Omaha Lead
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A STUDY ON

THE SOURCE OF ANOMALOUS LEAD CONCENTRATIONS IN SOILS FROM THE OMAHA COMMUNITY— OMAHA, NEBRASKA

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TABLE OF CONTENTS

1.0 Introduction.....6

2.0 Historical Background.....6

3.0 Lead Geochemistry.....8

4.0 Lead Speciation.....10

Methodology.....10

Sample Preparation

Point Counting

Precision and Accuracy

Plant Soils.....18

Park Soils.....28

Community Soils.....34

Statistical Study--Factor Analysis.....43

5.0 Bioavailability.....50

6.0 Lead Isotopic Study.....55

7.0 Apportionment.....61

8.0 Further Studies.....65

9.0 Conclusions.....66

10.0 References.....67

Tables

Table 1 Common Lead Sources....9

Table 2 Potential Source Samples: Locations and Bulk Lead Concentrations....14

Table 3 Community Soil Samples: Locations and Bulk Lead Concentrations....15

Table 4 Summary Speciation Results for Plant Soils....21

Table 5 Summary Speciation Results for Park Soils....31

Table 6 Summary Speciation Results for Community Soils....37

Table 7 Correlation Matrix....46

Table 8 Summary Bioavailabilty Results....52

Table 9 Lead Apportionment for Omaha Community Soils....63

Figures

Figure 1 Omaha Study Location Map....7

Figure 2 Summary of Plant-site Lead Speciation....19

Figure 3 Histogram of Lead phase particle-size from Plant-site....20

Figure 4 Summary of Park-site Lead Speciation....29

Figure 5 Histogram of Lead phase particle-size from Park-site....30

Figure 6 Summary of Community Lead Speciation....35

Figure 7 Histogram of Lead phase particle-size from Community Soils....36

Figure 8 Plots of Factor Loadings from Factor Analysis....45

Figure 9 Summary of Bioavailability Results....51

Figure 10 Lead Isotopic Summary....58

Figure 11 Lead Isotopic distribution for site lead forms.....59

Figure 12 Lead isotopic source characterizations.....60

1.0 INTRODUCTION

On August, 2000 Black and Veatch, on behalf of U.S. Environmental Protection Agency (USEPA) requested the Laboratory for Environmental and Geological Studies (LEGS), at the University of Colorado to undertake an apportionment /characterization study on residential soils from the central Omaha, Nebraska area. In response to this request a mineralogical and geochemical study was conducted on community and potential source soils in order to characterize the form(s) of lead, their isotopic character, and bioavailability . Samples were acquired from the former ASARCO lead refinery, and Gould secondary lead smelter, along with community soils by representatives of the USEPA. A site map, with sample locations and selected demographics are indicated on Plate 1.

2.0 HISTORICAL BACKGROUND

Historically, two lead smelters, the ASARCO Grant/Omaha Smelter and the Gould Secondary Smelter, have operated on the eastern edges of central Omaha, Nebraska along the banks of the Missouri River. Both facilities were likely to impact similar Omaha residential corridors, as the plants were virtually neighbors, although the ASARCO facilities historical operations were five times longer, Figure 1.

The Gould Secondary Smelter, operated from the early 1950's thru 1982. It was originally built to reclaim lead from storage batteries and other scrap sources, producing both native lead and antimony-lead ingots. The facility consisted of two reverberatory furnaces, and seven refining

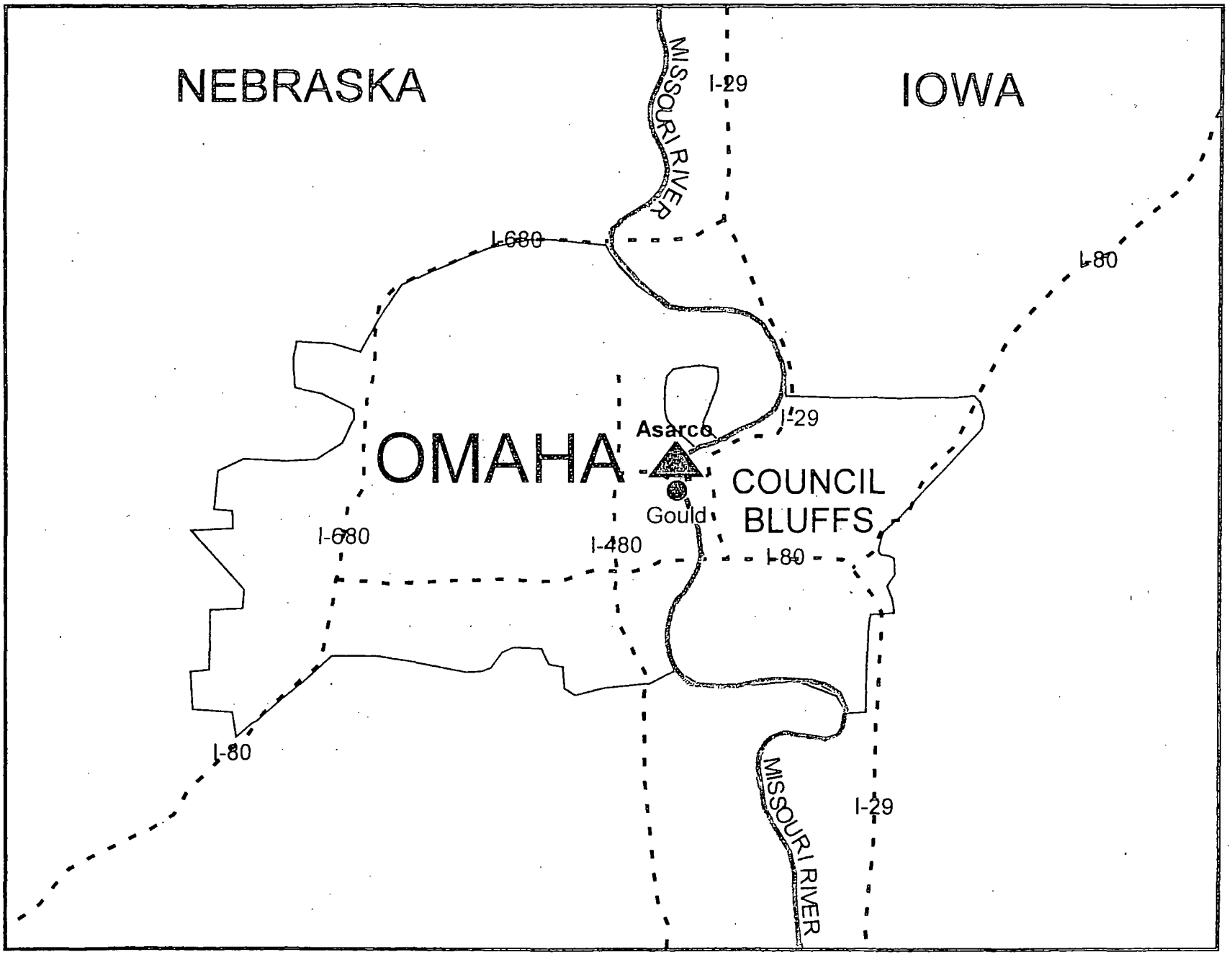


FIGURE 1. Omaha Site Location Map.

kettles. While smelting was carried out in a blast furnace constructed at the facility. The facility maintained a marginal draft system, and was repeatedly cited for elevated lead-in-air violations (2,000-8,000 mcg/m^3), Panitz, 1987. Baghouses (devices used to minimize stack emissions) were introduced to the facility in the early 1970's to limit the loss of metal from fumes, however the facility continued to exhibit uncontrolled emissions exceeding 1,000 mcg/m^3 until its closure in 1982. Facility soils were highly contaminated, with test borings ranging from 3800-152000 mg/kg Pb at 0-30" and up to 1700 mg/kg at 10'. (Neyer, Tiseo & Hindo, 1988).

The ASARCO smelter, initially referred to as the Grant and then later as the Omaha smelter, operated from 1871 thru 1997. It was built as a lead refinery, processing "pig" lead ingots, recovering Au, Ag, Cu, Zn, Te, Sb, and Bi. The facility consisted of two reverberatory and one blast furnace, for its copper circuit, eighteen refining kettles with six softening furnaces for its lead circuit, along with smaller, antimony and bismuth facilities. Baghouses, six in total, were introduced to the facility in the early 1900's to limit the loss of metal from fumes.

3.0 LEAD GEOCHEMISTRY

Lead is found in many minerals and is typically enriched in soils originating from shales/schists and argillaceous sediments. Uncontaminated soils have mean concentrations of 2-300 mg/kg (Fergusson, 1990), worldwide. The near neutral (6-8.5 pH) acidity of the local soils stimulate very low metal mobility, generally concentrating metals in the surface horizons by preventing there downward distribution over time, however, mobility may be enhanced by irrigation,

aeration, (Logan and Chaney, 1983).

Numerous sources of lead have led to elevated concentrations in surface soils. Table 1 is a compilation of the most common sources, their lead speciation, along with associated lead-soil concentrations (data from Barzi et al., 1996, Kabata and Pendias, 1993; Fergusson, 1990; and Drexler, per. communication, 1998).

Table 1. Compilation of common lead sources and associated soil-lead concentrations.

Source	Lead Speciation	Associated Soils Pb mg/kg
Anthropogenetic	Paint, Solder, Brass, Pb-Glass, Gasoline	100-17,000
Mining	Sulfosalts, PbS, $PbCO_3$, $PbSO_4$	100-96,000
Industrial Works	PbAsO, Pb, $PbSO_4$	100-600
Metal Processing	PbM*O, PbAsO , PbO, FePbO, $PbCO_3$, Slag, $PbCl_x$	100-12,000
Application of Pesticides	PbAsO,	200-2500
Fly Ash	Unknown	
Municipal Sludge	Unknown	80-7400

*M = typically As, Ca, Cd, Cu, Zn or Sb.

4.0 LEAD SPECIATION

Twenty-four samples from the ASARCO facility and eight samples from the GOULD facility (Table 2) along with twenty-eight samples from the surrounding community (Table 3.) were speciated for lead using electron microprobe (EMPA) techniques. Methodologies used for sample preparation, data collection, and data synthesis are described below. Although this reports primary emphasizes the species of lead found in the various media, secondary data was collected on arsenic, and antimony.

4.01 Methodology

Metal speciation was conducted on a JEOL 8600 electron microprobe (EMPA), operating at 15Kv (accelerating voltage) and 15-20 NanoAmp current, at the Laboratory for Geological Studies at the University of Colorado following the laboratory's SOP. One exception was made in the SOP, in that the samples were not sieved to <250 μm, as is most common for bioavailability determinations, but the 2mm fraction was used in order to be consistent with previous site studies in which lead sourcing and/or apportionment are the primary task (USEPA 1996, 1999, 2001 and CDPHE, 1998). The samples were all air dried and prepared for speciation analysis as outlined in the SOP . A combination of both an Energy Dispersive Spectrometer (EDS) and a Wavelength Dispersive Spectrometer (WDS) were used to collect x-ray spectra and determine elemental concentrations on observed mineral phases. All quantitative analyses are based on certified mineral and metal standards using a Phi Rho Z correction procedure.

Representative backscatter photomicrographs (BSPM) illustrating sample characteristics were acquired.

Data from EMPA will be summarized using three methods. The first method is the determination of FREQUENCY OF OCCURRENCE (F). This is calculated by summing the longest dimension of all the lead-bearing phases observed and then dividing each phase by the total length for all phases.

Equation 1.0 will serve as an example of how to calculate the frequency of occurrence for an

Lead- bearing compound.

F_{Pb} - Percent frequency of occurrence of lead in a single phase.

