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**X-Ray Fluorescence Investigation of Heavy-Metal
Contamination on Metal Surfaces in the Pilot Plant
Complex, Aberdeen Proving Ground, Maryland**

**Energy Systems Division
Argonne National Laboratory**

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Abstract

A field program using a portable x-ray fluorescence (XRF) instrument was carried out to obtain data on loadings of RCRA-regulated heavy metals in paint on metal surfaces within the Pilot Plant Complex at Aberdeen Proving Ground, Maryland. Measured loadings of heavy metals were sufficiently small that they do not present problems for either human exposure or the disposition of building demolition rubble. An attempt to develop an external calibration of the XRF instrument for cadmium, chromium, and lead was unsuccessful. Significant substrate effects were observed for cadmium and chromium; for accurate results for these elements, it appears necessary to calibrate by using a sample of the actual metal substrate on which the paint is located. No substrate effects were observed for lead, but the use of lead L-shell x-ray emission lines in the instrument mode utilized in this study appears to result in a significant underestimate of the lead loading due to self-absorption of these emissions.

1 Introduction

1.1 Background

Demolition in a controlled, safe, and environmentally acceptable manner is being planned for the buildings that constitute the Pilot Plant Complex (PPC) at Aberdeen Proving Ground (APG) in Maryland. Argonne National Laboratory (ANL) has undertaken a program to address environmental issues arising from the planned demolition and to develop a scope of work for the demolition process. The potential for contamination of the building demolition rubble by hazardous substances and the implications of that possible contamination for the disposal of the rubble are issues of concern. Contaminants that might be present in potentially significant amounts include heavy metals from paints used on such metal surfaces as structural steel members, doors, and door and window frames. This report presents the results and findings from a field measurement program undertaken in March 1995 to address the potential heavy-metal

contamination issue. Potential rubble disposal problems associated with contamination of painted surfaces by lead are addressed in a separate report (Brubaker et al. 1995).

The PPC currently comprises nine buildings. The Pilot Plant, Building E5625, is a four-story building consisting of a structural concrete and steel framework with walls made primarily of clay tile. The activities carried out in this building were primarily pilot-plant-scale testing of production methods for chemical warfare agents and other substances. The remaining buildings are much smaller and provided support for the activities in Building E5625. Table 1 lists these buildings and summarizes their histories of use. The code letter shown in Table 1 is the letter assigned to each building during this study. Building E5632, the refrigerator building (code H), was not included in this study due to the lack of metallic surfaces. Building E5626, the guardhouse (code F), also was not included in the sampling program described in this report. Figure 1 shows a current map of the complex.

1.2 Objective

The objective of the study was to determine the levels and spatial distributions of heavy metals, particularly cadmium, chromium, and lead, on structural members and other metallic surfaces within each building of the PPC. The measurements form the basis for an initial screening analysis for potential disposal problems involving the metal components of building demolition debris.

1.3 General Approach

Metallic surfaces were screened for the presence of the target metals by a sampling program that involved measurement of the heavy-metal loading at randomly selected points on structural members and other metallic surfaces within each building. A portable instrument based on the principle of x-ray fluorescence (XRF) was utilized for the measurements. Data collected during the field measurement program were downloaded from the XRF instrument into a data base that was subsequently analyzed.

Sampling was conducted on metallic surfaces in seven buildings in the PPC. The population of interest was the set of all possible independent XRF sampling units or areas (each approximately one square inch in area).

TABLE 1 Existing Pilot Plant Complex Buildings

Current Building Designation	Code Letter	Year Built	Uses
E5616	A	1942	Change house Pipe-fitting supply room Public toilet
E5617	B	1942	Lime house Test-equipment laboratory Pilot plant control building Dichloro-process hydrogenation control room Experimental laboratory
E5618	C	1942	Pump house Compressed-air house Plant neutralization system Air-compressor building
E5621	D	1942	Workshop Machine shop Machine, pipe, carpenter shop Inert-gas generator facility Gas-compressor building
E5625	E	1942	Pilot plant Agent filling GA pilot plant Agent transfer facility Process laboratory Pilot plant - toxics
E5626	F	1983	Guardhouse
E5627	G	1942	Laboratory and office Laboratory First aid station Quality control laboratory
E5632	H	1970	Refrigerator building
E5633	I	1942	Cooling tower Flammable-materials storehouse Drum storage

Source: Anderson et al. (1995).

2 XRF Heavy-Metal-Loading Measurements

2.1 Data Quality Objective

Regulations based on the Resource Conservation and Recovery Act (RCRA, Public Law 94-580 as amended) govern the disposition of rubble in a landfill. These regulations require that the total leachable content of various toxic substances, including several heavy metals, be less than specified levels. The total leachable content of a given substance is determined by conducting the Toxicity Characteristic Leaching Procedure (TCLP) (EPA 1986) on rubble samples and analyzing the leachate for that substance. It was initially expected that cadmium, chromium, and lead would be the toxic metals most likely to be present in significant amounts.

The results and findings of the sampling program are intended to support a decision either (1) to conduct further work to characterize the heavy-metal contamination or (2) to take no action regarding such contamination because the data have shown with sufficient confidence that problems are unlikely to arise.

