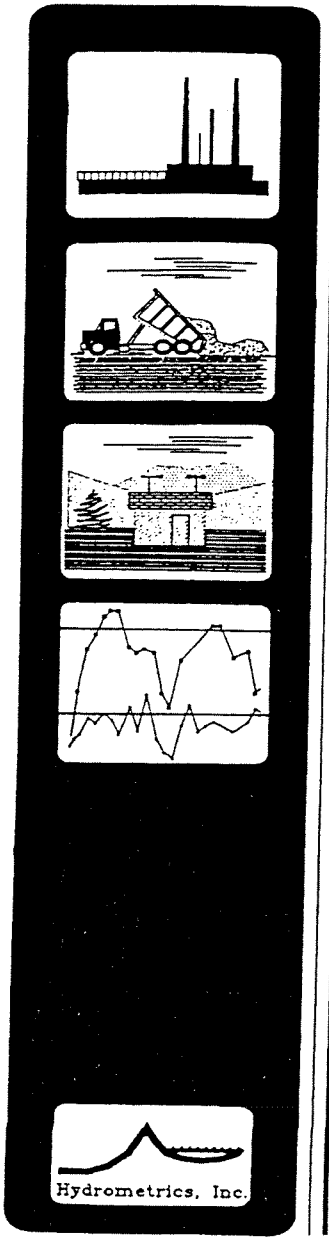
ATTACHMENT #3

East Helena Lead SIP Road Dust Control
Analytical Quality Assurance Plan

May 1995



East Helena Lead SIP Road Dust Control Analytical Quality Assurance Plan

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May 1995

EAST HELENA LEAD SIP

ROAD DUST CONTROL

ANALYTICAL QUALITY ASSURANCE PLAN

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EAST HELENA LEAD SIP

ROAD DUST CONTROL

ANALYTICAL QUALITY ASSURANCE PLAN

1.0 PROJECT ORGANIZATION AND RESPONSIBILITY

The East Helena Lead State Implementation Plan (SIP) Road Dust Control project calls for paved street dust to be analyzed for lead. Asarco has proposed that these samples be analyzed by XRF. This is a non-destructive analytical procedure which uses x-ray spectrum to characterize a sample.

The Hydrometrics, Inc. soils laboratory in East Helena, Montana is the analytical "data generator." Asarco East Helena Plant in East Helena, Montana is primary "data user/requester." The Laboratory Supervisor/QA Officer is the "data reviewer/approver." The responsibilities of QA personnel are as follows:

Project Manager Jon Nickel	Oversees all activities.
Office Manager Tom Wing	Oversees general operations of Laboratory.
Laboratory Supervisor/ QA Officer Linda Tangen	Oversees Laboratory QA/QC procedures, corrective actions and performance.
	Supervises laboratory personnel, equipment, procedures, and documentation.
Laboratory Technician Deanna Hersey	Prepares samples and performs XRF analyses.

2.0 DATA QUALITY OBJECTIVES

2.1 REQUIREMENTS FOR PRECISION, ACCURACY, REPRESENTATIVENESS, COMPLETENESS, AND COMPARABILITY

The overall goal of the Quality Assurance Project Plant (QAPP) is to ensure that data are acceptable for their intended uses, and are of sufficient quality to withstand the potential scrutiny of litigation. The PARCC parameters (precision, accuracy, representativeness, completeness and comparability) address these data quality requirements.

2.1.1 Precision

Precision can be defined as the degree of variability between replicate measurements. Precision is inversely related to the variability among the results obtained. It is expressed in terms of relative percent difference (RPD) of paired data (field and laboratory duplicates). The precision is a measure of the field sampling variability and laboratory analytical variability. The control limits are a relative percent difference (RPD) of 35% or less for field and laboratory duplicates for soil samples greater than 5 times the PRDL (Project Required Detection Limit). Control limits for low concentration data (< 5 X PRDL) are +/- 2 X PRDL. Precision calculations are described in Section 8.1.

2.1.2 Accuracy

Accuracy is the agreement between a measurement and the true value. Accuracy of XRF data will be assessed using laboratory control standards (LCS) and continuing calibration verification (CCV) standards. The control limits are a recovery rate of 75% to 125% for laboratory control standards and continuing verification standards. Accuracy calculations are described in Section 8.2.

2.1.3 Representativeness

Representativeness is the extent to which discrete measurements and testing accurately describe the sample source. Good representativeness is achieved through proper analytical

procedures. Analytical methods and procedures for analyses will follow the procedures outlined in this quality assurance project plan (QAPP).