PLD - An individual particle's longest dimension (microns)

$$F_{Pb} \text{ in phase-1} = \frac{\sum (PLD)_{phase\text{-}1}}{\sum (PLD)_{phase\text{-}1} + \sum (PLD)_{phase\text{-}2} + \sum (PLD)_{phase\text{-}n}} \qquad \text{Eq. 1.0}$$

$$\%F_{Pb} \text{ in phase-1} = F_{Pb} \text{ in phase-1} * 100$$

Thus, the frequency of occurrence of lead in each phase (F_{Pb}) is calculated by summing the

longest dimension of all particles observed for that phase and then dividing each phase by the total of the longest dimensions for all phases. The data generated thus illustrate which lead-bearing phase(s) are the most commonly observed in the sample or relative volume percent.

The second calculation used in this report determines the Percent RELATIVE MASS lead (RM_{Pb}) in a phase. These data are calculated by substituting the PLD term in the equation above with the value of RM_{Pb}. This term is calculated as defined below.

RM_{Pb} - Percent relative mass of lead in a phase

SG - Specific gravity of a phase (g/cm^3)

ppm_{Pb} - Concentration in mg/kg of lead in phase (see Table 2.0A, Appendix)

$$RM_{Pb} = F_{Pb} * SG * ppm_{Pb} \qquad \text{Eq. 2.0}$$

The advantage in reviewing the RELATIVE MASS lead determinations is that it gives one information as to which metal-bearing phase(s) in a sample is likely to control the total bulk concentration for lead. As an example, PHASE-1 may, by relative volume, contribute 98% of the sample, however it has a low specific gravity and contains only 1000 ppm lead, whereas PHASE-2 contribute 2% of the sample, has a high specific gravity and contains 850000 ppm of lead. In this example it is PHASE-2 that is the dominant source of lead to the sample.

The third calculation is to determine the MINERAL MASS lead (Min_{Pb}). In this calculation the RM_{Pb} is simply multiplied by the bulk concentration (mg/kg) of lead found in the sample:

$$Min_{Pb} = RM_{Pb} * Pb_{Bulk\ mg/kg} \qquad \text{Eq. 3.0}$$

Where Pb_{Bulk} is the bulk lead for the sample speciated. These values are most useful for geostatistical calculations, such as kriging, or apportionment since values are not forced to 100%.

4.02 Point Counting

Counts are made by traversing each sample from left-to-right and top-to-bottom. The amount of vertical movement for each traverse would depend on magnification and CRT (cathode-ray tube) size. This movement should be minimized so that NO portion of the sample is missed when the end of a traverse is reached. Two magnification settings should be used. One ranging from 40 to 100X and a second from 300 to 600X. The last setting will allow one to find the smallest identifiable (1-2 micron) phases.

The portion of the sample examined in the second pass, under the higher magnification, will depend on the time available, the number of lead-bearing particles, and the complexity of metal mineralogy. A maximum of 8 hours or 100 total particles will be spent per sample. This criteria is chosen to optimize the cost of EMPA analyses versus a statistically meaningful particle count.

Table 2. Potential Source Samples.

Sample Id	Location	Bulk Pb mg/kg
AZDSGP2212541	BH-1 3-4'	528
AZCNSGP2212542	BH-2 3-4'	52961
AZCSSGP2212543	BH-3 5-6.5'	8601
AZCSGP2212544	BH-4 5-5.5'	7958
AZDSGP2212547	BH-9 3-3.5'	22088
AZCESGP2212548	BH-10 3-3.5'	14407
AZCESGP2212550	BH-12 3.5-4'	61268
AZCESGP2212551	BH-13 2.5-3'	7129
AZCESGP2212552	BH-14 2.75-3'	13970
AZASGP2212553	BH-15 3-3.5'	45337
ASASGP2212554	BH-16 3-3.5'	50036
AZASGP2212557	Dead Man Trench 3'	103509
AZZSGPZA12563	MW-9D 0-2'	38260
AZZSGPZA12564	TH-5 0-2'	691
AZZSGPZA12565	TH-23 0-2'	1287
AZZSGPZA12566	MW-16 0-2'	144079
AZZSGPZA12568	TH-26 0-2'	4273
AZZSGPZA12569	TH-22 0-2'	4733
AZZSGPZA12571	MW-200G 0-2'	5109
AZZSGPZA12574	TH-9 0-2'	197206
AZZSGPZA12575	TH-1 0-2'	42220
AZZSGPZA12576	TH-21 0-2'	4201
AZZSGPZA12581	TH-18 0-2'	39190
AZZSGPZA12582	TH-34 0-2'	106665
Loc-1	HPA-1	2390
Loc-2	HPA-2	2590
Loc-3-6-9	HPA-3	1420
Loc-3-10-15	HPA-3 10-15'	449
Loc-4-7-10	HPA-4 7-10'	1590
Loc-5-10-12	HPA-5 10-12'	6170
Loc-7-9-11	HPA-7 9-11'	843
Loc-7-5-8	HPA-7 5-8'	1280

Table 3. Community Soil samples.

Sample ID	Bulk Pb mg/kg
11509	5788
1584	1129
1627	1080
1683	1289
5008B-1	374
5017F-1	659
5020B-2	485
5034B-1	355
5041B-1	142
5044B-1	304
5046Dz	2080
5048B-2	332
5055F-1	334
5056F-2	415
5059B-1	785
5060B-2	1649
5061F-2	261
5063F-2	534
5079B-2	841
5080B-2	328
5081F-2	436
5082B-1	365
5083B-1	1269
5083Dz	1240
5086B-1	NA
5087G	572
5088F-2	419
5098B-2	66

4.03 Precision and Accuracy

The precision of the EMPA speciation will be determined based on sample duplicates run every 20 samples. The accuracy of an analysis will be estimated from a statistical evaluation of point counting data based on the method of Mosimann (1965) these data will be tabulated in Tables 4-6 as $E^{95\%}$.

4.1 Potential lead sources to the Omaha community.

Based on a preliminary evaluation of the Omaha community and its historical growth it is believed that there are two primary sources to the elevated lead concentrations found in the community soils. These sources include; an anthropogenic input (paint, gasoline, solder/brass) and a pyrometallurgical input.

Both the ASARCO and GOULD facilities are characterized as pyrometallugical facilities and during their operational histories numerous sources of lead, primarily as fugitive emissions existed including:

Reverberatory furnaces

Lead kitchens (kettles)

Storage piles

Plant road dust

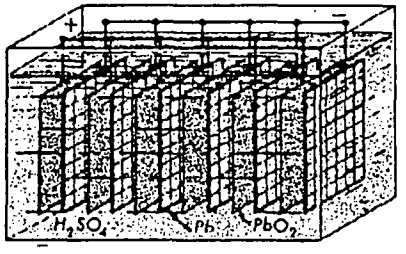
Baghouses/dust collectors

Few of these sources are available today for sampling, therefore, plant-site samples were limited to site-wide soils and borings.

Although both facilities are likely to produce significant quantities of PbO, and $PbCO_3$, some variations in lead speciation between the two smelter facilities can be predicted based on process knowledge. The ASARCO facility, with its copper converter will produce PbAsO, slag, and PbSbO. The lead refinery, will produce by products of $PbCl_x$, $PbSiO_4$, and lead oxides/sulfates of Bi and Zn. The GOULD facility on the other hand should have a greater association with native Pb, and $PbSO_4$, based on known lead-battery operation (Plate 2) along with oxides/sulfates of Cr based on internal documents.

PLATE 2.

Lead-Acid Battery



$$PbO_2 + Pb + 2H_2SO_4$$
$$\text{charge} \uparrow \quad \downarrow \text{discharge}$$
$$2PbSO_4 + 2H_2O$$

4.2 ASARCO-Plant-site Samples

Soil samples from the ASARCO facility were collected between 0-4.5 feet in depth and ranged

in bulk lead concentration from 500-197200 mg/kg. Plant samples studied to date have lead masses dominated (94% of the relative lead mass) by the following lead-bearing phases: PbO, PbMO, $PbCl_x$ and $PbCO_3$ Figure 2, Photos 1 and 2. The most common metals "M" associated with lead are As and Sb. Particle-size of lead phases are tri-modal in their distribution with modes at 2, 12 , and 200 microns, Figure 3 **(Particle-size information for all samples is provided on magnetic media)**. The 2 micron mode is dominated by both $PbCO_3$ and PbMO whereas the coarser modes contain $PbCl_x$ and PbO.

The soils within the ASARCO facility are not as homogeneous in lead speciation as one first may assume when looking at Figure 2. By examining Table 4 or Plate 1, one sees that approximately 62% of the samples had a single lead phase controlling the samples relative lead mass. Nearly 87% of the samples were dominated by only one or two lead phases. In fact, even PbS and $PbSO_4$ dominated the relative lead mass in some samples even though their facility-wide abundance was minor. It is likely this is a result of the multiple extraction circuits found at the facility ie. $PbCl_x$ from the dezincing circuit, PbO from the lead kitchens, and PbMO from the antimony and copper circuits.

Figure 2. Epa Omaha ASARCO "Plant Samples.

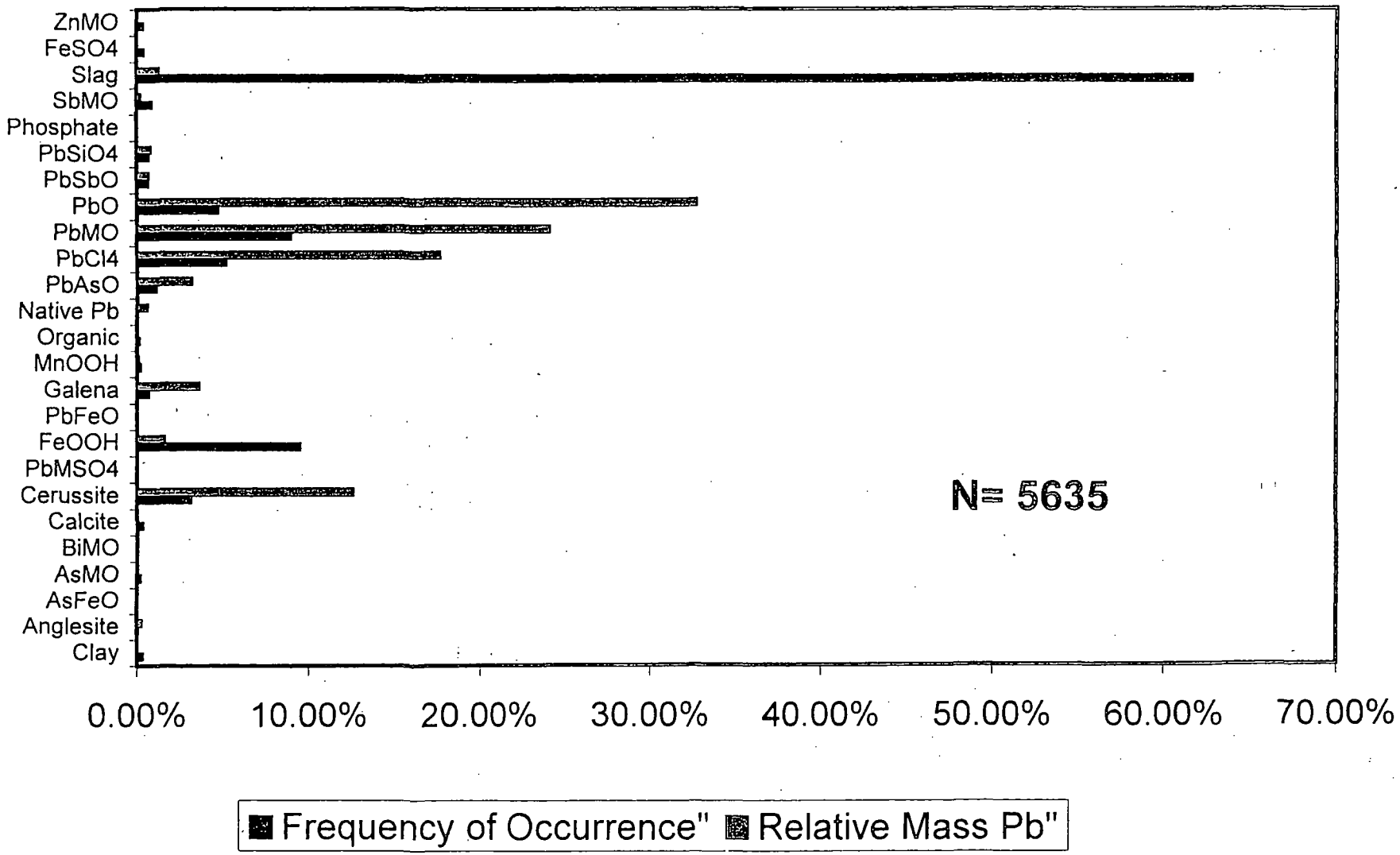


Figure 3. Histogram of Lead Phases from ASARCO Site.