Table 2 lists the metals that are included in the current RCRA regulations and for which TCLP regulatory levels exist. The regulatory levels are maximum TCLP leachate concentrations.

2.2 Sampling Strategy

Metal surfaces occur primarily in the form of structural steel members (such as I and H beams), metal window and door frames, and metal-covered doors. The surfaces in question are in the interior of each building with the exception of Building E5633 (code I), part of which is open to the environment. In each building, a random (judgmental) set of sampling locations was selected, with the distribution between structural and other surface types in approximate proportion to the relative surface areas involved. Table 3 shows the planned number of sampling locations in each building as well as the number for each type of surface.

TABLE 2 Metals Regulated under RCRA

Metal	TCLP Regulatory Level (mg/L)
Arsenic (As)	5
Barium (Ba)	100
Cadmium (Cd)	1
Chromium (Cr)	5
Lead (Pb)	5
Mercury (Hg)	0.2
Selenium (Se)	1
Silver (Ag)	5

Source: EPA (1993).

TABLE 3 Planned Numbers of Sampling Locations

Building	Structural Steel	Doors and Windows	Total Number
E5616 (A)	5	6	11
E5617 (B)	6	6	12
E5618 (C)	9	3	12
E5621 (D)	2	5	7
E5625 (E) 1st floor	40	6	46
E5625 (E) 2nd floor	30	6	36
E5625 (E) 3rd floor	34	6	40
E5625 (E) 4th floor	28	6	34
E5627 (G)	3	4	7
E5633 (I)	9	6	15

2.3 Collection of the Heavy-Metal-Loading Data

2.3.1 Methodology

Theory of XRF Operation. A TN Technologies Spectrace Model 9000 portable XRF Analyzer was used to make the heavy-metal-loading measurements. In the XRF process, a gamma ray collides with a K- or L-shell electron of a metal atom, dislodging it from its orbit and leaving a hole in the inner electron shell. This hole is immediately filled by an outer-shell electron. This readjustment of the atomic electron distribution is accompanied by the emission of an x-ray. The energy of the emitted x-ray is characteristic of the specific metal, and the intensity of the x-rays emitted is proportional to the concentration of that metal. The unit of energy is the kiloelectronvolt (keV). X-ray energy is directly proportional to the frequency and inversely proportional to the wavelength of the x-rays. An x-ray of energy 12.4 keV has a wavelength of about 1 angstrom (1×10^{-8} cm).

The XRF energy spectrum can be used to identify metals present in the sample by looking for emission lines characteristic for specific metals of concern. For example, lead produces L-emission lines at 10.5 and 12.6 keV and K-emission lines at 72.5, 74.5, and 84.8 keV. A sample that has spectral emission lines at these energies contains lead. The quantity of lead is determined by comparing the intensity of these emissions to the emission intensity from a standard containing a known quantity of lead.

In the TN Spectrace Model 9000 XRF Analyzer, samples are irradiated with gamma rays produced by three separate sources that together excite the entire spectrum of target heavy metals that the instrument is designed to detect. The sources are ^{109}Cd , ^{241}Am , and ^{55}Fe . The

instrument measures the energy spectrum of the x-rays emitted by the sample with a mercuric iodide detector. This spectrum is recorded, evaluated, and saved in memory by the instrument and is used to estimate the concentration or surface loading of a set of 25 metallic elements, including all those listed in Table 2. This spectrum contains other qualitative information about the sample and allows the analyst to determine the nature of the sample matrix, whether the XRF is operating properly, and if interferences are affecting the determination of the targeted element. The estimated metal concentrations may be read from the instrument display when the measurement is made. Results and spectra stored in the memory of the unit subsequently may be downloaded to a personal computer for archiving and additional analysis.

The data sets collected during the field program described in this report were censored automatically by the instrument. In addition to an estimated metal-loading value, the XRF instrument in the normal operating mode develops an estimated standard deviation based on counting statistics. If the loading value is less than the estimated standard deviation, the instrument considers the metal not to have been detected, and neither the value nor the standard deviation is reported. Accordingly, numerical loading values for many metals are not available for all measurements.

Procedures. The instrument was used in accord with the manufacturer's recommendations, with the Standard Operating Procedure written for the purpose, and with the requirements of the associated APG-approved Sampling Plan.

The basic operating procedures followed each day during the sampling program were as follows:

- A. Instrument setup and internal checks (performed at the start of each sampling day and as the manufacturer recommends during the sampling day)
 - 1. Unpack and assemble the instrument, and turn on the electronics.
 - 2. Verify the time and date, and update these if incorrect.
 - 3. Check the automatic results storage setting.
 - 4. Check the display threshold setting.
 - 5. Select the thin film application.
 - 6. Verify that real time is in use.
 - 7. Perform the automated standard operating check.
 - 8. Conduct the automated internal calibration procedure.
 - 9. Make any required adjustments.

B. Quality control measurements (see Section 2.4 for description)

1. Perform measurements on the blank and the high-concentration standards provided, and plot the results on the quality control charts; if one or more points are out-of-control, take the required corrective action.
2. Perform selected duplicate measurements.

C. Metal-loading measurements

1. Set the time of sample analysis.
2. Make the measurement.
3. Label and store the results electronically.
4. Manually record the results on the data logsheets developed for the purpose.

