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**AN X-RAY FLUORESCENCE SURVEY OF LEAD
CONTAMINATED RESIDENTIAL SOILS
IN LEADVILLE, COLORADO:
A CASE STUDY**

by

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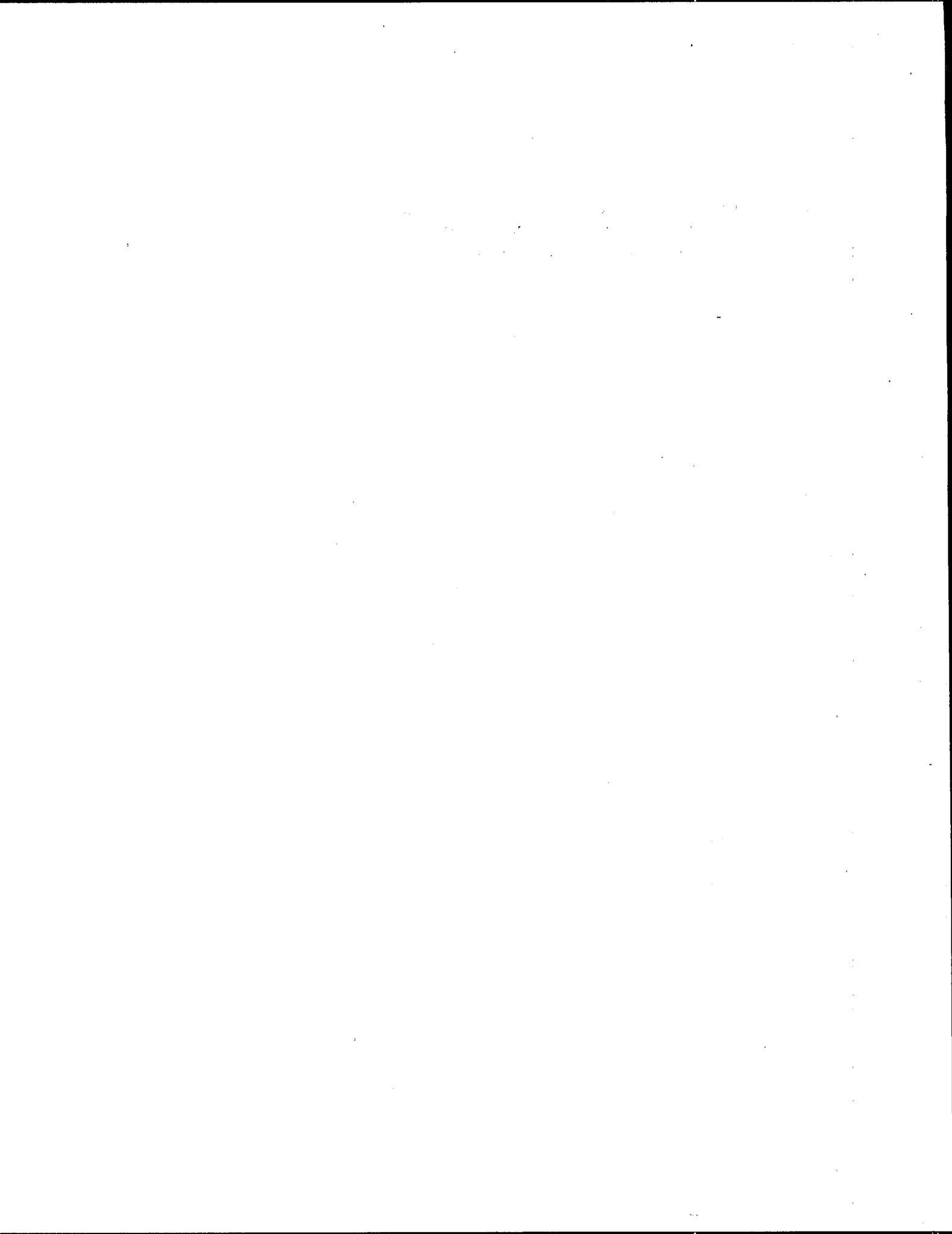
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FOREWORD

Continuing concern over the adverse impacts to human health due to exposure to lead has prompted characterization efforts at numerous sites across the United States. One of the primary potential exposure routes is through ingestion and inhalation of lead contaminated soils. This problem can be serious at old mining and smelting sites, especially in the western United States.

The California Gulch Superfund Site in Leadville, Colorado was added to the National Priority List (NPL) in 1983. It is an historic mining and smelting site that is currently the focus of extensive studies on soil lead contamination and bioavailability. Studies of ground and surface water impacts are also in progress. Personnel from the Environmental Protection Agencies (EPA) Environmental Monitoring Systems Laboratory at Las Vegas (EMSL-LV), the Denver office of Roy F. Weston, Inc., and Geostat Systems, Inc. (GSI) used field-portable X-ray fluorescence (FPXRF) to determine the spatial distribution of lead concentrations in residential soils.

This report details the FPXRF program sample collection, preparation, and analysis procedures, database management, and program quality assurance efforts at Leadville. The program clearly demonstrates that small, field portable XRF instrumentation can produce large quantities of acceptable quality data in a timely and cost-efficient manner when used properly.

When combined with the results of blood lead level and bioavailability studies, this data can help to develop a true assessment of the risks posed by lead in the residential soils of Leadville.

INTRODUCTION

Background

During the summer of 1991, over 3700 soil samples were collected and analyzed for lead content. These samples were collected from the edge of alley right-of-ways (alleyways) because of access difficulties, and from individual yards. The samples were analyzed using X-ray fluorescence spectrometry. A laboratory-grade Kevex 770 spectrometer was used to corroborate the analyses from three field-portable X-Met 880 spectrometers, which were then used to rapidly generate data of known quality.

Forty-five characterized Leadville residential soils were available at the onset of the survey. Ten of these samples were used to co-calibrate the Kevex 770 and three different X-Met 880 instruments, and the remaining 35 were used to confirm the calibrations. The first 850 samples were measured field moist after being brought to the field laboratory. They were then oven-dried and sieved, and approximately six grams of each subsampled into polyethylene X-ray cells. These prepared samples were analyzed on the Kevex and the X-Met 880s. Some of these samples were randomly subsampled for Contract Laboratory Program (CLP) analysis. Data comparability was demonstrated by correlating X-Met and Kevex results to each other and then to the CLP results.

All remaining field samples were analyzed field moist on one of the three X-Met 880 instruments. One sample from each preparation batch of 30 samples was selected for Kevex analysis and samples for CLP analysis were randomly selected from the entire sample suite. Results of the survey indicated that the X-Met 880s produced good quality data.