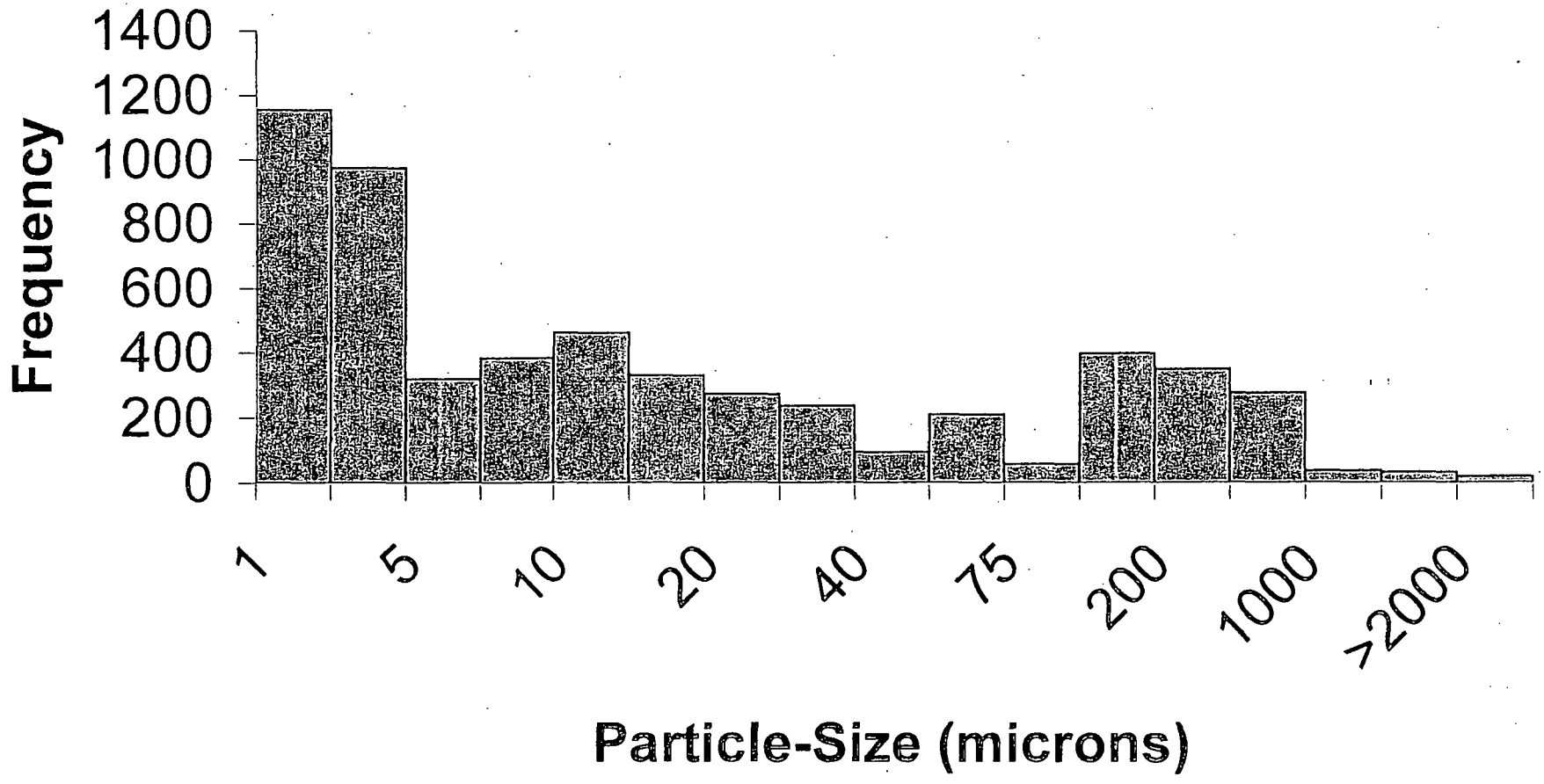


TABLE 4. Summary of Lead Speciation for ASARCO Plant Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
12541						
	Anglesite	0.2%	0.4%	0.0%	2	1.1%
	AsFeOOH	0.9%	0.1%	0.4%	0	2.1%
	Cerussite	1.1%	2.6%	0.0%	14	2.3%
	FeOOH	3.3%	0.3%	0.0%	2	4.0%
	PbAsO	1.0%	1.7%	5.7%	9	2.2%
	PbFeOOH	1.0%	0.3%	0.0%	2	2.2%
	PbMO	58.5%	93.0%	92.9%	491	11.1%
	PbMSO4	0.2%	0.4%	1.0%	2	1.1%
	PbS	0.2%	0.7%	0.0%	4	1.1%
	PbSiO4	0.3%	0.2%	0.0%	1	1.3%
	SbMO	0.1%	0.0%	0.0%	0	0.7%
	Slag	28.6%	0.4%	0.0%	2	10.2%
12542						
	FeOOH	5.8%	7.5%	0.9%	3981	2.2%
	FeSO4	0.2%	0.0%	0.1%	21	0.4%
	PbCl4	0.5%	13.2%	0.0%	7005	0.7%
	PbFeOOH	0.1%	0.4%	0.1%	217	0.3%
	PbMO	3.2%	64.3%	98.5%	34046	1.6%
	SbMO	0.1%	0.3%	0.2%	143	0.3%
	Slag	90.1%	14.3%	0.2%	7549	2.7%
12543						
	Anglesite	0.2%	1.3%	0.0%	110	0.5%
	Cerussite	0.5%	3.8%	0.0%	325	0.8%
	FeOOH	5.6%	1.9%	0.2%	164	2.7%
	FeSO4	0.4%	0.0%	0.0%	2	0.7%
	MnOOH	0.3%	0.3%	0.0%	25	0.6%
	Pb	0.7%	11.9%	0.0%	1025	0.9%
	PbCl4	0.1%	0.9%	0.0%	74	0.4%
	PbMO	11.8%	62.6%	96.8%	5386	3.7%
	PbMSO4	0.1%	0.7%	2.9%	59	0.4%
	PbS	1.3%	13.3%	0.0%	1146	1.3%
	Slag	79.1%	3.3%	0.1%	285	4.7%
12544						
	Cerussite	0.6%	18.0%	0.0%	1430	1.5%
	FeOOH	16.0%	20.7%	1.3%	1647	7.3%
	FeSO4	0.1%	0.0%	0.0%	2	0.7%
	PbAsO	1.5%	31.8%	85.5%	2527	2.4%
	PbMO	0.8%	16.7%	13.0%	1328	1.8%
	Slag	81.0%	12.9%	0.1%	1024	7.8%

TABLE 4. Summary of Lead Speciation for ASARCO Plant Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
12547						
	CaSiO4	2.5%	0.2%	0.0%	36	2.4%
	Cerussite	10.0%	34.8%	0.0%	7691	4.6%
	FeOOH	1.2%	0.2%	0.2%	41	1.7%
	FeSO4	0.7%	0.0%	0.2%	5	1.2%
	MnOOH	0.8%	0.4%	0.1%	79	1.4%
	Pb	4.0%	30.7%	0.0%	6771	3.0%
	PbMO	4.1%	9.5%	99.1%	2099	3.0%
	PbO	2.7%	16.2%	0.0%	3587	2.5%
	PbS	1.5%	6.7%	0.0%	1474	1.9%
	SbMO	0.3%	0.1%	0.4%	14	0.8%
	Slag	71.9%	1.3%	0.1%	292	6.8%
12548						
	Anglesite	1.7%	40.8%	0.0%	5884	2.3%
	PbAsO	0.2%	4.6%	55.2%	665	0.9%
	PbFeOOH	0.1%	0.4%	0.1%	54	0.6%
	PbMO	0.7%	12.2%	42.4%	1761	1.4%
	PbS	0.8%	26.8%	0.0%	3868	1.5%
	SbMO	0.5%	0.9%	1.8%	131	1.2%
	Slag	96.0%	14.2%	0.5%	2045	3.5%
12550						
	Cerussite	38.8%	74.5%	0.0%	45615	6.8%
	Clays	3.9%	0.3%	0.0%	154	2.7%
	FeOOH	9.5%	0.8%	0.2%	479	4.1%
	PbAsO	2.9%	3.9%	53.6%	2394	2.3%
	PbFeOOH	0.1%	0.0%	0.0%	20	0.5%
	PbMO	9.0%	11.6%	46.1%	7089	4.0%
	PbO	1.3%	4.4%	0.0%	2719	1.6%
	PbS	1.7%	4.2%	0.0%	2596	1.8%
	Slag	32.7%	0.3%	0.0%	202	6.6%
12551						
	Anglesite	2.6%	5.8%	0.0%	416	1.4%
	Cerussite	1.9%	5.1%	0.0%	360	1.2%
	Clays	4.3%	0.4%	0.0%	27	1.8%
	FeOOH	43.8%	5.1%	0.5%	363	4.4%
	FeSO4	0.6%	0.0%	0.0%	1	0.7%
	PbAsO	0.5%	1.0%	4.7%	72	0.6%
	PbMO	38.9%	70.6%	94.7%	5032	4.3%
	PbO	2.6%	12.0%	0.0%	852	1.4%
	Slag	4.8%	0.1%	0.0%	5	1.9%
12552						
	PbMO	0.4%	10.4%	98.1%	1460	0.6%
	PbMS	0.2%	4.4%	0.0%	610	0.4%
	PbS	1.3%	65.2%	0.0%	9115	1.1%
	Slag	98.1%	19.9%	1.9%	2785	1.4%

TABLE 4. Summary of Lead Speciation for ASARCO Plant Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
12553						
	Cerussite	2.9%	6.3%	0.0%	2868	1.8%
	FeOOH	5.1%	0.5%	0.5%	218	2.3%
	PbCl4	0.7%	1.3%	0.0%	581	0.9%
	PbMO	5.5%	8.1%	99.4%	3669	2.4%
	PbO	22.1%	83.0%	0.0%	37617	4.4%
	PbS	0.0%	0.1%	0.0%	53	0.2%
	Slag	63.6%	0.7%	0.1%	331	5.1%
12554						
	AsMO	0.1%	0.0%	0.0%	1	0.2%
	Calcite	0.7%	0.1%	0.0%	42	0.8%
	Cerussite	2.3%	6.5%	0.0%	3263	1.4%
	FeOOH	6.0%	0.7%	0.1%	369	2.2%
	MnOOH	4.9%	1.8%	0.0%	903	2.0%
	PbAsO	1.1%	2.3%	10.4%	1142	1.0%
	PbCl4	1.2%	3.0%	0.0%	1499	1.0%
	PbMO	33.4%	64.4%	84.7%	32203	4.5%
	PbMSO4	0.7%	1.4%	4.8%	687	0.8%
	PbO	3.3%	16.2%	0.0%	8089	1.7%
	PbS	0.8%	3.0%	0.0%	1490	0.9%
	Slag	45.7%	0.7%	0.0%	348	4.7%
12557						
	Calcite	5.2%	0.3%	0.0%	262	1.7%
	Cerussite	27.0%	29.7%	0.0%	30713	3.4%
	FeOOH	9.9%	0.5%	0.2%	485	2.3%
	PbAsO	2.2%	1.7%	29.8%	1797	1.1%
	PbMO	19.0%	14.0%	70.0%	14532	3.0%
	PbO	28.3%	53.8%	0.0%	55669	3.5%
	Slag	8.4%	0.0%	0.0%	50	2.1%
12563						
	Cerussite	0.4%	1.2%	0.0%	453	0.7%
	FeOOH	41.9%	5.5%	4.3%	2116	5.7%
	MnOOH	43.7%	17.3%	2.8%	6618	5.7%
	PbMO	4.1%	8.5%	82.3%	3255	2.3%
	PbO	12.3%	65.1%	0.0%	24892	3.8%
	SbMO	9.4%	1.9%	10.6%	733	3.3%
	Slag	31.3%	0.5%	0.1%	194	5.3%
12564						
	PbAsO	28.4%	44.2%	75.5%	305	39.5%
	PbMO	31.3%	46.6%	23.1%	322	40.7%
	PbSbO	7.5%	4.4%	0.0%	30	23.0%
	SbMO	32.8%	4.8%	1.4%	33	41.2%