Fieldwork for the structural definition phase of ANL's overall program for the PPC was carried out from May to October of 1994. Data from this effort were used to prepare the data logsheets on which measurements and other observations would be manually recorded during the heavy-metal-measurement field program. The field measurement program was initiated February 27, 1995, and was completed on March 8, 1995.

The data were recorded in two ways: manually on data logsheets and electronically by the Spectrace 9000 instrument. The logsheets contained information regarding the sample location (building, floor, and room), the structural survey, the analytes of interest, and general information about the measurements being made (date, time, sampling team members, logbook number, etc.).

2.3.2 Health and Safety

Field team members followed the APG-approved Health and Safety Plan at all times during the field program. Special safety considerations regarding radiation exposure arose due to the use of a portable device that uses the XRF principle. All manufacturer's recommendations and specified operating procedures were followed explicitly by ANL measurement team members, all of whom had received special training provided by the manufacturer and had been certified as qualified by the manufacturer prior to the start of the field program.

2.4 Quality Controls

A number of quality control (QC) provisions were incorporated into this study to ensure that the resulting data would be of known and adequate quality. Although the Spectrace 9000 spectrometer had been calibrated at the factory prior to its shipment to Argonne and internal automated calibration checks were performed regularly, an external calibration study was

performed to provide a set of data that either would confirm the factory and internal calibrations or could be used to correct the instrument readouts. Further, external QC/calibration checks were run periodically during the study to verify consistent instrument performance. Finally, data reproducibility and precision were evaluated by making at least one pair of duplicate measurements for each building within the PPC.

2.4.1 Calibration Data

Data accuracy in this study was to be ensured by using calibration standards for cadmium, chromium, and lead in thin films; these standards were obtained from the National Institute of Standards and Technology (NIST). A separate external calibration study was performed in which each standard was placed against a substrate blank and a set of readings obtained. Table 4 shows the standards used for each of the elements and also shows, for each set of data, the number of measurements made, the mean value obtained, the sample standard deviation, and the average standard deviation reported by the XRF instrument. Calibration sets were obtained by using a steel substrate blank intended to act as a surrogate metallic substrate.

Figures 2–4 show the calibration curves and regression equations obtained from these data; note that in the case of lead, the units of measurement have been changed to mg/cm^2 . In the

TABLE 4 Calibration Data Summary

Metal	Standard ($\mu\text{g}/\text{cm}^2$)	Number of Measurements	Mean ($\mu\text{g}/\text{cm}^2$)	Standard Deviation ($\mu\text{g}/\text{cm}^2$)	Instrument Standard Deviation ($\mu\text{g}/\text{cm}^2$)
Cadmium	blank	10	59.1	11.1	13.4
	26.6	5	75.2	19.5	13.7
	49.0	10	94.5	12.2	14.0
Chromium	blank	10	2.88	0.50	0.72
	15.0	5	12.64	0.27	0.93
	25.0	5	18.14	1.34	1.03
	48.0	10	35.75	1.42	1.30
Lead	blank	10	0.15	0.32	0.11
	43	5	46.3	0.41	1.9
	290	5	319	3.3	4.8
	1,020	5	1,045	15	12
	1,630	5	1,580	16	15
	3,530	10	2,754	25	20

FIGURE 2 Cadmium Calibration Curve

FIGURE 3 Chromium Calibration Curve

FIGURE 4 Lead Calibration Curve

regression equations, “meas” denotes the measured or observed metal loading and “ref” denotes the reference or standard value. The error bars shown in these figures represent the sample standard deviations as reported in Table 4; in the case of lead, the error bars are less than the size of the symbol used to show the data points. Table 5 summarizes the regression parameter values obtained. The uncertainties listed in Table 5 represent 95% confidence bands based on the indicated number of degrees of freedom. All regression coefficients given are highly significant statistically.

The calibration curves shown in Figures 2–4 could not be used in the actual data analysis. The reasons why were similar in the cases of cadmium and chromium. When the curves were applied to data obtained in the PPC buildings, approximately 80% of the calibrated cadmium-loading values were negative, as were approximately 40% of the chromium-loading values. The problem appears to be related to the use of a steel substrate blank during the collection of the calibration data. Calibration data had been obtained by placing the various standards on top of the steel blank and making replicate XRF measurements. The steel blank was intended to act as a surrogate for the metal substrates on which field measurements were to be made. It appears, however, that the blank did not accurately simulate the actual metal substrates. For cadmium and chromium, the XRF readings are sufficiently sensitive to the effects of different types of metal substrate that a piece of the actual field substrate is required for the calibration process. Concurrence with this interpretation of the calibration results was obtained in a telephone conversation with a technical representative of the instrument manufacturer (Rhea 1995). The

TABLE 5 Calibration Parameter Values

Parameter	Cadmium	Chromium	Lead
Degrees of freedom	23	29	34
Standard error (residuals)	13.2 $\mu\text{g}/\text{cm}^2$	1.24 $\mu\text{g}/\text{cm}^2$	0.0150 mg/cm^2
Intercept	$58.5 \pm 8.3 \mu\text{g}/\text{cm}^2$	$2.48 \pm 0.70 \mu\text{g}/\text{cm}^2$	$-0.0007 \pm 0.0430 \text{ mg}/\text{cm}^2$
Linear coefficient	0.720 ± 0.249	0.6850 ± 0.0226	1.12915 ± 0.08647
Quadratic coefficient	N/A	N/A	-0.09878 ± 0.0236
R ²	0.608	0.993	0.9999

interpretation of the field data is made somewhat ambiguous by the inability to separate effects arising from heavy metals in paints from effects due to the nature of the metal substrate.