2.1.4 Completeness

Completeness is achieved when the number of valid measurements is sufficient to satisfactorily address all important issues concerning this project.

2.1.5 Comparability

Comparability is the degree to which two or more data sets from the sample source are equivalent. These data sets will be reported so that comparisons may be made and conclusions drawn from the past, similar and anticipated future studies. Inherent compositional differences aside, discrete data sets may differ as a result of non-random (biased) sampling, variability in sampling technique, different sampling sites, and varied methods of analysis. In order to have confidence that data divergence is based on sample heterogeneity and not on the aforementioned variables, the following quality assurance mechanisms that will be used in this investigation can be categorized as prevention and correction:

2.1.6 Prevention

Prevention of defects in quality or quantity of measurements through planning and design of the investigation, documenting instructions and procedures, and employing experienced and qualified personnel.

2.1.7 Correction

Correction of conditions which could compromise the quality of samples or sample results, based on the review and inspection of measurements and measurement results. Corrective actions will be undertaken by laboratory personnel as described in Section 6.0 of this QAPP.

3.0 CHAIN-OF-CUSTODY

All samples must be traceable from the time the samples are collected until they are received by the laboratory. The laboratory is then responsible for custody during processing and analysis. A sample is under custody if:

1. It is in possession, or
2. It is in view, after being in possession, or
3. It was in possession and then was locked in a storage area to prevent tampering, or
4. It is in a designated secure area.

All samples will be accompanied by a chain-of-custody record. When shipping or transferring custody of samples, the following procedures will be observed.

1. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date and note the time on the record. This record documents sample custody transfer from the sampler to the laboratory.

2. Samples will be packaged properly for shipment and dispatched to the appropriate laboratory for analysis, with a separate custody record accompanying each shipment. Shipping containers will be sealed for shipment to the laboratory.

3. All shipments will be accompanied by the Chain-of-Custody Record identifying its contents. The original record will accompany the shipment and a copy will be retained in the project file.

4. All shipping receipts (freight bills, post office receipts, bills of lading, etc.) will be retained in the project file.

4.0 LABORATORY PROCEDURES

The Hydrometrics, Inc. Soil Laboratory (XRF field laboratory) will be the primary data generator for soil samples. The samples will be analyzed using the XRF instrumentation. Analytical methods, procedures, and detection limits for XRF techniques are summarized in Table 4-1.

TABLE 4-1. ANALYTICAL METHODS, PROCEDURES AND DETECTION LIMITS

PARAMETER	SAMPLE MATRIX	ANALYTICAL TECHNIQUE	SAMPLE PREPARATION	ANALYTICAL PROCEDURE	PROJECT REQUIRED DETECTION LIMITS (PPM)
Pb	STREET DUST	XRF	SIEVING AND GRINDING	QAPP PROCEDURES	10

5.0 XRF PROCEDURES

The basic principle behind the use of the X-ray spectrometer (XRF) is that elements in samples of soil produce a specific signature or spectral intensity peak when bombarded with X-rays. These spectral intensities relate to the concentrations of metals in the sample measured by traditional wet chemistry methods and/or concentrations of certified standards (values are determined by numerous analytical methods). In the Fundamental Parameters method, the measured spectral intensities for soil samples will be compared to spectral intensities measured for pure element standards and/or well characterized reference materials. The Fundamental Parameters method adjusts for matrix differences by theoretical formulas that are quite extensive and can only be efficiently calculated using special designed software and a powerful computer.

At least one reference standard closely approximating the sample matrix, should follow standard sampling, sample preparation, and analytical techniques to validate "theoretical formulas" used by the XRF software before the XRF is used for sample analyses. The concentration of lead in the reference standard shall be within the lead concentration range of the street dust samples. A reference standard meeting the previously criteria, will be analyzed at the beginning of the first run of the day. Calibration limits will be within 75 to 125% of the reported concentration. One continuing calibration verification standard (CCV) will also be analyzed after every 31st sample analyzed. The control limits will be within 75 to 125% of the reported concentration.

6.0 LABORATORY QUALITY CONTROL

6.1 INTERNAL AND EXTERNAL QC CHECKS

Quality control in XRF analyses will be established by analyzing internal QC samples. Frequencies and control limits for QC sample analyses are summarized in Table 6-1.

6.2 CONTROL CHARTS

XRF analyses will utilize control charts to monitor long-term instrument performance and to identify "out-of-control" situations. Control charts are used to trigger corrective actions when control limits are exceeded. Control chart results will only be used by analytical personnel to supplement the specific control limits listed in Table 6-1.