TABLE 4. Summary of Lead Speciation for ASARCO Plant Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
12565						
	AsFeOOH	0.6%	0.3%	2.2%	4	1.1%
	Cerussite	0.1%	0.9%	0.0%	12	0.4%
	FeOOH	3.5%	2.1%	0.3%	28	2.6%
	FeSO4	0.1%	0.0%	0.0%	0	0.5%
	MnOOH	1.2%	2.2%	0.1%	29	1.6%
	PbAsO	1.2%	12.1%	65.3%	155	1.6%
	PbCl4	0.1%	1.2%	0.0%	16	0.5%
	PbMO	2.0%	18.8%	29.5%	242	2.0%
	PbS	3.0%	53.0%	0.0%	682	2.4%
	SbMO	3.1%	2.9%	2.6%	37	2.5%
	Slag	85.1%	6.3%	0.1%	82	5.1%
12566						
	Calcite	1.4%	0.2%	0.0%	224	1.6%
	Cerussite	3.6%	8.8%	0.0%	12622	2.4%
	Clays	0.3%	0.0%	0.0%	39	0.8%
	FeOOH	5.1%	0.5%	0.1%	769	2.9%
	Organic	1.6%	0.0%	0.0%	37	1.6%
	PbAsO	5.3%	9.0%	42.9%	12976	2.9%
	PbMO	25.0%	40.6%	56.1%	58485	5.6%
	PbO	5.6%	23.3%	0.0%	33636	3.0%
	PbS	3.0%	9.3%	0.0%	13342	2.2%
	PbSbO	5.3%	3.4%	0.0%	4909	2.9%
	PbSiO4	6.3%	4.4%	0.8%	6339	3.2%
	SbMO	0.0%	0.0%	0.0%	11	0.3%
	Slag	37.4%	0.5%	0.0%	690	6.3%
12568						
	Anglesite	0.4%	1.6%	0.0%	68	1.4%
	BiMO	0.4%	0.3%	0.0%	13	1.4%
	Cerussite	4.8%	21.5%	0.0%	921	4.5%
	FeOOH	5.5%	1.1%	0.1%	46	4.9%
	FeSO4	0.3%	0.0%	0.0%	1	1.2%
	MnOOH	2.5%	1.4%	0.0%	61	3.3%
	PbAsO	4.4%	13.8%	76.3%	589	4.3%
	PbCl4	4.0%	15.5%	0.0%	661	4.2%
	PbMO	4.7%	14.3%	22.9%	609	4.5%
	PbO	2.8%	22.1%	0.0%	943	3.5%
	PbS	0.8%	4.5%	0.0%	192	1.9%
	PbSiO4	1.7%	2.2%	0.5%	93	2.7%
	SbMO	0.3%	0.1%	0.1%	3	1.1%
	Slag	62.5%	1.5%	0.0%	63	10.3%
	ZnMO	4.8%	0.2%	0.0%	8	4.5%

TABLE 4. Summary of Lead Speciation for ASARCO Plant Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
12569						
	Calcite	0.1%	0.0%	0.0%	2	0.5%
	Cerussite	1.5%	11.6%	0.0%	548	1.9%
	PbAsO	1.7%	9.0%	77.3%	427	2.0%
	PbCl4	0.1%	0.8%	0.0%	36	0.5%
	PbMO	1.5%	7.8%	19.4%	369	1.9%
	PbO	4.5%	60.3%	0.0%	2855	3.2%
	PbS	0.3%	3.3%	0.0%	154	0.9%
	PbSiO4	0.8%	1.8%	0.6%	87	1.4%
	SbMO	3.6%	1.9%	2.6%	88	2.9%
	Slag	85.9%	3.5%	0.1%	166	5.4%
12571						
	BiMO	0.8%	0.7%	0.0%	38	2.5%
	FeOOH	53.3%	13.1%	1.0%	668	13.7%
	MnOOH	26.2%	19.3%	0.3%	985	12.1%
	PbAsO	4.6%	18.6%	59.8%	951	5.8%
	PbCl4	0.7%	3.3%	0.0%	170	2.3%
	PbMO	10.8%	41.2%	38.5%	2106	8.5%
	Phosphate	1.4%	3.0%	0.0%	151	3.2%
	SbMO	2.1%	0.8%	0.4%	41	4.0%
12574						
	Calcite	1.1%	0.1%	0.0%	116	1.7%
	Cerussite	10.0%	11.8%	0.0%	23335	5.0%
	FeOOH	19.7%	1.0%	0.6%	1983	6.6%
	PbCl4	22.8%	23.1%	0.0%	45490	6.9%
	PbMO	16.7%	13.3%	99.4%	26276	6.2%
	PbO	24.7%	50.7%	0.0%	99938	7.1%
	Slag	4.3%	0.0%	0.0%	53	3.4%
	ZnMO	0.7%	0.0%	0.0%	14	1.3%
12575						
	Cerussite	2.2%	16.6%	0.0%	7017	2.0%
	Clays	1.1%	0.3%	0.0%	122	1.4%
	FeOOH	8.7%	2.8%	1.1%	1186	3.7%
	MnOOH	1.3%	1.3%	0.1%	535	1.5%
	PbAsO	0.5%	2.4%	39.9%	1022	0.9%
	PbMO	1.8%	9.1%	43.5%	3842	1.8%
	PbMSO4	0.2%	1.1%	13.6%	448	0.6%
	PbO	4.6%	59.8%	0.0%	25240	2.8%
	PbS	0.3%	2.4%	0.0%	1034	0.7%
	PbSiO4	0.3%	0.6%	0.4%	263	0.7%
	SbMO	0.9%	0.5%	1.3%	197	1.3%
	Slag	78.2%	3.1%	0.2%	1314	5.5%

TABLE 4. Summary of Lead Speciation for ASARCO Plant Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
12576						
	Anglesite	0.1%	1.1%	0.0%	46	0.7%
	Clays	8.2%	2.7%	0.0%	115	5.6%
	FeOOH	0.2%	0.1%	0.0%	4	0.9%
	MnOOH	3.0%	3.9%	0.2%	164	3.5%
	PbAsO	0.5%	3.7%	29.9%	154	1.5%
	PbCl4	0.5%	4.3%	0.0%	182	1.4%
	PbMO	4.4%	29.5%	69.5%	1238	4.2%
	PbS	3.7%	46.7%	0.0%	1961	3.8%
	Phosphate	0.0%	0.1%	0.0%	5	0.4%
	SbMO	0.1%	0.0%	0.1%	2	0.5%
	Slag	57.8%	3.0%	0.1%	127	10.0%
	ZnMSiO4	21.4%	4.8%	0.3%	202	8.3%
12581						
	AsMO	1.4%	0.1%	0.4%	46	1.4%
	AsMSO4	0.4%	1.9%	4.6%	750	0.7%
	FeOOH	7.1%	2.3%	0.2%	894	3.1%
	FeSO4	2.1%	0.1%	0.1%	52	1.7%
	PbAsO	3.5%	18.5%	56.6%	7235	2.2%
	PbMO	8.6%	42.9%	38.2%	16826	3.4%
	PbO	2.4%	30.3%	0.0%	11887	1.8%
	PbS	0.1%	0.9%	0.0%	347	0.4%
	Slag	74.6%	2.9%	0.0%	1153	5.3%
12582						
	AsMO	2.1%	0.0%	0.7%	41	1.9%
	Cerussite	0.1%	0.1%	0.0%	133	0.4%
	FeOOH	20.8%	1.4%	0.7%	1495	5.4%
	PbCl4	58.6%	78.5%	0.0%	83784	6.6%
	PbMO	16.0%	16.8%	98.1%	17891	4.9%
	PbO	1.0%	2.8%	0.0%	2999	1.4%
	PbSiO4	0.4%	0.2%	0.2%	199	0.9%
	SbMO	1.1%	0.1%	0.4%	123	1.4%

** For all similar tables: %F = Frequency percent, %RM-Pb = Percent relative mass lead, %RM-As = Percent relative mass arsenic, Pb-Min = Mineral lead (ppm), and E-95% = Error at the 95% confidence limit. All terms are fully defined in text.

4.3 GOULD Park-site Samples

Park samples studied were collected from borings, ranging in depth between 0-12 feet with bulk lead concentrations between 450-6200 mg/kg. Samples lead masses were dominated (93% of the relative lead mass) by the following lead-bearing phases: PbO, $PbCO_3$ and Native Pb Figure 4 and Table 5. Particle size of lead phases are near log normal in their distribution with a preponderance of the overall population between 1 and 10 microns, Figure 5. A 5 micron mode is dominated by $PbCO_3$ whereas the coarser, 10 micron mode contains Native Pb and PbO , Photos 3 and 4.

Again, the speciation summary in Figure 4 is perhaps misleading. Over 75% of the GOULD samples were dominated by $PbCO_3$, Table 5 or Plate 1. The dominant occurrence of $PbCO_3$ at a battery recycling facility is perhaps in question, but it is likely the result of the oxidation of native lead to $PbCO_3$ in high pH-Eh environments. As documented by Garrels and Christ, 1965 and Kabata and Pendias, 1984, under normal, near-surface conditions $PbCO_3$/PbO, and $PbSO_4$ are the stable lead forms and the stability of native lead would require reduced alkaline conditions. The author has found this to be a common transition in the many shooting ranges studied across the country, USDOD 2001-2002.

Figure 4. EPA Omaha Gould "Park" Samples.