From the beginning, two major issues were of concern. First, was whether a single matrix model for the X-Mets would be adequate to analyze all soils within the area to be surveyed. Comparison of the X-Met and CLP data for the same samples indicated this to be the case. Second, was whether the alleyway samples and the nearby residential yard samples were of a single population. The non-parametric Kolmogorov-Smirnov procedure and the paired-wise sample t-test indicated no significant differences in the alleyway and yard samples; thus inferences could be made in unsampled yards from nearby alleyway easement samples.

History

Mining activity in the vicinity of Leadville was traced to the 1859 discovery of placer gold in California Gulch. The decline of the placer deposits led to the search for and discovery of lode gold in 1868. This discovery failed to reverse the decline, but in 1874 a heavy mineral that had been interfering with the placer operations was identified as silver-bearing lead carbonate. The ensuing silver boom was such that by 1880, there were enough mines to keep a number of smelters in operation.

Eventually, the mining and processing turned from the oxidized, carbonate ores to the less desirable sulfide ores of the more mundane metals, lead and zinc. Activity since has been cyclic, following trends in the base metals markets. Total metal production to 1966 was about 24,000,000 tons. There is currently only one active major operation in the area, ASARCO's Black Cloud Mine. The last smelter ceased operations in 1960.

The extensive underground mining activity left a legacy of drainage tunnels, perhaps most notably the Yak tunnel, and numerous mine waste rock and tailings piles dotting the landscape, almost entirely to the east and upslope of the town. The processing activities, which were scattered around the town, left behind large amounts of slag. Owing to the relative inefficiency of the recovery methods of the time, much of the waste material contains high amounts of lead and zinc, along with some other metals.

A preliminary EPA site evaluation took place in 1982 and 1983, and the site was placed on the NPL in 1983. The initial concern was on the effluent from the Yak tunnel. A surge pond and treatment system have since been constructed to deal with this aspect of the mining legacy. However, as is sometimes the case around old mining districts, material has been taken from abandoned dumps for use as fill, slag has been used as railroad ballast, and it has been crushed for use on streets in the winter. This use, taken in conjunction with the spread of smelter dust and wind transport of fine grained particles from various dumps, prompted concern about the effects of lead on people living in the town, especially the children.

Site Description

The town of Leadville lies about 100 miles southwest of Denver. It is situated on the western slope of the Mosquito Range, just east and upslope of the Arkansas River, at an elevation of approximately 10,200 feet. The mining activity was predominantly on the eastern side of town, along the drainages of California, Evans, Stray Horse, Oregon, Malta and Georgia Gulches. The area lies within the Colorado Mineral Belt and is highly mineralized⁽¹⁾.

The soils in the affected area are sandy loams to gravelly sandy loams, with varying amounts of admixed slags and tailings. The Leadville sandy loam predominates, with lesser amounts of Pierian and Troutville gravelly sandy loams present⁽²⁾. Large piles of slag and tailings are also scattered around the site.

Migration of Waste Materials

Contaminant transport occurred from natural processes, such as wind and water dispersion, but in Leadville as previously stated, the problem was exacerbated by human impacts, ranging from smelter stack emissions to slags that were crushed and spread on icy roads and used for railroad ballast. Tailings and mine waste rock were thoroughly mixed into local soils by over a century of mining and commercial activities where these materials

were often used for fill material.

In addition, many homes are built among the waste rock/tailings piles, or immediately adjacent to them. The tailings piles in particular are used as recreational areas by many off-road motorcycle riders and are criss-crossed with trails. Children also have access to these areas as unsanctioned playgrounds.

The Role of EMSL-Las Vegas

At the request of EPA Region 8, an intensive effort was mounted by the EMSL-LV Technology Support Center to gather a large amount of data on the surficial (0-4") spatial distribution of lead in the residential soils of Leadville during the 1991 field season. Owing to the rapid and economical approach afforded by FPXRF equipment and methodology, the EMSL-LV FPXRF team became an integral part of the program design group, along with personnel from Roy F. Weston, Inc., Denver, and Geostat Systems, Inc., of Golden, Colorado.

The study was designed to achieve three primary goals. First, to demonstrate the ability of the FPXRF instrumentation to generate quantitative data of known quality. Second, to gather sufficient data to allow the use of geostatistics to determine the optimal sample spacing for further sampling (to be determined by Geostat Systems, Inc.). Third, to define areas of contamination in specific concentration ranges of <500 mg/kg, 500-1500 mg/kg, and >1500 mg/kg.

To achieve these goals prior to field work, EMSL-LV participated in the writing of a Sampling and Analysis Plan and a Quality Assurance Project Plan as part of the Workplan for XRF⁽³⁾. Once the plans were written and accepted, the EMSL-LV mobile XRF laboratory was moved to Leadville, and a temporary field laboratory was set up for sample preparation and analysis. In addition, a database management system was designed and implemented to handle the large amount of data generated by the XRF program.

Once on site, the next step was to run a feasibility study to demonstrate that the data generated by the FPXRF instruments would meet the data quality objectives of the project. The remainder of this report is dedicated strictly to XRF aspects of the program.

PRINCIPLES OF X-RAY FLUORESCENCE

XRF spectrometry is based on the principle that photons produced from an X-ray tube or radioactive source bombard the sample to produce fluorescence. The incident photons impinge on the electron cloud of the atom. Among other events, this process creates vacancies in one or more of the inner shells. The vacancies cause instability within the atom. As the outer electrons seek stability by filling the vacancies in the inner shells, the atom emits energies as X-ray photons. The emitted energy (fluorescence) from a particular shell is characteristic of the atom in which it was produced and is equal to the difference in bonding energy between the outer shell electron and the vacant shell. Most elements under

the photon bombardment fluoresce simultaneously to produce a spectrum of characteristic radiation. It is this spectrum that the XRF detector senses and counts.

There are two types of XRF spectrometers, energy dispersive and wavelength dispersive. The principal differences are in the method of detection of the fluorescent energies of the specimen and the method of quantifying the analytes of interest. For more detailed information on X-ray fluorescence, the reader is referred to Jenkins *et al.*⁽⁴⁾.

THE X-MET 880

The X-Met 880 used on the Leadville site is a field-portable, energy dispersive XRF spectrometer marketed by Outokumpu Electronics, Inc., Langhorne, PA. The unit is self-contained, battery powered, microprocessor based, and weighs 8.5 kg. The surface analysis probe is specifically designed for field use. The X-Met 880 is hermetically sealed and can be decontaminated with soap and water. The probe includes two radioisotope sources, Americium-241 and Curium-244, a proportional tube counter, and the associated electronics. The source is protected by a Nuclear Regulatory Commission approved safety shutter. The electronic unit has thirty-two calibration memories called "model". Each model can be independently calibrated for as many as six elements. Using a multivariate regression procedure with the proper isotope sources, the instrument can be calibrated to measure elements from silicon to uranium. Unknown sample intensities are then compared to the calibration curves to yield quantitative concentrations.