6.3 CORRECTIVE ACTION

Corrective actions are the responsibility of analytical personnel and are described in Table 6-1.

6.4 DETECTION AND QUANTITATION LIMITS

Table 4-1 lists the project required detection limits (PRDL) for lead in soil (10 ppm). Instrument detection limits (IDL) must be less than the PRDL. Instrument detection limits are determined after calibration by calculating the lower limit of detection (LLD) from numerous samples with concentrations near the expected IIDL. The 99% confidence limit of these were used for the reported IDL. The following formula is used to calculate the IDL:

$$IDL = 3\sqrt{N_b \times \frac{VK}{N_p}}$$

Where: N_b = Background Intensity Counts
N_p = Peak Intensity Counts
VK = Known Value of Sample

TABLE 6-1. SUMMARY OF LABORATORY CONTROL PROCEDURES - XRF

PROCEDURE	TASK ELEMENTS	FREQUENCY REQUIREMENT	CONTROL LIMIT	CORRECTIVE ACTIONS
1. Verification of laboratory QC samples	Duplicates	1 in 10 samples or a minimum of 1 duplicate per sample set	RPD +/- 35% Duplicate values within +/- 2 X PRDL for values <5 times PRDL	If duplicate sample results are out of control, flag all data associated with that duplicate sample with "*".
	Laboratory Control Standard (Standard Reference Material or standard with concentrations determined by wet chemistry)	1 at beginning of first run	LCS Recovery 75%-125%	If results for the LCS are out of control, terminate analysis, correct problem, and reanalyze samples associated with that LCS.
2. Instrument calibration	Instrument calibration frequency and control limits	Instrument calibrated the Fundamental Parameters Methods (instrument does not need to be recalibrated after initial calibration other than a case of x-ray tube or detection failure)	Standard correlation of determination (r^2) greater than .95 (determined at the time of calibration by regression analysis)	Recalibrate
3. Instrument calibration verification	Continuing calibration verification standard (standard used for calibration)	1 in 32 samples	CCV recovery 75%-125% (or within 95% confidence limits for the standard)	If results for the CCV are out of control, terminate analysis, correct problem, verify calibration, and reanalyze samples associated with that CCV.
4. External QC Checks	Outside laboratory confirmation of sample split	1 per calendar quarter	No limits. Report results in quarterly report.	No corrective action
	Blind field sample	1 per calendar quarter	No limits. Report results in quarterly report.	No corrective action

7.0 REPORTING

Analytical reports will be reviewed by the Laboratory Supervisor/QA Officer for data input accuracy and to assure quality control standards have been met.

Analytical reports will include:

1) Copy of the Chain of Custody

2) Results of the sample analysis
   a. Name of procedure used
   b. Name of samples with laboratory codes
   c. Units
   d. Laboratory duplicate values and RPD calculations

3) Quality control report
   a. Laboratory control standard values with recovery rate calculations
   b. Continuing calibration verification standard values with recovery rate calculations

8.0 ASSESSING DATA PRECISION AND ACCURACY

8.1 PROCEDURES FOR CALCULATING PRECISION

From the summarized information on the precision form, the relative percent difference (RPD) of each laboratory duplicate pair calculated separately as:

$$RPD = \frac{|S - D|}{(S + D)/2} X\ 100,$$

where: S = First Sample Value (original);
D = Second Sample Value (duplicate).

Perfect precision would result in 0% RPD.
Any RPD value exceeding the control limits of = 35% for soils.

8.2 PROCEDURES FOR CALCULATING ACCURACY

From the summarized information on the accuracy form, the percent recovery of the LCS and CCV are calculated separately as:

$$\%\ Recovery\ of\ LCS\ or\ CCV = \frac{VA}{VK} \times 100$$

Where: VA = Analytical Value of LCS and CCV;
VK = Known (or certified) Value of LCS and CCV;

Perfect accuracy would be 100 percent recovery.

APPENDIX A

STANDARD OPERATING PROCEDURES

PRE-ANALYTICAL SOIL HANDLING AND PREPARATION ©
(HS-SOP-83-5/95)

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Hydrometrics, Inc. Consulting Scientists, Engineers & Contractors

STANDARD OPERATING PROCEDURE

PRE-ANALYTICAL SOIL HANDLING AND
PREPARATION FOR SILT ©
(HS-SOP-83-5/95)

1.0 PURPOSE

The purpose of this procedure is to prepare samples for XRF analysis. All soil samples collected for analysis will be prepared using this procedure.