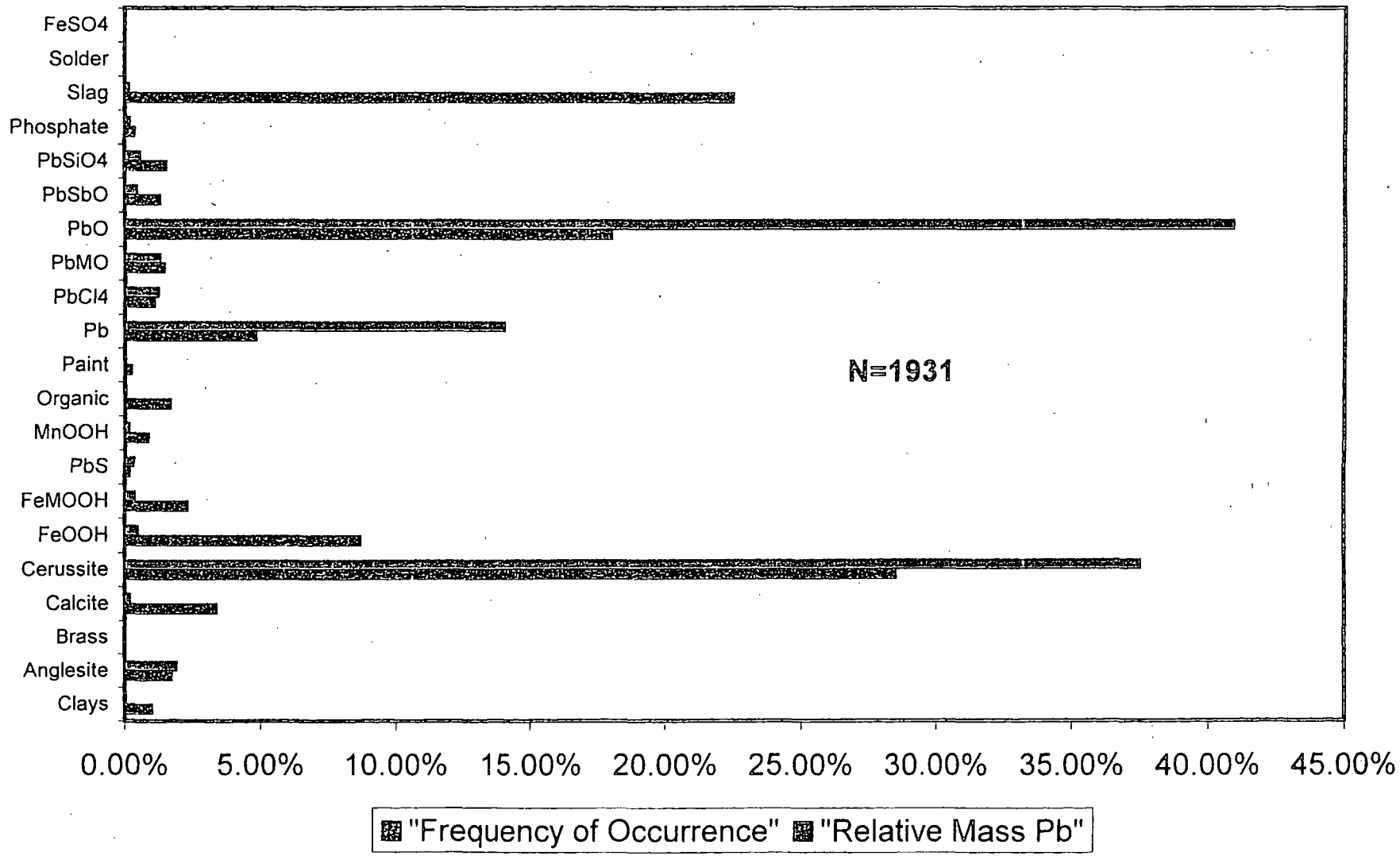


Figure 5. Histogram of Lead Phases from Gould Site.

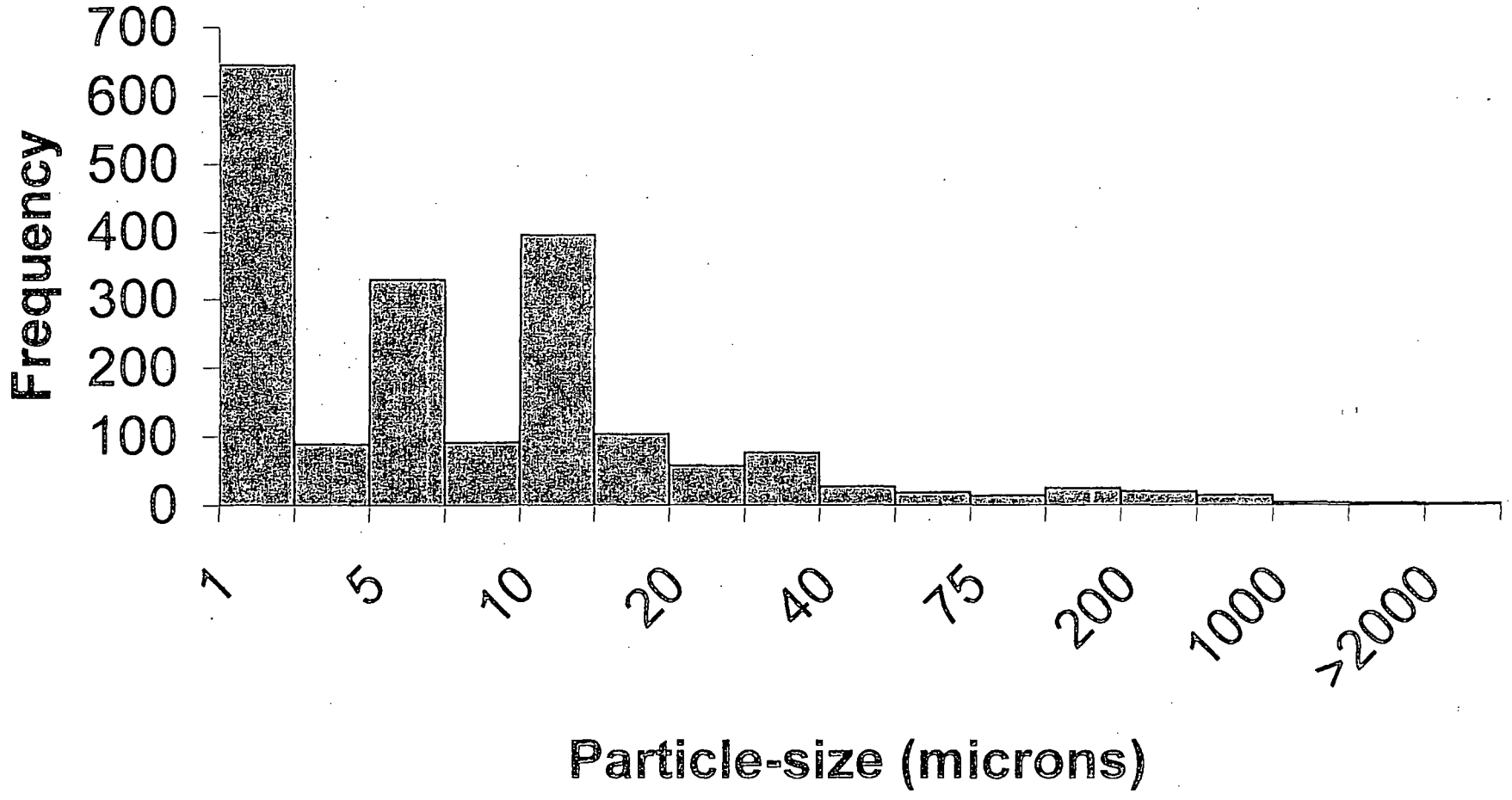


TABLE 5. Summary of Speciation Results for Gould "Park" Samples.

		%F	%RM-Pb	%RM-As	Min-Pb	E-95%
Loc-1						
	Anglesite	0.16%	0.36%	0.00%	20	0.6%
	Cerussite	27.02%	74.06%	0.00%	4108	6.2%
	FeMOOH	20.12%	6.67%	62.55%	370	5.6%
	FeOOH	1.48%	0.17%	3.67%	10	1.7%
	Galena	0.49%	1.71%	0.00%	95	1.0%
	Paint	2.24%	0.32%	0.28%	18	2.1%
	PbMO	0.67%	1.23%	20.76%	68	1.1%
	PbO	2.26%	10.67%	0.00%	592	2.1%
	PbSb Chlorate	0.58%	0.42%	0.00%	23	1.1%
	PbSbO	4.43%	3.21%	0.00%	178	2.9%
	Phosphate	0.56%	0.58%	0.03%	32	1.0%
	Slag	40.01%	0.58%	12.71%	32	6.9%
Loc-1-Dup						
	Cerussite	42.10%	84.64%	0.00%	4694	12.0%
	FeOOH	20.98%	1.81%	58.96%	101	9.9%
	Galena	0.27%	0.68%	0.00%	38	1.3%
	MnOOH	1.06%	0.28%	0.62%	15	2.5%
	PbSbO	11.69%	6.22%	0.00%	345	7.8%
	PbSiO4	7.30%	4.20%	35.26%	233	6.3%
	Phosphate	2.66%	2.02%	0.16%	112	3.9%
	Slag	13.94%	0.15%	5.01%	8	8.4%
Loc-2						
	Anglesite	6.00%	6.51%	0.00%	535	2.8%
	Cerussite	59.36%	76.50%	0.00%	6288	5.8%
	FeMOOH	1.01%	0.16%	4.91%	13	1.2%
	FeOOH	8.99%	0.50%	35.05%	41	3.4%
	Galena	0.40%	0.66%	0.00%	54	0.7%
	Organics	1.43%	0.01%	0.00%	1	1.4%
	PbO	5.26%	11.70%	0.00%	961	2.6%
	PbSbO	0.49%	0.17%	0.00%	14	0.8%
	PbSiO4	8.41%	3.10%	56.28%	255	3.3%
	Phosphate	1.33%	0.65%	0.11%	53	1.4%
	Slag	7.31%	0.05%	3.64%	4	3.1%
Loc-3-6-9						
	Anglesite	1.11%	1.88%	0.00%	69	2.0%
	Brass	1.22%	0.01%	0.00%	TR	2.1%
	Cerussite	43.77%	87.87%	0.00%	3203	9.4%
	FeOOH	29.99%	2.59%	86.28%	94	8.6%
	MnOOH	22.90%	5.92%	13.72%	216	7.9%
	PbO	0.41%	1.40%	0.00%	51	1.2%
	PbSbO	0.61%	0.32%	0.00%	12	1.5%

TABLE 5. Summary of Speciation Results for Gould "Park" Samples.

		%F	%RM-Pb	%RM-As	Min-Pb	E-95%
Loc-5						
	Anglesite	2.20%	1.37%	0.00%	228	1.2%
	Calcite	9.63%	0.32%	0.00%	53	2.4%
	Cerussite	17.74%	13.12%	0.00%	2183	3.0%
	Clays	2.89%	0.07%	0.00%	12	1.3%
	FeOOH	0.30%	0.01%	72.92%	2	0.4%
	Native Pb	13.69%	22.42%	0.00%	3729	2.7%
	PbC14	3.13%	1.98%	0.00%	329	1.4%
	PbCrSO4	2.89%	1.45%	0.00%	242	1.3%
	PbO	46.40%	59.20%	0.00%	9849	4.0%
	PbSbO	0.14%	0.03%	0.00%	4	0.3%
	Phosphate	0.12%	0.03%	0.62%	6	0.3%
	Slag	0.86%	0.00%	26.46%	1	0.7%
Loc-7-5-8						
	Cerussite	4.57%	35.64%	0.00%	1557	3.6%
	FeOOH	12.92%	4.32%	57.06%	189	5.8%
	Galena	0.16%	1.59%	0.00%	69	0.7%
	PbO	3.73%	50.15%	0.00%	2191	3.3%
	PbSbO	2.51%	5.17%	0.00%	226	2.7%
	Slag	76.11%	3.13%	42.94%	137	7.3%
Loc-7-9-11						
	Cerussite	44.49%	93.01%	0.00%	1258	9.1%
	FeOOH	8.53%	0.77%	13.29%	10	5.1%
	PbMO	4.03%	5.64%	78.13%	76	3.6%
	Solder	0.38%	0.11%	0.11%	1	1.1%
	Slag	42.57%	0.47%	8.47%	6	9.0%
Loc3-6-9-Dup						
	Cerussite	50.99%	95.03%	0.00%	3464	12.5%
	FeOOH	15.43%	1.23%	75.63%	45	9.1%
	MnOOH	9.88%	2.37%	10.09%	86	7.5%
	PbMO	0.91%	1.14%	0.00%	41	2.4%
	Slag	22.80%	0.22%	14.28%	8	10.5%
Loc-3-10-13						
	FeOOH	80.00%	45.13%	35.63%	203	21.0%
	PbMO	3.08%	27.06%	17.05%	122	9.0%
	FeSO4	9.23%	1.05%	47.32%	5	15.2%
	PbSbO	7.69%	26.75%	0.00%	120	14.0%

TABLE 5. Summary of Speciation Results for Gould "Park" Samples.