In the case of lead, the quadratic calibration curve leads to a different problem. In this case, several field measurements could not be calibrated because they were above the maximum value attained by the quadratic function shown in Figure 4. This behavior is related to the manner in which the instrument was operated and to the procedure used by the instrument to produce a reading for lead. In this study, the "thin-film" mode of operation was used because it permitted the determination of all the target heavy metals in one measurement. In this mode, the instrument uses the lead L-shell x-ray emission lines to estimate the lead-surface loading. The L-lines are easily reabsorbed by lead in the sample and are therefore useful only for measurements on very thin films. The lead standards above 1 mg/cm^2 all show an increasing amount of self-absorption, leading to an increasingly large negative error in the measurement. Similar problems were also expected in the actual field measurements. Again, concurrence with this interpretation of the calibration results was obtained in a telephone conversation with a technical representative of the instrument manufacturer (Rhea 1995).

In the case of lead, there seems to be no significant effect arising from different metal substrates. Excellent linear calibration curves had been obtained for lead on both steel and concrete substrates in an earlier study (Brubaker et al. 1995), where a different instrument (from the same manufacturer) that used the lead K-shell lines instead of the L-shell lines had been used. In that study, the steel blank gave systematically higher readings than did the concrete blank. The lack of a significant substrate effect in that study is consistent with the use of L-shell emission lines, which would not be expected to "see" below a very thin surface layer.

2.4.2 Calibration Checks and Control Charts

The performance of the XRF analyzer during the study was monitored through the use of control charts based on the instrument's responses to blanks and to the highest concentration calibration standards for each target metal. These QC data were acquired by the operators.

periodically throughout each day of field measurements and were immediately plotted onto the control charts.

Plots of the XRF metals control-chart data are shown in Figure 5. In each part, the vertical axis represents the QC measurement value, and the horizontal axis represents the sequential measurement number. The period of time spanned by these plots is from approximately noon on March 1, 1995, to approximately noon on March 8, a total of five working days.

In part A, the cadmium data are shown; the open circles denote measurements made with the 49 $\mu\text{g}/\text{cm}^2$ standard, and the filled circles denote measurements made with the blank. Horizontal lines are drawn at the two mean values of 94.5 and 59.1 $\mu\text{g}/\text{cm}^2$, respectively. Upper and lower control limits were set at the mean value plus and minus three times the standard deviation obtained in the calibration measurements; the corresponding values are (131.1, 57.9) for the standard and (92.4, 25.8) for the blank. For simplicity, these control limits are not indicated in part A of Figure 5. Although points plotted in part A are within control limits, except the three open circles at the far right side of the figure, it appears that the instrument behavior was qualitatively different from measurement 9 onwards as compared with measurements 1-8.

Part B shows the QC data for chromium. Again, the open circles denote measurements made with the high-concentration standard, in this case 48 mg/cm^2 , and filled circles denote measurements made with the blank. In part B, the upper and lower control limit lines are shown, but lines at the mean values are omitted for simplicity. The mean values and control limit values are given by $35.75 \pm 4.26 \text{ mg}/\text{cm}^2$ for the high-concentration standard and $2.88 \pm 1.50 \text{ mg}/\text{cm}^2$ for the blank. From the figure it is apparent that all measurements were within control limits up to measurement 9, and that this and all subsequent measurements indicate a problem with the instrument.

Part C shows the lead QC data. Again, the open circles denote measurements made with the high-concentration standard, in this case 3.53 mg/cm^2 , and the filled circles denote measurements made with the blank. The upper and lower control limit lines are shown for the standard data, but the mean value line is omitted for simplicity. The mean and the control limits for the blank are not distinguishable from zero on this plot. The mean values and control limit values are given by $2.754 \pm 0.075 \text{ mg}/\text{cm}^2$ for the standard and $0.00015 \pm 0.00096 \text{ mg}/\text{cm}^2$ for the blank. From the figure, it is apparent that again all measurements were within control limits up to measurement 9. In this case, measurement 9 on the standard seems in control, but all subsequent measurements indicate a problem with the instrument. The measurements on the lead blank were essentially all zero, even when the instrument was working properly.

Figure 5 indicates gaps in some of the data; specifically, cadmium high-concentration standard data and all lead data are missing for measurements 10 and 11. Also, lead blank data are missing for measurements 13 and 14. All chromium QC measurements were zero after measurement 8. The gap at points 10 and 11 arises because the field measurement team, realizing

FIGURE 5 XRF Metals Control-Chart Data

that a problem existed with the chromium measurements following measurement 9, immediately repeated the blank measurements twice, thereby generating measurements 10 and 11. The blank measurement for chromium is also used for cadmium, but the lead blank is physically different. The field team continued taking data, however, until an accident on March 8 disabled the instrument completely, at which point the field measurements were terminated.