THE KEVEX 770

The Kevex 770 is a laboratory-grade, energy dispersive XRF instrument marketed by Fisons Instruments, San Carlos, CA. The instrument contains a 198 watt, Rh anode, liquid-cooled X-ray tube, and a cryogenically cooled, lithium drifted silicon solid state detector. Optimal excitation conditions for analytes ranging from Na to U can be achieved using tube direct excitation with filters or using secondary targets for essentially monochromatic excitation. The higher resolution of the Kevex (over five times that of the X-Met) allows for excellent qualitative scans for analytes that interfere with the analytes of interest.

Calibration curves were chosen over Fundamental Parameters (FP)¹ for quantitating the analytes of interest. It was decided in committee that calibration curves based on a suite of site specific calibration standards would be a more robust approach than using FP.

INSTRUMENT CO-CALIBRATION

Forty-five residential soil samples from a 1990 sampling effort by Walsh and Associates, Denver, Colorado, were available with corresponding EPA CLP analytical results.

¹Fundamental Parameters is a mathematical approach which resolves analyte interferences and produces quantitative results for all analytes in the sample.

Each sample was poured from its eight ounce jar into a pan, dried overnight at 100 °C, and then sieved through a two mm sieve. The sample was then rolled 20 times corner-to-corner on a piece of kraft paper down the long axis of the subsequent ellipsoid shape of the pile of soil. Approximately ten, half gram samples were extracted from the pile of soil and placed in a 31 mm polyethylene X-ray cell which was sealed with 0.2 mil thick polypropylene film. Ten of these samples which spanned the full concentration range were used to "co-calibrate" the four XRF instruments (site specific soil standards). The remaining samples were used to verify the accuracy of the calibration procedures. There were four instruments used in this study: one Kevex 770 and three X-Met 880s. Correlations between CLP results and the results from the four instrument verifications are shown in Figure 1.

Site specific soil standards were used to compensate for physical (particle size, bulk density, heterogeneity) and chemical (spectral) matrix effects that impact instrument response when analyzing soils. Calibration curves for one matrix usually give incorrect results when used to analyze samples of a different matrix.

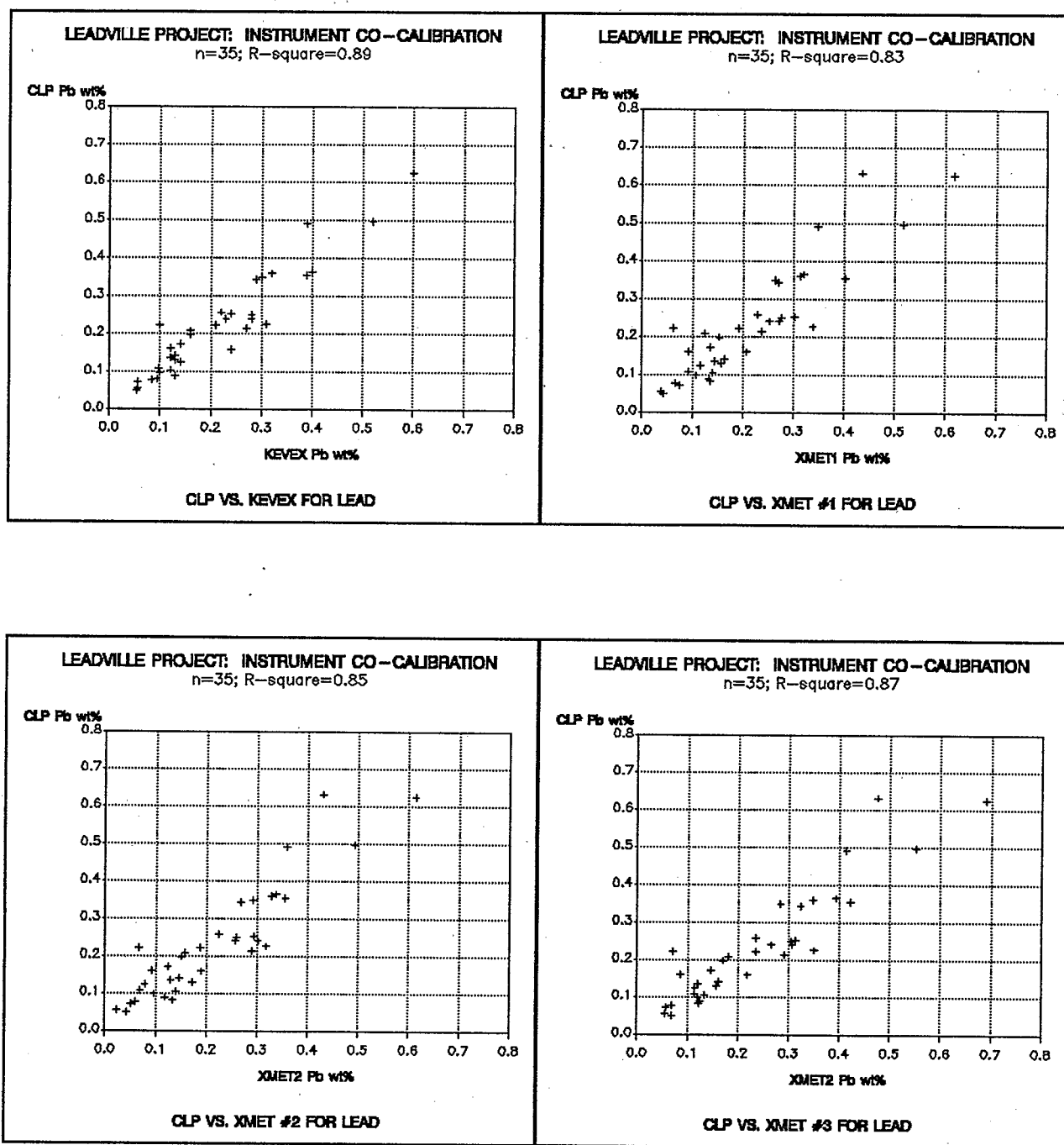


Figure 1. Calibration results for the Kevex and X-Mets 1, 2, and 3.