		%F	%RM-Pb	%RM-As	Min-Pb	E-95%
Loc-4-7-10						
	Cerussite	40.03%	88.62%	0.00%	1409	7.6%
	FeOOH	32.50%	3.09%	51.21%	49	7.3%
	Galena	1.15%	3.23%	0.00%	51	1.7%
	PbMO	1.74%	2.58%	34.11%	41	2.0%
	FeSO4	0.19%	0.00%	3.48%	Tr	0.7%
	PbSbO	1.01%	0.59%	0.00%	9	1.6%
	PbSiO4	2.59%	1.64%	7.01%	26	2.5%
	Slag	20.85%	0.24%	4.20%	4	6.3%
Loc-7-5-8-Dup						
	Anglesite	0.62%	1.64%	0.00%	72	1.1%
	Cerussite	26.04%	81.69%	0.00%	3568	6.0%
	FeOOH	17.69%	2.38%	62.85%	104	5.2%
	Organics	15.77%	0.33%	0.00%	14	5.0%
	PbMO	0.36%	0.76%	16.01%	33	0.8%
	PbO	2.07%	11.19%	0.00%	489	1.9%
	Solder	0.18%	0.08%	0.13%	3	0.6%
	PbSbO	0.44%	0.37%	0.00%	16	0.9%
	PbSiO4	0.78%	0.70%	4.74%	30	1.2%
	Phosphate	0.23%	0.28%	0.02%	12	0.7%
	Slag	35.82%	0.59%	16.26%	26	6.6%

4.4 Community Soils

Although this study was initiated when anomalously high, bulk lead concentrations within the Omaha site were identified, the community soil sample set (Plate 1) includes soils with varied bulk lead concentrations (60-2400 mg/kg). These samples have lead masses almost exclusively (74% of the relative lead mass) dominated by phosphates, $PbCO_3$, MnOOH, and a mixed lead (a combination of $PbCO_3$ + $PbSO_4$+ PbO), with minor contributions from other lead forms, Figure 6. The particle- size distribution for all lead species is near log normal, Figure 7. The phosphate and $PbCO_3$ particles are smaller, and generally cemented, Photos 5-6, with a median particle size of 2 microns, while the mixed lead (and MnOOH are generally much coarser at 95 microns, Photo 7.

The community soils contain source-traceable lead forms, (slag, $PbCl_x$, PbAsO, PbMO, PbSbO, and $PbSiO_4$) ,Table 6, providing good evidence that pyrometallugical activity contributed to the elevated lead concentrations. However, the "soil interacting" phases: Mn oxide, Fe oxide and phosphate are more prevalent as is typical in developed soil environments. These phases than are the result of soluble lead sorbing onto Mn, Fe, and/or P minerals that are found in soils. Good physical evidence can be seen in Photo 7 supporting both the transition of lead in $PbCl_x$, $PbCO_3$ and paint to these soil phases.

Figure 6. EPA Omaha Soil Samples.

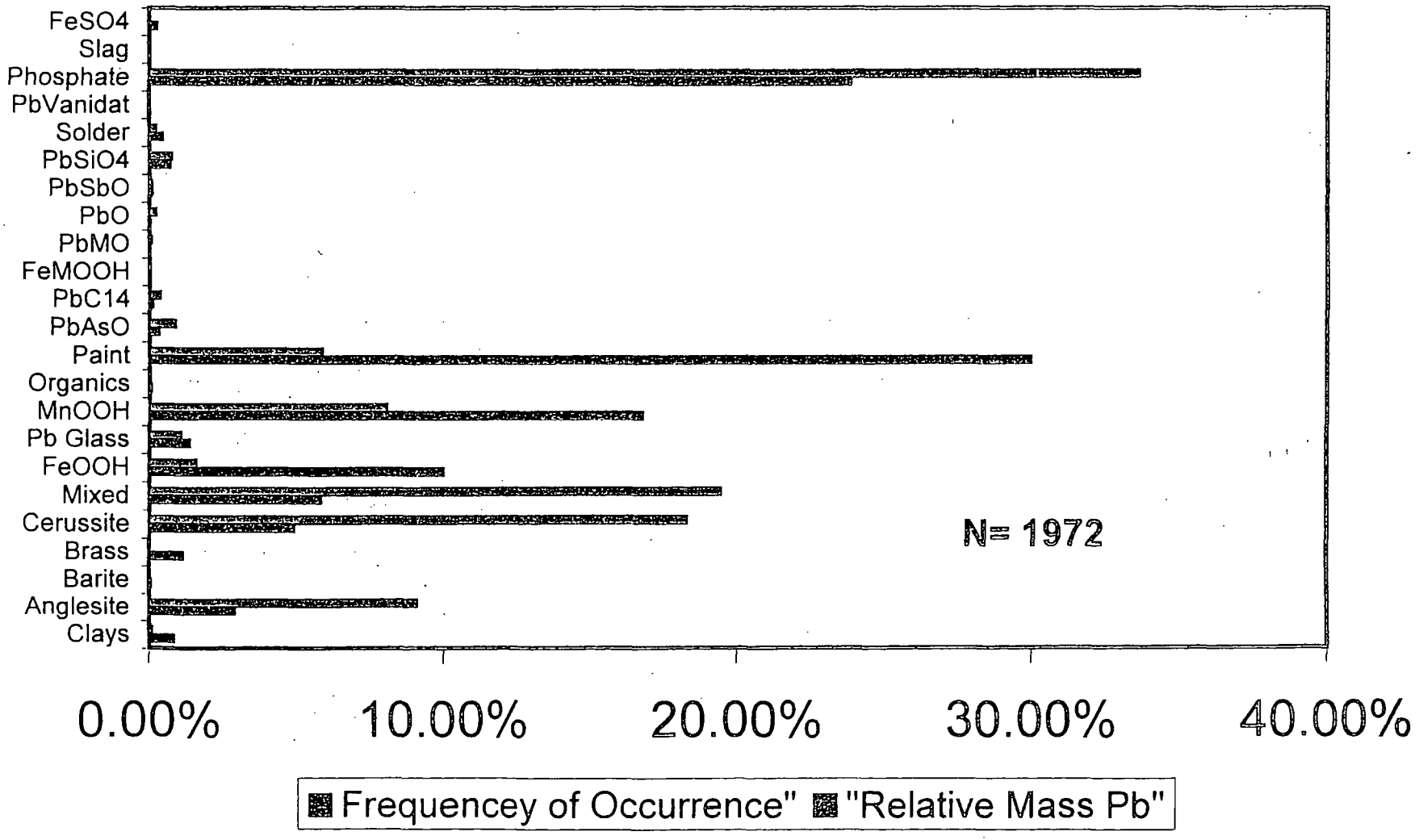


Figure 7. Histogram of Lead Phases from Community Soils.

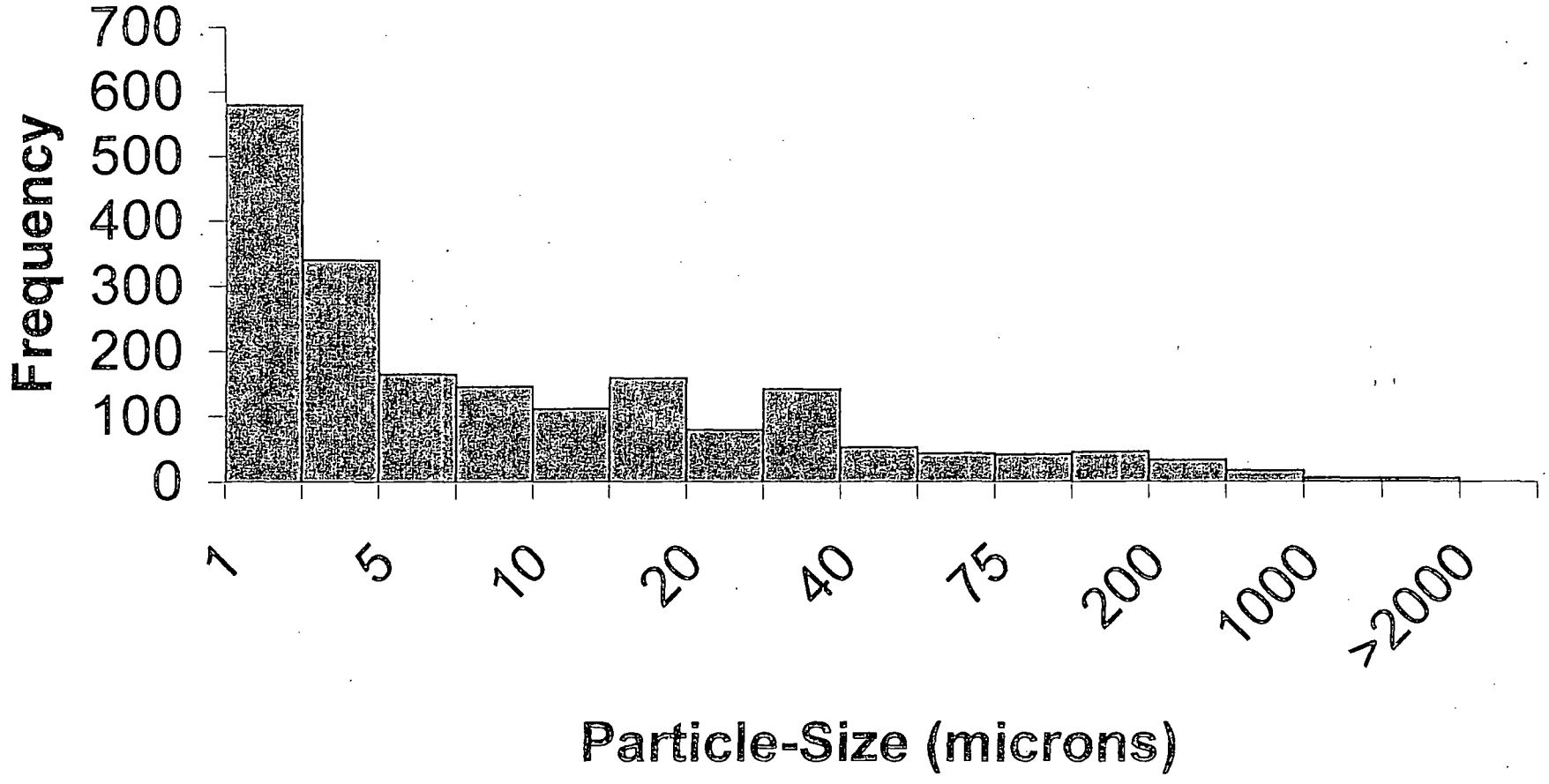


TABLE 6. Summary of Speciation Results for Community Soil Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
11509						
	Anglesite	28.76%	46.49%	0.00%	2691	5.45%
	Clay	2.40%	0.15%	0.00%	9	1.84%
	FeOOH	6.85%	0.57%	66.65%	33	3.04%
	Mixed Lead	5.26%	9.09%	0.00%	526	2.69%
	MnOOH	11.39%	2.82%	23.08%	163	3.82%
	Paint	5.89%	0.60%	2.86%	35	2.83%
	Cerussite	9.50%	18.25%	0.00%	1056	3.53%
	PbCl4	0.69%	1.13%	0.00%	66	1.00%
	Phosphate	28.40%	20.67%	5.76%	1196	5.43%
	Solder	0.87%	0.23%	1.65%	13	1.12%
1584						
	Anglesite	0.11%	0.61%	0.00%	7	0.50%
	Barite	0.40%	0.01%	0.00%	Tr	0.95%
	FeOOH	14.68%	4.24%	62.89%	48	5.37%
	MnOOH	31.37%	27.18%	28.01%	307	7.04%
	Paint	31.01%	10.99%	6.64%	124	7.02%
	PbCl4	0.29%	1.65%	0.00%	19	0.81%
	Phosphate	21.49%	54.72%	1.92%	618	6.23%
	Solder	0.65%	0.60%	0.54%	7	1.22%
1627						
	FeOOH	18.81%	3.76%	71.03%	41	13.33%
	MnOOH	22.57%	13.53%	17.76%	146	14.26%
	Paint	10.19%	2.50%	1.92%	27	10.32%
	Cerussite	1.57%	7.29%	0.00%	79	4.24%
	Phosphate	38.32%	67.50%	3.02%	729	16.59%
	Solder	8.54%	5.43%	6.27%	59	9.54%
1683						
	Anglesite	1.75%	2.73%	0.00%	35	2.46%
	FeOOH	6.58%	0.52%	2.60%	7	4.65%
	Mixed Lead	3.81%	6.36%	0.00%	82	3.60%
	MnOOH	22.31%	5.33%	1.84%	69	7.82%
	Paint	6.71%	0.66%	0.13%	8	4.70%
	Cerussite	34.41%	63.78%	0.00%	822	8.92%
	PbAsO	5.61%	7.30%	95.27%	94	4.32%
	PbCl4	0.13%	0.21%	0.00%	3	0.68%
	Phosphate	18.68%	13.11%	0.15%	169	7.32%
5008B-1						
	Phosphate	100.00%	100.00%	100.00%	647	0.00%