Apparently the instrument was not functioning properly after QC measurement set number 8, which was taken at about 11:30 a.m. on March 7, 1995. Discussions with the field measurement team and examination of the field logbook showed that during the early afternoon on March 7, the instrument was severely jarred. A bipod being used to support the instrument's weight during a measurement tipped over, causing the instrument to fall from a height of about 2 ft. It is now believed that the instrument was damaged by this incident. Consequently, all field data collected after the 11:30 a.m. QC check (QC measurement set number 8) were discarded. All prior field data collected are considered valid.

2.4.3 Detection Limits

The limits of detection of heavy metals for the Spectrace 9000 instrument were estimated from the data generated in the calibration study described in Section 2.4.1. A standard deviation was calculated for each set of measurements made with the calibration standards and the steel substrate blank. These standard deviations, which represent the random error of measurement, were used in estimating the detection limits.

The SW-846 method (EPA 1986) defines the detection limit to be the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. Each SW-846 detection limit was calculated by multiplying the one-tailed Student's t-statistic for the 99% confidence level and the appropriate number of degrees of freedom by the standard deviation obtained when using the blank (for cadmium and chromium) or the lowest available standard (43 $\mu\text{g}/\text{cm}^2$ for lead). Table 6 shows the results.

TABLE 6 Detection Limits

Metal	Standard	Degrees of Freedom	Standard Deviation ($\mu\text{g}/\text{cm}^2$)	t-Statistic ^a	Detection Limit ($\mu\text{g}/\text{cm}^2$)
Cadmium	blank	9	11.1	2.821	31
Chromium	blank	9	0.50	2.821	1.4
Lead	43 $\mu\text{g}/\text{cm}^2$	4	0.41	3.747	1.5

^a At 99% confidence level.

2.4.4 Duplicate Measurements

The field measurement team made at least one pair of duplicate measurements in each outbuilding of the PPC as well as three pairs on the fourth floor and one pair on the third floor of Building E5625 before the field program was terminated on March 8. A maximum total of eight pairs of duplicate data remained after values made suspect by QC considerations were discarded. This total was reduced in many instances when the XRF instrument did not report a value for a metal of interest from one or both measurements. As explained in Section 2.3.1, values are not reported when the value estimated by the instrument is less than the simultaneously estimated standard deviation. Thus, for the RCRA-regulated metals, sufficient duplicate data to allow statistical analysis exist only for silver, barium, cadmium, and lead. Table 7 summarizes the duplicate data for these metals. In each case, the average value of the differences between duplicate measurements is well below not only the sample standard deviation but also the estimated standard deviation of the mean, which is obtained by dividing the sample standard deviation by the square root of the number of degrees of freedom. The number of degrees of freedom is one less than the number of valid pairs of measurements. These results indicate that, as expected, no systematic differences appear in the duplicate measurements.

The sample standard deviations cited in Table 7 represent the standard deviations associated with differences between two measured values. As such, they should be larger than the corresponding population standard deviations, estimates of which are given in Table 6, by a factor equal to the square root of two, or approximately 1.414. The standard deviations cited in Tables 6 and 7 for cadmium very nearly satisfy this requirement; compare the value $14.6 \mu\text{g}/\text{cm}^2$ with 1.414 times the value cited in Table 6, or $15.7 \mu\text{g}/\text{cm}^2$. On the other hand, the standard deviation cited in Table 7 for differences between duplicate lead measurements, $141.2 \mu\text{g}/\text{cm}^2$, is approximately 243 times the value shown in Table 6 multiplied by 1.414, rather than approximately equal to it.

One possible explanation for the discrepancy in the standard deviations for the lead case is that the standard deviation of measured values increases significantly as the measured value itself increases; see Table 4 in which the standard deviation associated with measurements using the highest concentration standard was almost two orders of magnitude greater than that

TABLE 7 XRF Heavy-Metal Duplicate-Data Summary

Parameter	Silver	Barium	Cadmium	Lead
Mean difference ($\mu\text{g}/\text{cm}^2$)	-0.2	60.2	-2.3	19.4
Standard deviation ($\mu\text{g}/\text{cm}^2$)	4.6	382.9	14.6	141.2
Degrees of freedom	5	7	7	7
Standard deviation of the mean ($\mu\text{g}/\text{cm}^2$)	2.1	144.7	5.5	53.4

associated with measurements on the blank and on the lowest concentration standard. The standard deviation shown in Table 6 is only for measurements on the lowest concentration standard, but duplicate field measurements were made at arbitrary points in the buildings. The average of the standard deviations reported by the XRF instrument for the individual lead measurements used in the analysis of duplicates is $10.4 \mu\text{g}/\text{cm}^2$ (the corresponding average lead loading is $909.3 \mu\text{g}/\text{cm}^2$). This value may be taken as an estimate of the standard deviation of the population used in the duplicate measurements and can be used instead of the value cited in Table 6. Multiplying this value by 1.414 gives $14.7 \mu\text{g}/\text{cm}^2$, which is still an order of magnitude less than the value cited in Table 7. Apparently, the dependence of lead standard deviations on lead loading values cannot completely account for this discrepancy. This discrepancy suggests that the variability of duplicate field measurements for lead, and by extension the variability of field measurements for lead in general using L-shell XRF techniques, is substantially higher than that of replicate measurements made on a standard for the purpose of calibration.