2.0 EQUIPMENT

Microwave or
Drying Oven
Shatter Box Grinder or
Mill Grinder
Mylar (4.5 mm)

Ziplock Bags (one gallon size)
Kraft paper bags (100 g. size)
XRF Instrument
XRF Soil Cups
200 Mesh Sieve
Sieve Shaker (Horizontal Action)

3.0 PROCEDURE

1) Collect Sample (200-2000 grams).

2) Record sample into laboratory log book and give sample laboratory and archive code. Mark sample bag with laboratory code.

3) Dry sample by microwave or in drying oven if needed to achieve uniform split. Drying temperature not to exceed 110° C.

4) Homogenize and split sample into 100-150 gram size using "cone and quartering method." Save one 100-150 gram section of sample, archive section(s) equaling at least 200 grams and discard remaining sample into contaminated waste container.

"Cone and Quartering Method"

A) Place entire sample onto clean freezer paper.

B) Roll sample back and forth using all sides of paper. This is to be done until aggregate size is uniformly distributed in a cone fashion.

C) Sample is then divided into "pie" sections until sections equal 100-150g. A larger section may be needed if more than 80% of sample is greater than 200 mesh

5) Dry 100-150g sample section in microwave or drying oven until sample is friable. Drying temperature should not exceed 110° C.

6) Disaggregate and screen sample using a decontaminated #200 stainless steel mesh screen and tared pan. Disaggregation is accomplished by sieving sample using a sieve shaker for 10 minutes. Weigh pan containing minus 200 mesh. Repeat the sieving in 10 minute intervals until the difference between two successive pan sample weights is less than 3 percent when the tar weight of the pan has been subtracted. Do not sieve longer than 40 minutes. Discard over size sample into contaminated waste container. Screen is to be decontaminated by using compressed air in between each sample. The mortar and pestles will be decontaminated using compressed air, rinsed with distilled water and wiped dry.

7) Grind undersize sample using a shatterbox grinder for a period of 2 minutes (more may be required depending on matrix of sample) to achieve <400 mesh size. Three samples may be ground at the same time using a Spex 8510 model with adapter. Sample may also be ground using a mill type grinder for a period of 2 minutes or longer if required. Grinder is cleaned thoroughly by spraying with compressed air in between each sample. Mill grinder is additionally cleaned by grinding clean silica and spraying with compressed air. All grinding and decontaminating is to be done under a well ventilated hood. Canister type respirators are to be worn supplied with particulate HEPA filters when working with samples containing high concentrations of these materials.

8) Cool ground sample.

9) Place »10g sample into XRF sample cup. Tamp sample to a consistent depth and density within the cup. Place Mylar on cup and anchor with a plastic ring. Mark cup with sample code. Remaining sample is to be placed into a kraft paper sample bag, marked with sample code and archived. After analyses, XRF sample cup is to be archived.

APPENDIX B

STANDARD OPERATING PROCEDURE

SPECTRACE 5000 EDXRF ROUTINE SOIL ANALYSIS ©
(HL-SOP-53-2/95)

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STANDARD OPERATING PROCEDURE

SPECTRACE 5000 EDXRF ROUTINE SOIL ANALYSIS ©
(HL-SOP-53-2/95)

1.0 PURPOSE

The purpose of this procedure is to provide the analyst with a guideline for XRF analysis. All soil samples collected for the determination of analytes by XRF will be analyzed using this procedure.

2.0 EQUIPMENT

Spectrace 5000 Energy Dispersive X-Ray Fluorescence Spectrometer

3.0 PROCEDURE

1) Unlock XRF at rear of instrument and turn on the computer.

2) Calibrate instrument to copper energy line by the following:

TYPE: C:\EDXRF
PRESS:<ENT> <F5>
TYPE: \??? - Name of the program containing the energy calibration setup.
PRESS: <ENT>
Place copper disk into position #16 of carousel.
Enter into program containing calibration setup.
PRESS: <F7> <SPACEBAR>

3) Check system status display by the following:

TYPE: <F2> <F4>
Check "Fast Disc Rate" - this should be between 100 and 150/sec. If not, adjust the Fast Discriminator with a tool supplied by Spectrace to bring the rate into the correct range (must be visually instructed before attempting with procedure).

4) Print system status display by the following:

PRESS: <PRINT SCRN>
PRESS: <F10> <F10>

5) Run intensity correction program by the following:

Put Intensity Correction sample into position #1.
Highlight Procedure #8.
PRESS: <F1> <ENT>
The report of the check standard factor will automatically print out. Record into daily calibration log book along with the: **gain dac, zero dac, fast discriminator (from system status hardcopy); date, time, initials of the analyst and whether the liquid nitrogen dewar tank was filled.**

6) Run quality control and unknown samples by the following:

Review quality control standards set for each project. These standards must be consistently followed in order for results to be considered "valid."