TABLE 6. Summary of Speciation Results for Community Soil Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
5017F-1						
	Anglesite	1.77%	4.80%	0.00%	45	3.09%
	Clay	0.88%	0.10%	0.00%	1	2.19%
	FeOOH	3.83%	0.53%	21.14%	5	4.49%
	MnOOH	65.85%	27.38%	75.76%	258	11.11%
	Cerussite	16.68%	53.83%	0.00%	508	8.73%
	PbSiO4	0.20%	0.18%	1.86%	2	1.04%
	Phosphate	10.79%	13.19%	1.24%	125	7.27%
5020B-2						
	Brass	1.56%	0.06%	0.00%	1	3.08%
	FeOOH	4.11%	2.94%	46.06%	24	4.94%
	MnOOH	1.03%	2.21%	2.40%	18	2.51%
	Paint	90.95%	79.95%	50.99%	644	7.14%
	Phosphate	2.35%	14.84%	0.55%	119	3.77%
5034B-1						
	Barite	3.41%	0.05%	0.00%	Tr	4.71%
	Clay	3.72%	0.50%	0.00%	2	4.91%
	FeOOH	17.65%	3.08%	68.22%	15	9.90%
	MnOOH	11.46%	6.00%	9.23%	29	8.27%
	Cerussite	0.62%	2.52%	0.00%	12	2.04%
	PbSbO	1.55%	1.66%	0.00%	8	3.20%
	PbSiO4	1.86%	2.16%	12.34%	11	3.51%
	Phosphate	51.70%	79.56%	4.16%	390	12.97%
	Solder	8.05%	4.47%	6.05%	22	7.06%
5041B-1						
	Brass	10.94%	0.10%	0.00%	Tr	16.97%
	FeOOH	34.38%	5.88%	97.06%	7	25.82%
	Cerussite	4.69%	18.65%	0.00%	23	11.49%
	Phosphate	50.00%	75.37%	2.94%	94	27.18%
5044B-1						
	Clay	2.08%	0.44%	0.00%	2	5.60%
	FeOOH	30.83%	8.42%	11.51%	36	18.10%
	FeSO4	2.50%	0.14%	10.74%	1	6.12%
	MnOOH	47.08%	38.57%	3.66%	167	19.57%
	Cerussite	1.25%	7.95%	0.00%	34	4.36%
	PbAsO	4.58%	20.46%	73.42%	88	8.20%
	PbSbO	0.83%	1.40%	0.00%	6	3.56%
	PbSiO4	0.83%	1.52%	0.53%	7	3.56%
	Phosphate	8.75%	21.07%	0.07%	91	11.08%
	Slag	1.25%	0.04%	0.06%	Tr	4.36%

TABLE 6. Summary of Speciation Results for Community Soil Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
5046DZ						
	Clay	3.51%	0.43%	0.00%	8	3.01%
	FeOOH	8.94%	1.40%	62.70%	28	4.66%
	MnOOH	12.01%	5.66%	17.55%	112	5.31%
	Paint	10.50%	2.02%	3.68%	40	5.01%
	Cerussite	0.36%	1.30%	0.00%	26	0.97%
	PbCl4	0.09%	0.28%	0.00%	5	0.49%
	PbMO	0.04%	0.11%	3.88%	2	0.34%
	PbSiO4	0.18%	0.19%	2.14%	4	0.69%
	Phosphate	63.83%	88.35%	9.33%	1744	7.85%
	Solder	0.53%	0.27%	0.73%	5	1.19%
5048B-2						
	FeOOH	51.14%	10.44%	44.15%	54	32.66%
	Paint	5.68%	1.42%	0.25%	7	15.12%
	Cerussite	1.14%	5.40%	0.00%	28	6.92%
	PbMO	5.11%	16.27%	54.94%	84	14.39%
	Phosphate	36.93%	66.47%	0.66%	342	31.53%
5055F-1						
	Brass	43.55%	0.85%	0.00%	5	16.67%
	FeOOH	1.20%	0.43%	9.56%	3	3.67%
	MnOOH	37.01%	39.99%	61.20%	252	16.23%
	Cerussite	0.17%	1.44%	0.00%	9	1.39%
	PbMO	0.17%	0.97%	17.00%	6	1.39%
	PbSiO4	0.69%	1.65%	9.39%	10	2.78%
	Phosphate	17.21%	54.67%	2.85%	344	12.69%
5056F-2						
	FeOOH	1.16%	0.61%	17.20%	5	3.70%
	MnOOH	5.35%	8.48%	16.58%	74	7.80%
	Paint	85.92%	55.68%	63.88%	489	12.05%
	Phosphate	7.57%	35.23%	2.34%	309	9.16%
5059B-1						
	Barite	0.45%	0.01%	0.00%	Tr	1.91%
	Brass	0.37%	0.01%	0.00%	Tr	1.75%
	Clay	6.36%	1.50%	0.00%	12	6.98%
	FeOOH	26.35%	7.97%	70.26%	63	12.59%
	MnOOH	49.40%	44.84%	27.44%	356	14.29%
	Cerussite	0.07%	0.53%	0.00%	4	0.78%
	PbSiO4	0.30%	0.60%	1.37%	5	1.56%
	Phosphate	16.69%	44.54%	0.93%	353	10.66%

TABLE 6. Summary of Speciation Results for Community Soil Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
5060B-2						
	Clay	0.38%	0.03%	0.00%	1	1.20%
	FeOOH	6.72%	0.73%	68.81%	14	4.86%
	Mixed Lead	29.03%	66.55%	0.00%	1290	8.81%
	MnOOH	3.39%	1.11%	7.24%	22	3.51%
	Paint	35.85%	4.82%	18.37%	93	9.31%
	Cerussite	1.92%	4.90%	0.00%	95	2.67%
	PbSiO4	0.03%	0.03%	0.62%	1	0.36%
	Phosphate	22.60%	21.81%	4.82%	423	8.12%
	Solder	0.07%	0.02%	0.14%	1	0.51%
5061F-2						
	Brass	21.75%	0.49%	0.00%	3	12.33%
	FeOOH	31.66%	13.26%	80.69%	75	13.90%
	MnOOH	35.23%	44.27%	18.71%	251	14.28%
	Phosphate	11.36%	41.98%	0.60%	238	9.49%
5063F-2						
	Anglesite	1.90%	5.26%	0.00%	62	3.91%
	FeOOH	6.27%	0.88%	36.68%	10	6.93%
	Mixed Lead	10.64%	31.44%	0.00%	372	8.81%
	MnOOH	48.15%	20.38%	58.67%	241	14.29%
	Paint	6.38%	1.11%	1.87%	13	6.99%
	Cerussite	3.81%	12.51%	0.00%	148	5.47%
	Phosphate	22.84%	28.42%	2.78%	337	12.00%
5079B-2						
	Anglesite	0.06%	0.22%	0.00%	4	0.44%
	Barite	0.06%	0.00%	0.00%	Tr	0.44%
	Clay	0.11%	0.02%	0.00%	Tr	0.63%
	FeOOH	23.51%	4.71%	38.64%	95	7.89%
	FeSO4	0.85%	0.03%	16.08%	1	1.71%
	MnOOH	6.06%	3.65%	2.08%	73	4.44%
	Paint	2.49%	0.61%	0.20%	12	2.90%
	Pb Glass	33.99%	33.45%	0.00%	672	8.81%
	Cerussite	0.06%	0.26%	0.00%	5	0.44%
	Pb Vanidate	0.06%	0.11%	0.00%	2	0.44%
	PbFeOOH	0.17%	0.10%	0.35%	2	0.77%
	PbO	0.91%	7.30%	0.00%	147	1.76%
	PbSiO4	14.90%	19.90%	42.07%	400	6.62%
	Phosphate	16.77%	29.64%	0.57%	596	6.95%

TABLE 6. Summary of Speciation Results for Community Soil Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
5080B-2						
	Brass	9.39%	0.15%	0.00%	1	10.62%
	FeOOH	31.02%	9.46%	15.69%	54	16.84%
	MnOOH	42.45%	38.83%	4.47%	220	17.99%
	PbAsO	3.67%	18.31%	79.73%	104	6.85%
	PbSbO	3.67%	6.90%	0.00%	39	6.85%
	Phosphate	9.80%	26.34%	0.10%	149	10.82%
5080B-2-Dup						
	Barite	0.28%	0.01%	0.00%	Tr	1.10%
	Clay	2.12%	0.38%	0.00%	2	3.01%
	FeOOH	12.27%	2.81%	45.20%	16	6.85%
	MnOOH	55.90%	38.41%	42.90%	218	10.37%
	Cerussite	0.28%	1.48%	0.00%	8	1.10%
	PbSbO	0.46%	0.65%	0.00%	4	1.42%
	PbSiO4	1.48%	2.25%	9.34%	13	2.52%
	Phosphate	26.48%	53.48%	2.03%	303	9.22%
	Solder	0.74%	0.54%	0.53%	3	1.79%
5081F-2						
	Anglesite	0.08%	0.28%	0.00%	2	0.69%
	FeOOH	16.41%	3.12%	79.03%	22	9.29%
	MnOOH	9.54%	5.43%	9.57%	38	7.37%
	Organics	2.29%	0.07%	0.00%	1	3.75%
	Paint	36.64%	8.54%	8.82%	59	12.09%
	Cerussite	8.40%	37.11%	0.00%	257	6.96%
	PbCl4	0.84%	3.17%	0.00%	22	2.29%
	PbSbO	1.45%	1.70%	0.00%	12	3.00%
	Phosphate	24.20%	40.50%	2.43%	281	10.75%
	Solder	0.15%	0.09%	0.14%	1	0.98%
5082B-1						
	FeOOH	27.59%	8.66%	60.83%	70	20.10%
	MnOOH	58.62%	55.23%	26.93%	446	22.15%
	PbSiO4	3.10%	6.50%	11.76%	52	7.80%
	Phosphate	10.69%	29.61%	0.49%	239	13.89%
5088F-2						
	FeOOH	15.23%	4.69%	2.69%	30	15.75%
	FeSO4	47.72%	2.96%	97.02%	19	21.89%
	MnOOH	4.57%	4.22%	0.17%	27	9.15%
	Phosphate	32.49%	88.14%	0.12%	561	20.53%

TABLE 6. Summary of Speciation Results for Community Soil Samples.