The two sets of measurements differ in two ways: (1) calibration data were obtained using a single steel-substrate blank and (2) the XRF instrument was not repositioned between successive calibration measurements. Duplicate measurements in the field, however, were obtained on different metallic surfaces and generally involved repositioning the instrument prior to making the second measurement. The higher variability in the lead data may result from inhomogeneities in the surface-metal loading on a distance scale comparable to the size of the XRF instrument window, approximately 1 in., or from effects due to differences in the substrate. It is not clear why only some metals and not others would be affected. Also, no evidence for significant substrate effects for lead measurements was found in the calibration-curve fitting process, as discussed earlier.

Figure 6 shows normal probability plots of one set of lead calibration data (that obtained using the $0.29 \text{ mg}/\text{cm}^2$ standard) and the duplicate lead data. The calibration data has been "Studentized," that is, the mean of that set of data has been subtracted from each measurement and the difference divided by the standard deviation of the data set. A single standard deviation should not be used to scale the duplicate data, since the lead standard deviation varies with the lead loading. In the figure, the difference between the two members of each pair of duplicate values was divided by the mean of the two corresponding instrument standard deviations. A normal probability plot has the property that data falling approximately on a straight line are approximately normally distributed (Snedecor and Cochran 1989). The calibration data shown in part A generates a reasonable facsimile of a straight line, while the duplicate data (part B) appears to have an inverted S-shaped curve. Such a curve is indicative of a distribution having much more pronounced tails than the normal distribution does; such a distribution generates many more values that appear to be outliers when compared with normally distributed data. Samples from such a distribution also tend to have significantly higher standard deviations, and this difference in the shape of the probability plots is consistent with the finding of significantly different standard deviations.

Figure 7 shows normal probability plots of one set of cadmium calibration data (that obtained using the blank) and the duplicate cadmium data. The two sets of data were scaled in ways similar to those used for the data in Figure 6. In this case, both data sets plot as

FIGURE 6 Lead Calibration- and Duplicate-Data Distributions

FIGURE 7 Cadmium Calibration- and Duplicate-Data Distributions

approximate straight lines, indicating that both are approximately normally distributed. This result is consistent with the finding discussed above that the standard deviations for cadmium are approximately consistent with each other. The reasons for this difference in behavior between lead and cadmium are not known.

Figures 8–11 show probability plots of duplicate measurement data for silver, barium, cadmium, and lead. In these figures, the duplicate data have been scaled two different ways. In the top part of each figure, the relative difference, defined as the difference divided by the mean of the two corresponding loading values, is plotted. In the bottom part of each figure, each difference has been divided by the mean of the two corresponding standard deviation values reported by the XRF instrument. These two approaches to scaling the duplicate data were

FIGURE 8 Silver Duplicate-Data Distribution

FIGURE 9 Barium Duplicate-Data Distribution

adopted to see if a systematic increase in data variability associated with higher metal loadings could explain the behavior noted above. As can be seen from the figures, barium and lead behave in qualitatively the same way, and silver and cadmium have behavior similar to each other. Inverted S-curves are seen for the barium and lead data, while the silver and cadmium duplicate data appear to be normally distributed. Again, the reasons for these differences in behavior are not known.

FIGURE 10 Cadmium Duplicate-Data Distribution

FIGURE 11 Lead Duplicate-Data Distribution

3 Data Summary and Analysis

Table 8 summarizes the number of XRF measurements made in PPC buildings. The building code and total number of locations at which measurements were made for each building are given in the first two columns. Subsequent columns give, for each RCRA-regulated element, the number of values obtained in each building that were greater than one and greater than two instrument standard deviations. Very few data were obtained for arsenic and selenium, and only a limited amount of data was obtained for mercury and chromium. Relatively more data are available for the other elements. The "greater than one instrument standard deviation" criterion is used by the instrument to automatically censor data, as explained in Section 2.3. Assuming the errors of measurement are normally distributed, measured values greater than one and two standard deviations above zero imply detection at confidence levels of approximately 84% and 98%, respectively.

Table 9 summarizes the data obtained for the entire PPC. No clear and systematic differences among buildings were observed in the data. Due to the automatic censoring of data, results are not available for each element at each measurement location. In order to avoid a significant upward bias in estimating the true mean loading of each element, loading values that were less than the instrument standard deviation, and hence were not reported, must be taken into account. The procedure followed in this study was to estimate a default value that was approximately equal to one-half of the median instrument standard deviation reported. This procedure is equivalent to assuming that the unknown values are uniformly distributed over a range of values from zero to the median instrument standard deviation, so that their average value is approximately equal to the assumed default value, as desired. The number of default values used and the value itself are given in Table 9 for each element. No default values were used for arsenic and selenium due to the lack of data on which to base the estimate. The statistics for those elements reflect only the reported values and are not representative of the true distribution of values.

