9900 onto the samples in the petri dishes. No sample homogenization or preparation took place. Overall the Fe values of the two instruments are close enough for semi-quantitative work, but the values for the priority metals Cu, Zn, and Pb are diverse for the two instruments and need further investigation. The authors suggest that further comparative work in the laboratory with rigorous QA/QC would determine which XRF system is better suited for field work.

STATISTICS

The replicate precision on the standards of the Martin Marietta XRF system ranged from 1.2 percent RSD for Zn to a maximum of 34.4 percent RSD for Pb on the NBS SRM 1648 (Table 5). The second column for each element represents the 90° rotation in the same horizontal plane after the seven-replicate analysis. The difference in the two sets of analyses could reflect the effect due to surface morphology from different areas within a sample which can affect the X-rays the detector senses.

The duplicate precision on routine samples of the Martin Marietta XRF system ranged from 0.88 percent RSD to a maximum of 10.19 percent RSD on the three samples run (Table 6). The relatively high percent RSD's which appear with sample G-20 could occur due to the counting statistics and being close to the instrument's detection limit. The more controlled studies need to be done in this area.

In Figure 10, the bar graph is a plot of the percent relative root mean square deviation verses the elements Fe, Cu, Zn, and Pb for each method. The data from Table 1 was used to calculate the mean percent error (MPE) using the formula:

$$MPE = \sum_{i=1}^{3} \frac{|X_i - T_i|}{3T_i} \times 100$$

where:

X_i = recovered concentration for a method
T_i = NBS certified concentration

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TABLE 5. REPLICATE ANALYSES OF THE NBS SRM 1648
(Data supplied by Martin Marietta)

Flux Factors	Gross backscatter (counts per second)					
	Fe X100	Fe X100	Zn X1000	Zn X10	Pb X1000	Pb X10
A-1	3.464	6.150	2.818	1.853	5.795	1.563
A-2	3.289	5.999	2.203	1.854	2.870	1.629
A-3	3.225	5.909	2.820	1.873	4.857	1.541
A-4	3.401	5.818	2.951	1.871	2.333	1.640
A-5	3.206	6.429	3.909	1.830	3.469	1.642
A-6	3.316	6.371	2.531	1.813	3.810	1.596
A-7	3.684	5.887	3.523	1.843	2.578	1.564
mean	3.369	6.080	2.974	1.848	3.673	1.596
s.dev.	0.166	0.243	0.572	0.022	1.265	0.041
%RSD	4.927	3.997	19.23	1.167	34.44	2.569

TABLE 6. COMPARISON OF PERCENT RSD OF DUPLICATE ANALYSES BY XRF

Elements	IDL	Samples		
		G-10	G-20	G-30
Fe	---	57,729	38,321	57,050
		52,947	33,990	58,350
%RSD		4.32	5.99	1.13
Cu	250	1,056	373	726
		919	304	743
%RSD		6.95	10.19	1.15
Zn	200	2,979	449	3,316
		3,022	417	3,490
%RSD		0.73	3.70	2.55
Pb	70	14,943	343	12,138
		14,840	282	11,927
%RSD		0.35	9.76	0.88

The NBS certified value is assumed to be the "true" concentration. Each method of analysis recovered concentrations equal to or less than the true concentration for each element. The deviation from the true concentration of each element represents the effect of both bias and lack of precision or MPE for each method. What is interesting to note is that while the Parr bomb method shows the lowest MPE of the three methods, the XRF is within a few MPE of the CLP for Fe, Cu, and Pb. The Zn values for XRF exhibited a lower observed MPE than the CLP values. The overall precision and bias of the results from the CLP and XRF methods are within acceptable scientific limits ($\pm10\%$).

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