At Leadville, at least four different matrices were expected to occur: a carbonate tailings matrix, a sulfide tailings matrix, slag, and local soil. An assumption was made that since human activity over the last century thoroughly mixed these matrices in the residential portion of the town, a single set of calibration curves could be used. The ten calibration samples came from locations scattered across the townsite, and the success of the calibration confirmation and subsequent CLP corroboratory analyses indicated that the assumption was valid.

SAMPLE HANDLING

It was originally intended that once X-Met correlation to the Kevex was clearly shown to be acceptable (i.e., $R^2 > 0.7$) on a significant number of samples (800-1000), the X-Mets would be taken into the field for in situ analysis. This was to be done for the sake of expedience, but the field sampling crews proved so efficient that sample analysis continued in the laboratory for the duration of the program. Access to residential lots was extremely limited at the beginning of the program, so transects were surveyed on public properties which were mostly along the unpaved shoulders and edges of alley rights-of-ways, usually only a few feet from backyard property lines.

FIELD SAMPLING

Intrusive samples were collected at 25-foot intervals along the transects. At each sample location, a volume of soil approximately six inches in diameter and four inches deep was thoroughly disaggregated with a pick and shovel. The soil was turned onto itself seven times to reduce heterogeneity and to allow a surface measurement technique to represent a volume. This was the surface upon which in situ analysis was originally intended to be performed. Approximately 300 to 500 grams of soil was scooped into a large plastic bag, labeled and custody sealed, then double bagged and placed in a cooler for transport to the field laboratory. All samples were obtained under chain of custody. Upon arrival at the field laboratory, all samples were logged in and remained under locked custody.

SAMPLE PREPARATION

The First 850 samples

Each bag was opened and the field moist samples were analyzed in the bag three times (by placing the probe in the bag), thoroughly shaking the sample in the bag between analyses. This mode of analysis was deemed analogous to in situ analysis, if the program had gone to in situ analysis.

Each sample was then transferred to a Pyrex loaf dish and oven dried overnight at 100 °C. The dried sample was passed through a ten mesh (2 mm) sieve onto a three by three foot piece of kraft paper where the sample was rolled onto itself 20 times to reduce heterogeneity. Approximately six grams taken in 10-12 subsamples was placed into a 31 mm

diameter polyethylene X-ray cell and sealed with 0.2 mil polypropylene film. The cupped sample was then analyzed on the Kevex and again on one of the three X-Mets. The remaining dried soil was put into archive, still under chain-of-custody. All Pyrex loaf dishes were decontaminated with an Alconox/distilled water solution, rinsed with distilled water, and air dried.

All X-Met measurements were done in triplicate and the values averaged partly due to the relatively short acquisition time (30 seconds livetime), but mostly to obtain a more representative composite value of each sample. A sample is measured only once on the Kevex due to the long acquisition time (200 seconds livetime²).

The Rest of the Samples

Once good correlation was established between X-Met and Kevex analysis (see Figure 2), only one in ten samples was dried, cupped, and analyzed on the Kevex. The X-Met procedure continued in the same manner throughout the rest of the program; that is, samples were brought in by the field crews, analyzed in triplicate in the plastic bag, and then archived.

DATABASE MANAGEMENT

A database management system was developed using the Statistical Analysis Software supported by the SAS Institute Inc., Cary, NC. Screens were designed to look exactly like the data recording forms. Along with all the analytical data (all triplicate measurements and associated QC samples), other data including easting, northing, analytical date and time, sample type, instrument ID, and a unique serial number for each sample were tracked by the management system.

Data were entered in batches (30 samples per batch) and as each batch was completed, it was printed out and 'hand' checked against the data recording forms for entry errors. All changes made to the database were tracked by a comparison procedure, and a printout of each set of changes made to the data set was put into the hard copy dataset for documentation purposes.

QUALITY CONTROL

As the database grew, comparison plots were periodically generated between the Kevex and the X-Mets to assess the degree of correlation, as was done with the co-calibration, thus demonstrating internal consistency within the data collection effort. Once the CLP corroboratory data were available, the same type of correlation was generated, confirming the accuracy of the data.

²At an average deadtime of 40 percent, this equates to 280 seconds acquisition time per sample.

INTERNAL CONSISTENCY

Figure 2a shows the correlation between dry Kevex results and moist X-Met results and 2b shows the correlation between dry Kevex and dry X-Met results. Note that when the samples are dried and cupped and reanalyzed on the X-Met, the correlation improves only five percent. The X and Y axis have been cut off at 1.0 weight percent for illustrative purposes (21 points in excess of 1.0 weight percent are removed from 2a and the R^2 drops from 0.90 to 0.85; 17 points are removed from 2b with no change in R^2). These plots show excellent correlations, and provide assurance of good internal consistency throughout the program.

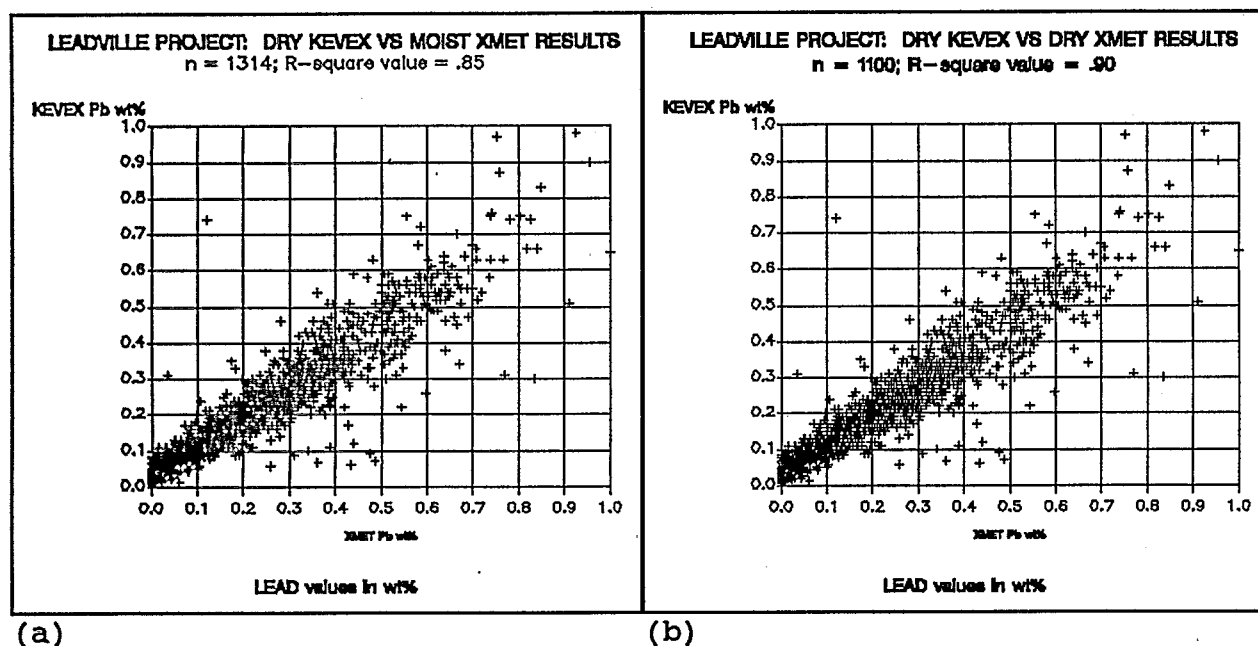


Figure 2. Correlation plots between Kevex and moist/dry X-Met.