The mean value, standard deviation, and standard deviation of the mean are the standard sample summary statistics based on the indicated number of values. The maximum value is the largest reported value observed. The median is that value above and below which half the measurements lie. Because it is less sensitive to extreme values, the median is often considered a truer indication of the "center" of the distribution, especially when the distribution of values is highly skewed, as is the case for many of the elements examined in this study. A high degree of positive skewness is suggested when the median is significantly lower than the mean. The interquartile range is the difference between the seventy-fifth and twenty-fifth percentile values; half of the data lie within this range. The interquartile range, being less sensitive to extreme values, is a more robust measure of the spread in the distribution than is the standard deviation. The interquartile range is less than the standard deviation for distributions having long tails and greater for distributions having less pronounced tails.

The values of heavy-metal loading observed are rather low on average and do not appear to pose any problems for human exposure or for disposition of building demolition rubble.

TABLE 8 Summary of XRF Measurement Counts^a

Building	Total ^b	Silver		Arsenic		Barium		Cadmium		Chromium		Mercury		Lead		Selenium	
		>1σ	>2σ	>1σ	>2σ	>1σ	>2σ	>1σ	>2σ	>1σ	>2σ	>1σ	>2σ	>1σ	>2σ	>1σ	>2σ
A	11	10	8	0	0	11	11	10	9	0	0	2	1	11	11	1	0
B	12	7	3	0	0	11	9	7	6	6	5	3	0	12	12	0	0
C	12	8	6	1	0	12	10	11	8	8	5	0	0	12	12	1	0
D	7	3	2	0	0	7	7	4	3	4	4	4	0	7	7	1	1
E	24	17	12	2	1	21	19	21	16	10	7	9	4	23	23	2	1
G	7	6	4	0	0	7	7	6	4	0	0	3	0	7	7	0	0
I	12	8	4	0	0	12	11	11	9	9	8	3	1	12	12	1	0
Total	85	59	39	3	1	81	74	70	55	37	29	24	6	84	84	6	2

^a Number of measurements greater than one and two instrument standard deviations (>1σ and >2σ, respectively).

^b Total number of locations at which XRF measurements were taken.

TABLE 9 Summary Statistics of Uncalibrated XRF Measurements ($\mu\text{g}/\text{cm}^2$)

Statistic	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
Mean value	25.2	1.9	552	36.8	27.0	1.55	1,213	1.4
Standard deviation	70.7	1.2	1,326	23.6	88.0	1.03	1,018	0.84
Number of values	85	3	85	85	85	85	85	6
Standard deviation (mean)	7.67	0.81	144	2.56	9.55	0.11	110.4	0.34
Maximum value	422	3.0	9,302	117	598	4.8	4,113	2.9
Median value	12.2	1.9	132	38.0	0.4	1.12	1,115	1.1
Interquartile range	15.3	—	537	30.0	2.49	1.15	1,654	—
Default value ^a	3.11	—	0.76	5.79	0.41	0.97	0.47	—
Number of default values	26	0	4	15	48	61	1	0

^a See text for explanation.

The distributions of values greater than one instrument standard deviation for the elements of interest, excluding arsenic and selenium, are shown in Figures 12–23. Two figures are shown for each element: one showing a histogram of values and one showing a log-probability plot of the reported values. Relatively high values in combination with many lower values can be seen in most of these figures.

If data are log-normally distributed, they plot approximately as a straight line on a log probability plot. None of the elements examined have linear log probability plots, indicating that these elements are not even approximately log-normally distributed. Similarly, plots of the values themselves on linear probability plots (not presented) show that the distributions of values obtained are not even approximately normally distributed. The best explanation of the observed distributions is that they represent the superposition of several subpopulations, corresponding to the use of multiple but different types of paint in different areas. The number of measurements is inadequate to clearly delineate subpopulations, although some differences can be seen in a comparison between results from different types of metal surface and in the presence of “hot spots” in the data.

Table 10 presents the summary statistics for data obtained on structural steel members and on doors and door and window frames. There is no clear difference between these two types of surface for silver, arsenic, cadmium, mercury, or selenium loadings. There appears to be somewhat more lead and chromium and somewhat less barium per unit area on structural steel than on doors and windows. These differences are not considered particularly significant.

Localized hot spots exist for some elements; these localized areas of relatively high loading are not considered high enough to present problems of exposure or disposition. Figures 12 and 13 show that three relatively high silver-loading values were obtained. All three were in excess of $350 \mu\text{g}/\text{cm}^2$, and all three occurred in Building E5625 (code E), fourth floor, room 12. One value was measured on a structural member and two values were on metal associated with doors and/or windows. The next highest silver value measured was approximately $30 \mu\text{g}/\text{cm}^2$.

Three out of the four highest barium measurements also occurred in room 12 in Building E5625 but not at the same locations. The values occurred on structural steel members and were all in excess of $3,500 \mu\text{g}/\text{cm}^2$. Two other high values, including the maximum value reported ($9,302 \mu\text{g}/\text{cm}^2$) occurred in room 1 of Building E5633 (code I).

The two highest cadmium values, 116.8 and $112.6 \mu\text{g}/\text{cm}^2$, also occurred in Building E5625, fourth floor, room 12, at the same locations as two of the three high silver values (one on a structural member and one on a window frame).