View prepared sample in XRF cup. Check for even distribution of particles. If necessary, tap the cup until particles are distributed evenly. Place cup carefully into the carousel.

After XRF cups are appropriately placed in carousel:

PRESS: <F1>
TYPE: # - Number of samples to be run
PRESS: <ENT>
TYPE: ~~## ######~~ - Laboratory sample code
PRESS: <ENT>
After all lab codes are entered, recheck codes by:
PRESS: <F10>
Repeat above procedure by pressing <ENT> after each lab code is displayed correctly or edit lab codes when needed before pressing <ENT>

After all lab codes have been entered correctly, place carousel into the XRF by aligning pins with correct slots. Tighten thumb screw only slightly. Check all cups for proper placement. Close lid carefully. The energy level will increase and x-rays will engage at this point. When spectrum appears on screen, the analysis has begun.

If x-rays fail to engage:

Check front and back panel doors to ensure they have been properly latched. The latch for the front panel is located in the back of the XRF behind the back panel. This handle should point down. Turn the key to lock the back panel. Also, check the lid for proper latching. When lid is closed and program has started, a clicking sound can be heard (this is the latching of the lid). If no click is heard, push down slightly on lid and listen for a click. If lid again fails to latch, or if there are other problems, refer to the

operator's manual or call Spectrace Instruments (415) 967-0350 and ask for a technician.

To stop the program at any time:
PRESS: <F10> This will also back out of each screen or menu.

If paper misfeeds:
Adjust printer and set "on line".

If printer error message displays on screen:
Type: <R> - Report will print from the point of interruption.

If data is unreadable:
Highlight the procedure the samples were run from.
PRESS: <F2> <F6> <F7> Entire report will print.
PRESS: <F10> <F10> This will put you back into main menu.

If program is disrupted during analyses:
=>If samples were run using a single procedure:
Check hard copy for last sample result and run samples with missing results.

=>If samples were run using a combined procedure (ex. 6+7 Unknown):
Highlight each single procedure comprising the combined procedure and follow proceeding instructions (ex. Highlight procedure 6 first to print out report, repeat for procedure 7 to print out report).
PRESS: <F2>
HIGHLIGHT: "SPECTRUM PROCESSING"
PRESS: <F1>
TYPE: ## - Number of samples that were run before disruption (if this is an unknown number, type in 16).
PRESS: <ENT> Wait until samples are processed.
HIGHLIGHT: "ANALYSES TECHNIQUE"
PRESS: <F1> Report will print out.

If screen displays error message "ZERO DAC AT LIMIT":
PRESS: <F7> <F4> <F10> <F10>
If spectrum displays on screen, reanalysis has begun. If not, use the procedure described in "*If program is disrupted during analyses:*."

7) Copy project Results file to disk by the following:

Go to program directory prompt:
PRESS: <F10>
TYPE: Y

Copy ASCII Results file:
Insert disk in drive (B:)
TYPE: COPY RESULTS A (or B drive): ??###### (Project, Year, Month, Day)
PRESS: <ENT>
ex) EH940724 (East Helena Project, 1994, July 24th)

To convert Results file to Lotus 123 (if needed):
PRESS: <F10>
TYPE: Y CONV123
PRESS: <ENT>
TYPE: N Y ??###### (Project, Year, Month, Day)
PRESS: <ENT>

To copy Lotus 123 file to disk:
TYPE: COPY ??######.WKS A (or B drive):

8) Erase project Results (and Lotus 123) file by the following:

Go to program directory prompt:
PRESS: <F10>
TYPE: Y

Erase Results file:
TYPE: ERASE RESULTS

Erase Lotus 123 file:
TYPE: ERASE ??######.WKS

4.0 MAINTENANCE

1) Fill dewar tank with liquid nitrogen at the beginning of the day on Tuesdays and Fridays or twice a week. Safety glasses and autoclave gloves must be worn when filling. XRF should sit idle for approximately 20 minutes after filling. Check fast discriminator rate (directions preceding) to make sure it is within range before calibrating. Order liquid nitrogen from supplier every three weeks.

2) Keep carousel area free of dust and dirt. Replace mylar on detector when dirty or severely scratched (must be visually instructed before attempting this procedure).

3) Unplug computer and XRF during power surges such as electrical storms.

4) Leave computer on in between sample runs. The XRF must be energy calibrated each time the computer is turned on.