QUALITY CONTROL CHARTS

In order to monitor instrument stability, quality control check samples (QCCS) were measured before and after each block of ten samples on each X-Met, and with each batch of 13 samples on the Kevex³. A low- and a mid-calibration range of QCCS selected were used to verify the calibration curves.

³The Kevex 770 has a 16 place autosampler. Each batch of samples consisted of 1 tube flux monitor standard, 2 QC standards, and 13 routine samples.

The low-range sample was used to calculate detection limits (discussed in section entitled "PRECISION, ACCURACY AND DETECTION LIMITS" below), and the mid-range was plotted in a control chart to monitor instrument stability. These control charts are shown in Figure 3.

There are notable differences in the charts that need explanation. There were considerably more samples run on X-Met Number One than on the Kevex, thus the difference in a horizontal sense. There was only one set of QCCS run on the Kevex; however, there were at least three sets run on X-Met Number One due to breakage of the polypropylene film and loss of sample. What was not foreseen, mainly because the authors had not engaged in an XRF survey of this magnitude, was that time would wreak havoc with the QCCS. The 0.2 mil polypropylene film, through which the samples are X-rayed, developed small holes with time and the soil leaked out. Consequently, the film had to be replaced periodically and, being highly electrostatic, it extracted portions of the very fine fraction from the soil, thus biasing the standard. Occasionally, the film would simply break and another QCCS would have to be used. The bias between the different QCCS samples could be seen as several distinct concentration groupings, the first break being at run number 117 (for X-Met Number One). All of these potential sources of error manifested themselves, particularly in the control chart for X-Met Number One, because the majority of the samples were analyzed on this instrument. Also, the QCCS were analyzed in triplicate on the X-Mets and were shaken and tapped between each measurement. The least variability is evident from the Kevex chart because considerably fewer samples were run on this instrument and samples were run only once, thus much less abuse of the polypropylene film occurred.

In retrospect, the QCCS should have been pulverized and pressed to pellets, alleviating the biases with time. The accuracy of the X-Met is clearly displayed in the correlation between CLP and X-Met data (see Figure 4). Ninety-six of the 140 samples sent to the CLP were run on X-Met Number One ($R^2 = 0.86$).

CLP VERSUS X-METS

Figure 4 shows the correlation plots between combined X-Met and CLP and between the Kevex and CLP. These plots show very good agreement between XRF measurements and those of the CLP, thus supporting the high degree of accuracy achieved in this field survey. The higher R^2 value for the less sophisticated X-Mets is probably a result of the triplicate measurement average accounting for the heterogeneity of the sample better than the single, longer measurement used on the Kevex.

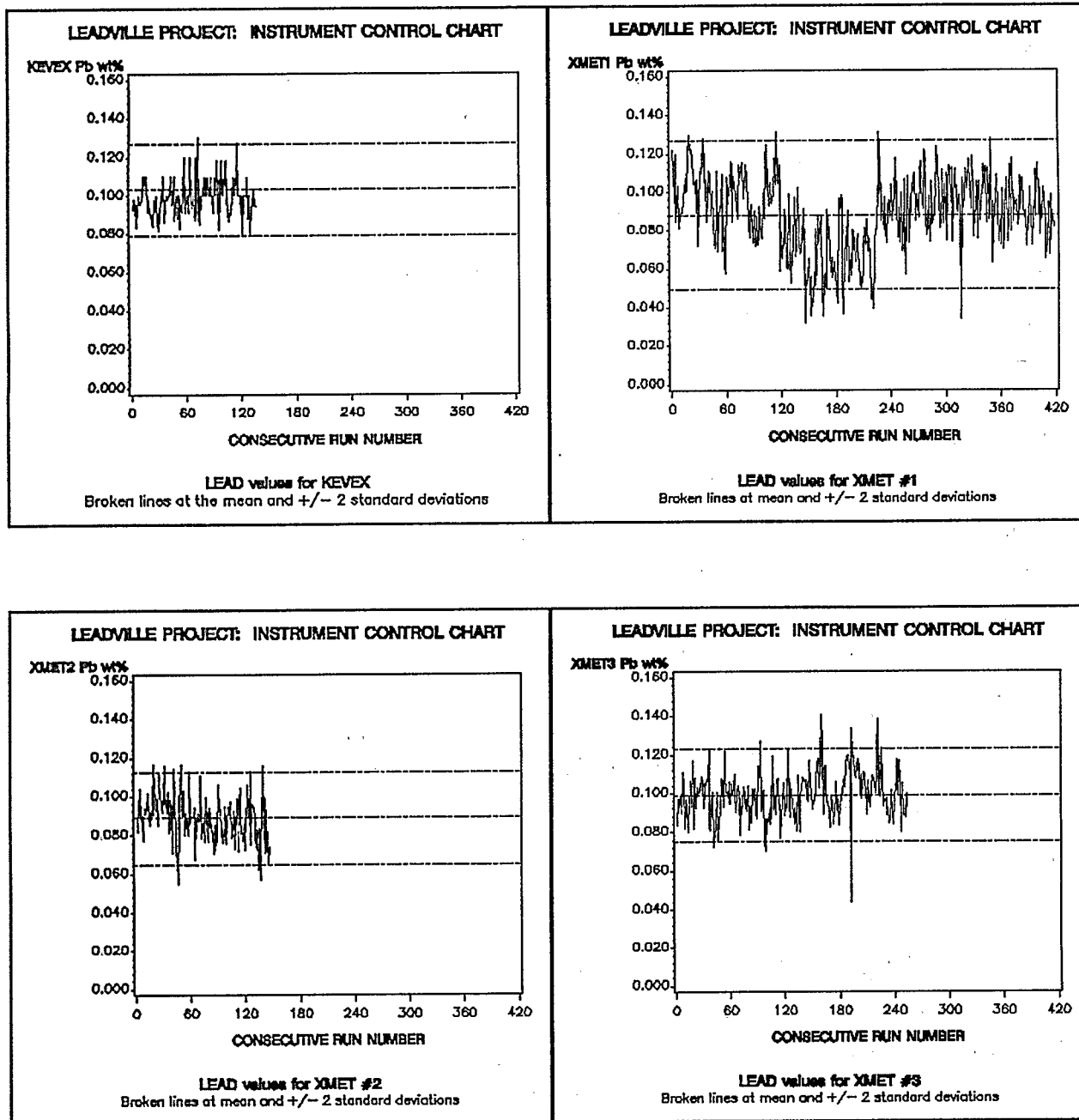


Figure 3. Quality control charts for Kevex and X-Met #1.