Six of the seven highest chromium values, which ranged from 110 to $598 \mu\text{g}/\text{cm}^2$ and averaged $301 \mu\text{g}/\text{cm}^2$, appear at the six measurement locations in room 2, Building E5633 (code I),

FIGURE 12 Frequency Distribution of Silver

FIGURE 13 Log Probability Plot for Silver

FIGURE 14 Frequency Distribution for Barium

FIGURE 15 Log Probability Plot for Barium

FIGURE 16 Frequency Distribution for Cadmium

FIGURE 17 Log Probability Plot for Cadmium

FIGURE 18 Frequency Distribution for Chromium

FIGURE 19 Log Probability Plot for Chromium

FIGURE 20 Frequency Distribution for Mercury

FIGURE 21 Log Probability Plot for Mercury

FIGURE 22 Frequency Distribution for Lead

FIGURE 23 Log Probability Plot for Lead

TABLE 10 Summary Comparison of Metal-Loading Data for Structural Steel, Doors, and Door/Window Frames^a

Part A. Structural Steel Members

Statistic	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
Average	19.7	1.9	438.1	36.33	36.27	3.1	1,351	1.3
Standard deviation	48.0	1.6	998.2	21.69	107.2	0.8	1,096	0.4
Count	55	2	55	55	55	15	55	3
Maximum	364	3	4,940	12.6	597.5	4.8	4,113	1.7
Median	13.9	1.9	91.7	38	0.41	3.2	1,290	1.2
Default	3.11	—	0.76	5.79	0.41	—	0.47	—
Number of default values	15	0	3	8	30	0	1	0
Percent of default values	27.3	0	5.5	14.6	54.6	0	1.8	0

Part B. Doors and Door/Window Frames

Statistic	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
Average	35.3	1.9	761.7	37.8	9.96	2.9	960	1.4
Standard deviation	100	—	1,783	27.16	23.7	0.8	813.2	1.3
Count	30	1	30	30	30	9	30	3
Maximum	422	1.9	9,302	116.8	95.3	3.9	2,725	2.9
Median	8.45	1.9	200	39.5	0.41	2.9	866.5	0.8
Default	3.11	—	0.76	5.79	0.41	—	0.47	
Number of default values	11	0	1	7	18	0	0	0
Percent of default values	36.7	0	3.3	23.3	60	0	0	0

^a Metal loading values in micrograms per square centimeter.

all on structural steel members. This "room" is actually exposed to the outside, so the high values for chromium are probably associated with the use of an exterior grade paint. At these sampling locations, the corresponding barium levels are much lower than most other values, and the corresponding lead levels are somewhat higher than "normal."

An examination for other correlations among the different elements was made by computing the correlation coefficient between measurements for silver, barium, cadmium, chromium, and lead. For this calculation, only values greater than twice the instrument standard deviation were used. Insufficient data existed to look for correlations involving arsenic, mercury, and selenium. Table 11 presents the results.

Two of the correlations examined were statistically significant at the 99% confidence level — those between silver and cadmium and between lead and chromium. All others failed to be statistically significant at the 95% level. The two significant correlations can be explained entirely by the correlation between the highest values as discussed above.

TABLE 11 Metal-Loading Correlation Matrix^a

Metal	Silver	Barium	Cadmium	Chromium	Lead
Silver	1.000 (39)	-0.111 (36)	0.797** (26)	-0.221 (11)	-0.255 (38)
Barium	b	1.000 (74)	-0.130 (50)	-0.147 (17)	-0.024 (73)
Cadmium	b	b	1.000 (55)	-0.048 (18)	-0.225 (55)
Chromium	b	b	b	1.000 (29)	0.527** (28)
Lead	b	b	b	b	1.000 (84)

^a The top value in each grouping is the correlation coefficient between measurements of the two given metals; only values greater than twice the instrument standard deviation were used. The value in parentheses is the number of measurements for which both metal-loading estimates satisfied the above criterion. Entries marked by a double asterisk (**) are significant at the 99% confidence level. All other entries fail by a substantial margin to be significant at the 95% level.

^b The matrix is symmetric about the diagonal; entries below the diagonal have been omitted for clarity.

4 Summary and Conclusions

A field program was carried out to obtain data on loadings of RCRA-regulated heavy metals in paint on metal surfaces within the PPC at APG. A portable instrument utilizing the principle of XRF was used to make these measurements.

Measured loadings of heavy metals were sufficiently small that they are not considered to present any problems related to either human exposure or to the disposition of building demolition rubble.

External calibration of the XRF instrument was attempted for cadmium, chromium, and lead. In all cases (although for different reasons), the calibrations could not be used, and all values used in the analysis of this report are the original values as reported by the XRF instrument. Significant substrate effects were observed for cadmium and chromium; to obtain accurate results for these elements, it appears necessary to calibrate the XRF instrument by using a sample of the actual metal substrate on which the paint is located. No substrate effects were observed for lead, but the use of the lead L-shell x-ray emission lines in the instrument mode utilized in this study appears to cause a significant underestimate of the lead loading due to self-absorption of these emissions. Because of these difficulties in interpreting the results, the conclusions reached in this study must be regarded as tentative.

5 References

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