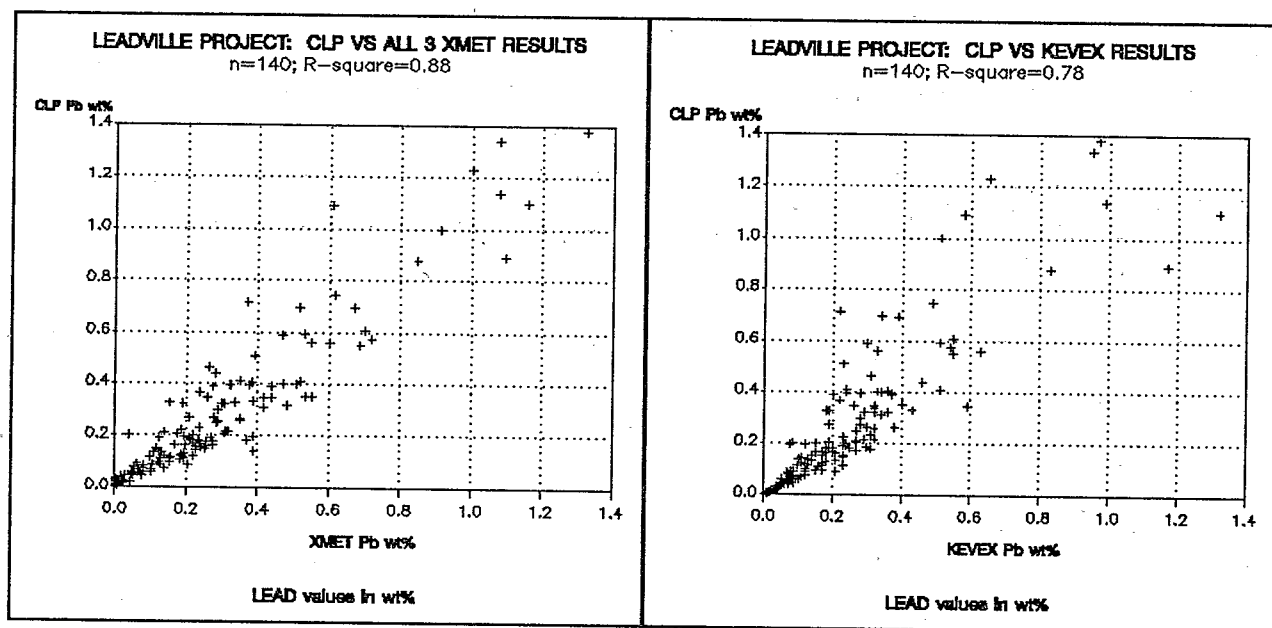


Figure 4. Correlation plot between CLP and combined X-Mets, and Kevex.

PRECISION, ACCURACY AND DETECTION LIMITS

The system precision can be estimated from the moist field duplicates. These samples were split in the field after the in situ preparation of the soil. The sampling trowel would scoop alternately to two bags and each sample went through the system in an identical manner. The analysis of a routine sample and its field duplicate often occurred in different batches, so there is a large time component in the overall variability of these duplicates. The frequency distribution and univariate statistics shown in Figure 5 are on the percent relative standard deviation (%RSD, or percent coefficient of variation) between the routine sample and its field duplicate for samples over 0.05 wt% (500 ppm) Pb. At the 95th percentile, %RSD is 27, so a very conservative estimate of precision is $\pm 27\%$. This is not just analytical error but includes field sampling error and sample preparation errors as well.

Accuracy can be estimated from the correlation with the CLP. With an 88% correlation (Figure 4, left plot), the accuracy can be estimated at approximately $\pm 6\%$ (half of the 12% non-correlation).

Using the American Chemical Society (ACS)⁽⁵⁾ definition of detection limits⁴, the low-calibration level of QCCS estimated a quantitation limit (QL) of approximately 0.16 wt% lead. Given the errors introduced by the unstable QCCS standards, this detection limit is probably artificially high. This assumption is supported by Figure 2a. At the origin of both these plots, a "take off" point for X-Met detection can be seen on the Y-axis at or below 0.1 wt% lead. Note that the QL goes down slightly for the dried samples. Based on Figure 2a, an empirical QL for lead measurements in this program is set at approximately 0.1 wt% (1000 ppm).

⁴The ACS defines a minimum instrument detection limit as 3 times the standard deviation of a series of nonconsecutive blanks or low level check samples, and a quantitation limit as 10 times the standard deviation.

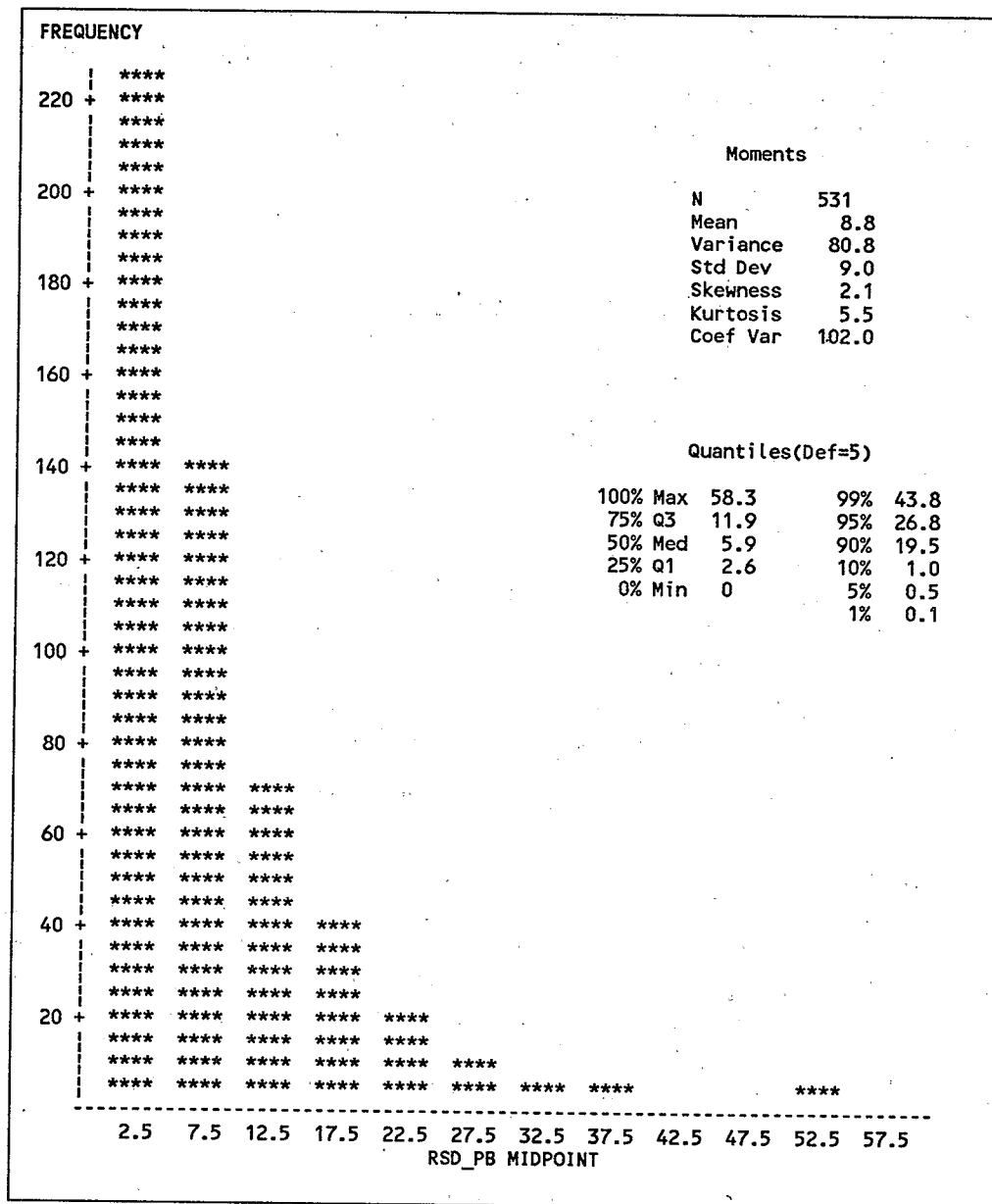


Figure 5. Frequency distribution of %RSD for moist field duplicates.

TOTAL VERSUS ESTIMATION ERROR

The above precision and QL estimates seem high when compared to those obtained from a laboratory, but there were in excess of 3700 samples obtained in this program. Decisions on the spatial distribution of lead in Leadville will not be based on the individual samples, but rather on a geostatistical model of those samples. Consider the following equation:

$$\sigma_F^2 + \sigma_P^2 + \sigma_A^2 + \sigma_E^2 = \sigma_T^2$$

where:

σ_F^2 = Field sampling variance (or error)

σ_P^2 = Sample preparation variance

σ_A^2 = Analytical variance

σ_E^2 = Estimation variance

σ_T^2 = Total variance

The goal of any QA program is to minimize the total error, the right side of the equation. The largest error on the left side of the equation is generally the estimation error⁽⁶⁾. This error is reduced by reducing the sample spacing, thus increasing the number of samples. Raising the analytical quality of the data from Level two to Level three, or from Level three to Level four, as defined by the EPA⁽⁷⁾, will have very little effect on the total error in a study of this magnitude. Significantly increasing the number of samples, however, can have a considerable effect on reducing the total error.

FALSE POSITIVES/FALSE NEGATIVES

The cross plots generated for comparison of X-Met data to CLP data (Figure 4) also provide the basis for another useful tool. By projecting lines at the chosen action level from each axis, the plot is divided into quadrants that can be used to estimate the per cent false positive and false negative analyses. Assuming that the CLP values are the "true" values, the upper left quadrant contains the false negative data points, and the lower right quadrant contains the false positive data points. We constructed a series of such plots at various action levels, the results of which are given in Table 1, below, two of which are shown in Figure 6.

The percentage of false positives is generally higher than false negatives, which suggests that at Leadville, at least, the X-Met measurements err toward the conservative side, i.e., "clean" soil will be unnecessarily called "dirty" more often than "dirty" soil being called "clean". However, because all of the data will be used to generate a model, the impact of a small percentage of false measurements will be minimized and smoothed during the data interpretation procedures. If, however, a large percentage of the data points were to fall in the false positive/false negative quadrants for a critical action level, this would indicate a serious compromise in the data quality.

Action Level (ppm)	False Positive	False Negative
500	2 (8.7%)	3 (2.5%)
1000	9 (22.0%)	2 (2.0%)
1500	13 (22.4%)	3 (3.6%)
2000	21 (26.6%)	6 (9.5%)
2500	13 (14.6%)	4 (7.5%)
3000	8 (8.4%)	8 (17.0%)

Table 1. False positives and false negatives generated at six action levels.

POPULATION TESTING

As explained above, residential access was extremely limited at the beginning of the field season, so the first 50% or more of the samples came from shoulders of alleys in direct proximity with residences. The obvious question was whether the contaminant concentrations along the alleyways were significantly different from contaminant concentrations in nearby residential soils (i.e., are alley samples representative of yard material?). To answer this question, 38 'cells' were located where samples were taken both within alley rights-of-way and in the nearby residential yards. The paired-sample t-test and the nonparametric Kolmogorov-Smirnov procedures of the SAS software were used to show that, with very few exceptions, there is no significant difference between contaminant concentrations in the alleys and in the nearby yards.

The results of the tests on the individual cells are shown in Table 2. The test results are shown for test size 0.05.

Two testing methods were employed, one a parametric statistical approach (2-sample t Test), the other a nonparametric statistical test (Kolmogorov-Smirnov Test). The two approaches were tried because the distribution of data values was tending toward the lognormal, but not strongly so. Thus in order to cover all the bases, both methods were tried. Of the 38 pairwise comparisons of yard and nearby alleyway samples, five were significantly different using the parametric test, while only two were significantly different using the nonparametric test. This confirms the more nearly lognormal distribution of values. Both methods point to the same conclusion, that the two populations are essentially the same.

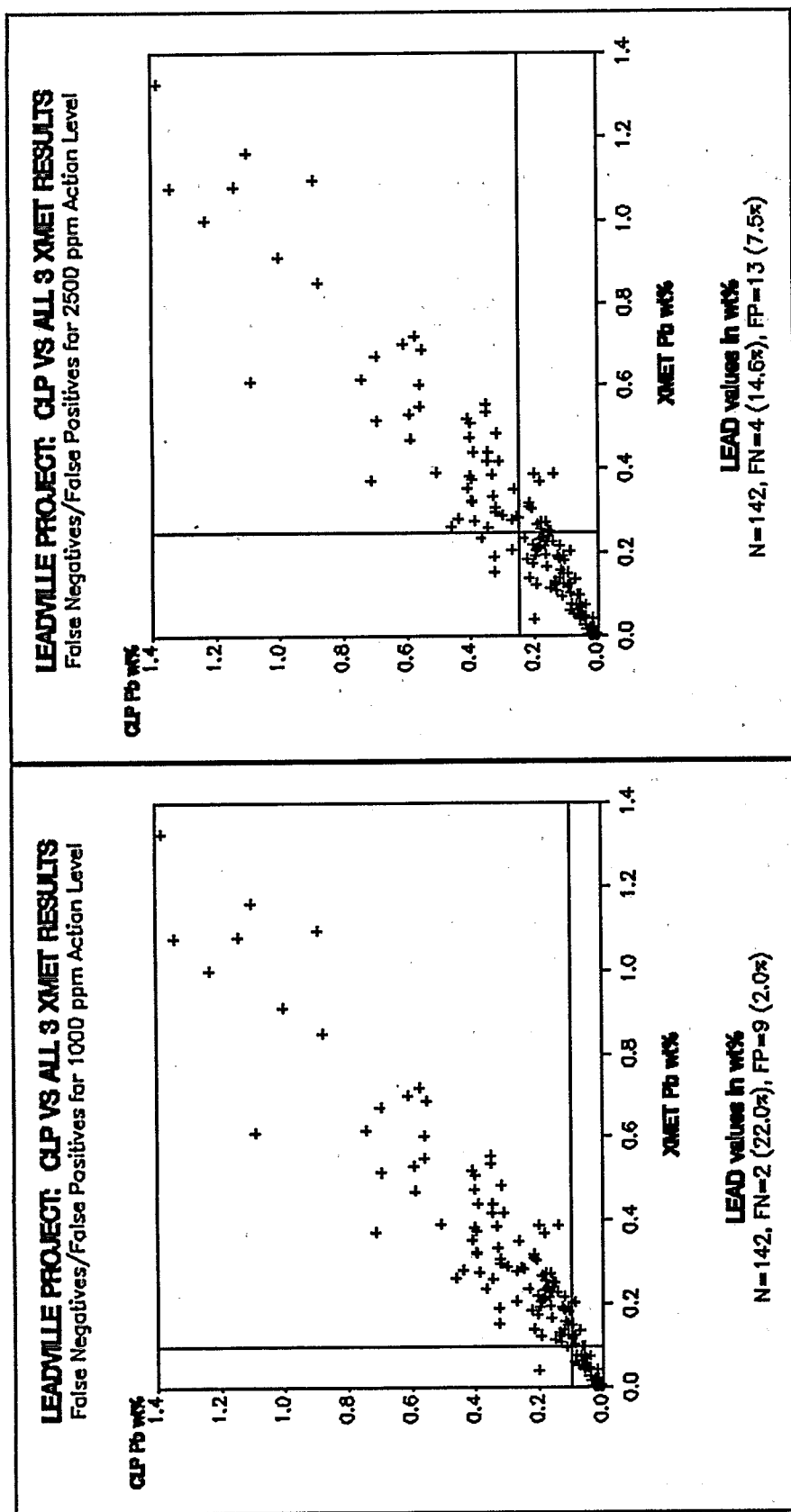


Figure 6. False negatives and false positives generated at two different action levels.

Cell Number	t Test	KS Test	Cell Number	t Test	KS Test
1	NSD	NSD	21	NSD	NSD
2	NSD	NSD	22	NSD	NSD
3	NSD	NSD	23	NSD	NSD
4	SD	NSD	24	NSD	NSD
5	NSD	NSD	25	NSD	NSD
6	NSD	NSD	26	NSD	NSD
7	NSD	NSD	27	NSD	NSD
8	NSD	NSD	28	NSD	NSD
9	NSD	NSD	29	NSD	NSD
10	NSD	NSD	30	NSD	NSD
11	NSD	NSD	31	SD	SD
12	NSD	NSD	32	NSD	NSD
13	NSD	NSD	33	NSD	NSD
14	NSD	NSD	34	NSD	NSD
15	SD	NSD	35	NSD	NSD
16	NSD	NSD	36	NSD	NSD
17	NSD	NSD	37	SD	SD
18	NSD	NSD	38	SD	NSD
19	NSD	NSD			
20	NSD	NSD			

Table 2. List of results of t-test and Kolmogorov-Smirnov (KS) test. "NSD" means no significant difference, "SD" means significant difference.

CONCLUSIONS

The lead concentration data generated by FPXRF on residential soils in Leadville is optimal for producing concentration isopleth maps that depict gross contamination patterns across the townsite. The large number of sample points analyzed minimizes errors in estimating values at unsampled points, yielding a more representative depiction of contaminant distribution than a smaller data set of higher data quality.

A very large number of samples (>3700) were analyzed in a period of about three months, allowing for cost- and time-effective determination of spatial patterns of contamination distribution.

Precision and accuracy of the data generated are good, being $\pm 27\%$ and $\pm 6\%$ respectively. The levels of false positives and negatives are also quite low.

The initial assumption that residential soils in Leadville were of a very similar matrix (with respect to XRF) appears to have proven valid. The close agreement between XRF results and randomly chosen samples analyzed by CLP methods indicates that the single matrix model used with the X-Met 880 instruments was a reasonable approach to dealing with a soil whose initial components were distinctly different, but presumably well mixed by residential and mining activities over a long period of time.

Lead data from alleyway samples can be used to infer lead concentrations in the soil of nearby yards. Statistical analyses showed no significant differences between lead values in backyards and values in nearby alleyways.

As a recommendation, any long-term future work (greater than two weeks) using FPXRF should use pelletized QCCS. It is virtually impossible to prepare identical QCCS from loose soil, which is falsely interpreted as inter-instrument bias. With extended use, the fine soil fraction leaks through holes in the polypropylene biasing the sample, which falsely translates to instrumental drift (intra-instrument bias). Pulverization of the QCCS material prior to splitting minimizes inter-instrument bias, and pressing the pulverized soil into a pellet produces a stable, homogeneous check standard, thus removing the intra-instrument bias.

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