		F%	%RM-Pb	%RM-As	Min-Pb	E-95%
5083B-1						
	Anglesite	2.23%	9.25%	0.00%	205	2.33%
	Clay	1.56%	0.26%	0.00%	6	1.96%
	FeOOH	2.28%	0.48%	28.82%	11	2.36%
	MnOOH	12.01%	7.64%	31.63%	170	5.13%
	Paint	51.66%	13.44%	32.64%	298	7.89%
	Cerussite	4.03%	19.89%	0.00%	442	3.11%
	Phosphate	26.23%	49.03%	6.91%	1089	6.95%
5083DZ						
	Anglesite	10.05%	15.50%	0.00%	370	5.78%
	FeOOH	10.91%	0.86%	75.13%	21	5.99%
	MnOOH	13.85%	3.27%	19.87%	78	6.64%
	Paint	0.57%	0.06%	0.20%	1	1.45%
	Cerussite	31.16%	57.10%	0.00%	1364	8.90%
	Phosphate	33.45%	23.22%	4.80%	555	9.07%
5086B-1						
	FeOOH	33.51%	7.54%	76.55%	74	12.59%
	MnOOH	28.73%	19.41%	13.67%	191	12.07%
	Paint	5.38%	1.49%	0.61%	15	6.02%
	Cerussite	2.00%	10.46%	0.00%	103	3.73%
	PbCl4	0.17%	0.78%	0.00%	8	1.11%
	PbMO	0.26%	0.91%	7.40%	9	1.36%
	PbSiO4	0.09%	0.13%	0.34%	1	0.79%
	Phosphate	29.86%	59.28%	1.42%	585	12.21%
5087G						
	FeOOH	5.82%	0.46%	54.25%	5	5.65%
	FeSO4	0.21%	0.00%	22.81%	Tr	1.11%
	Mixed Lead	42.55%	70.72%	0.00%	692	11.93%
	MnOOH	5.98%	1.42%	11.61%	14	5.72%
	Paint	7.98%	0.78%	3.72%	8	6.54%
	Cerussite	0.35%	0.64%	0.00%	6	1.42%
	PbCl4	0.03%	0.04%	0.00%	Tr	0.39%
	PbSiO4	0.03%	0.01%	0.43%	Tr	0.39%
	Phosphate	37.05%	25.92%	7.19%	254	11.65%
5098B-2						
	Brass	66.70%	1.60%	0.00%	1	65.32%
	PbSiO4	33.30%	98.40%	100.00%	61	65.32%

4.4 Statistical Study--Factor Analysis

A limited statistical evaluation of the speciation results was conducted in order to determine lead phase associations within source groups and in particular relate these associations to those found in residential soils in order to strengthen any apportionment conclusions. Matrixes were constructed using sixteen variables and 'n' cases (depending on the number of samples) for each of the three major sample groups to determine covariance. For a factor analysis the number of variables used was limited to valid cases identified by the procedure. All analyses were performed using *STATISTICA*. The variables included data from the Omaha speciation study (Min_{pb}), and bulk metals concentrations. Table 7 illustrates the results for the Omaha residential soils, ASARCO site, and Gould site, respectively. The most significant correlations between variable pairs have been marked in **bold** in Table 7. Many of these correlations support the categories established later in Chapter 7.

Review of the ASARCO plant matrix indicates that their bulk lead concentrations are most significantly correlated (r^2>.80, $p<0.05$) with the presence of $PbSO_4$ - $PbSiO_4$- PbO, although $PbCO_3$-PbMO-PbAsO-PbS (0.61-0.76, $p<0.05$) are also important. Some inter-phase correlations are also very significant (eg. $PbSiO_4$-$PbCl_x$, r^2=1.0, $p<0.05$) reflecting plant processes. Finally, $PbSiO_4$ is the most highly correlated lead phase (r^2.87-1.0 with 6 of the 16 variables).

Significant correlations among the GOULD "Park" samples are not as common, this is most likely a result of the smaller data set (N=8). Bulk lead concentrations in these samples are most

strongly correlated to the presence of PbO (r^2=.93, $p<0.05$).

Four observations that one can make from the residential soil data, Table 7, which are most important to this study are; 1) the total lack of a significant (r^2 =-.04 to -.10) correlation between $PbSO_4$-$PbCO_3$-PbO (the three most common lead paint pigments) and the occurrence of paint. These data support the fact that the occurrence of these three phases in residential soils is most likely pyrometallurgical in origin., 2) bulk lead concentrations are most significantly correlated to the presence of $PbSO_4$-$PbCl_x$-$PbCO_3$-Phosphate (r^2 = .64 to .88, $p<0.05$) 3) the three pyrometallurgical lead forms (PbO, PbFeO, and $PbSiO_4$,) show the greatest "commonality" among the correlation variables, 4) $PbCl_x$-$PbSO_4$-Slag and phosphate have significant correlations (r^2= 0.41-0.67, $p<0.05$) suggesting that the lead sorbed to phosphate is pyrometallugical in origin.

To further investigate the above correlations a preliminary factor analysis study was conducted. Four factors were identified in most data sets (Gould had only two), using principal components (the number of factors selected are determined following the method of Kaiser, 1960 ie. NO eigenvalues <1.0), accounting for approximately 64% of the variance. The factors represent lines of maximal variance about the data sets. Each consecutive factor is defined to maximize the variability not captured by the preceding factor.

Factor loadings for residential soils, Figure 8A, graphically show a strong co-location of the pyrometallugical phases $PbCO_3$, $PbCl_x$, and $PbSO_4$ along with phosphate and clay, accounting for 23% of the variance. Another, PbO, PbFeO, and $PbSiO_4$ control 20% of the population variance and PbAsO and PbSbO about 11%.

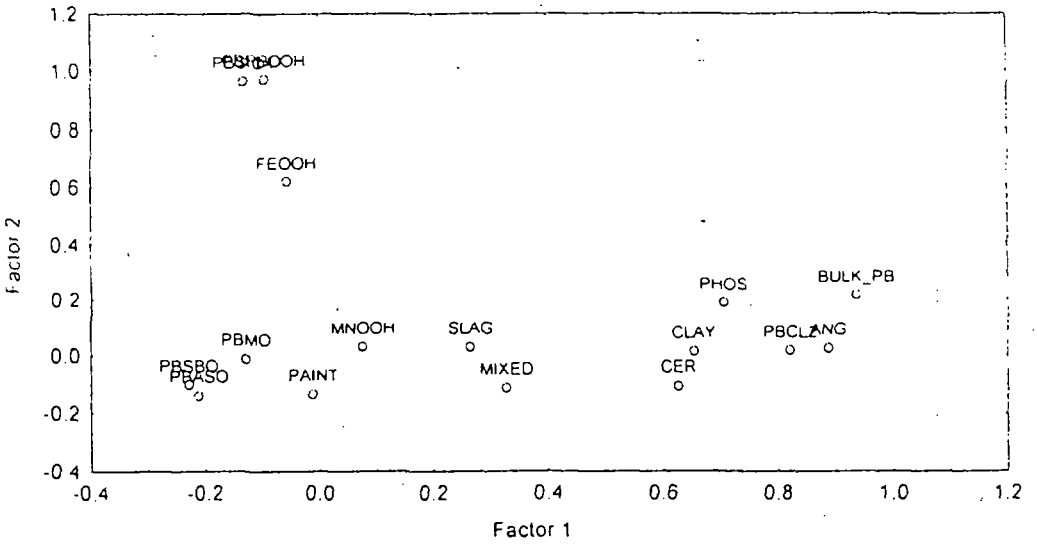
The Gould site soils are difficult to interpret do to the elimination of many (8 out of 16) variables

because of invalid cases. A significant, co-location for FeOOH, slag and PbSbO accounts for 50% of the variance, while $PbCO_3$ accounts for 20%, Figure 8B.

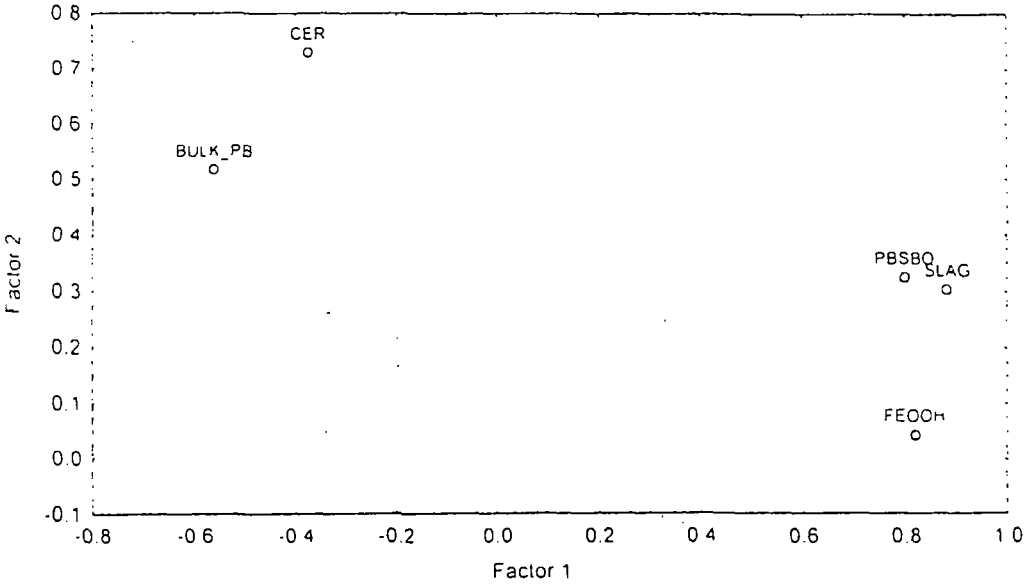
Factor loadings for the ASARCO site soils indicate significant, co-locations for PbAsO, PbMO, PbS, and $PbSiO_4$, accounting for 32% of the population variance. An additional population accounting for 18% of the variance includes; FeOOH, MnOOH and SbMO, Figure 8C.

Figure 8. Factor loadings (first two factors representing > 50% of variance) for: A) Residential soils, B) Gould Site, and C) ASARCO Site.

A.



B.



C.

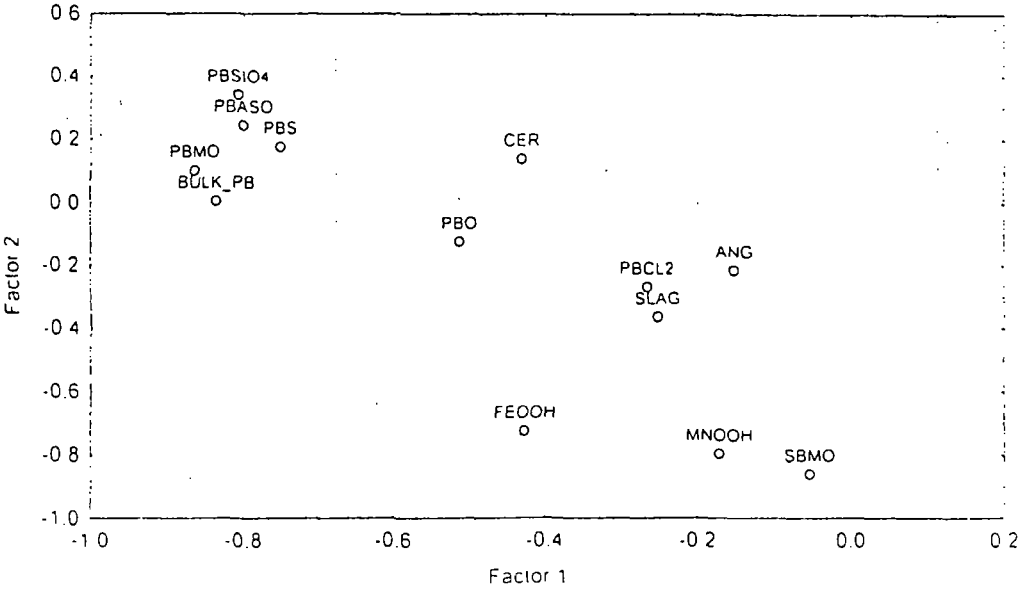


Table 7. Correlation matrix for Residential Yard Samples

	Ang	Cer	FeOOH	MnOOH	PbAsO	PbClx	PbFeO	PbMO	PbO	PbSbO	PbSiO4	Phos	Slag	Paint	Mixed	Bulk Pb
Ang	1.0	.60	-.01	.04	-.08	.89	-.05	-.06	-.05	-.08	-.07	.41	-.05	-.04	.27	.88
Cer	.60	1.0	-.21	-.05	.10	.45	-.10	-.10	-.10	-.12	-.14	.23	-.09	-.10	.09	.66
FeOOH	-.01	-.21	1.0	.44	.03	.06	.47	.19	.47	.13	.47	.09	-.02	-.19	-.22	.05
MnOOH	.04	-.05	.44	1.0	.05	.07	-.10	-.20	-.10	.05	-.07	.02	-.04	-.19	-.20	.05
PbAsO	-.08	.10	.03	.05	1.0	-.10	-.07	-.08	-.07	.62	-.09	-.29	-.07	-.15	-.10	-.14
PbCl2	.89	.45	.06	.07	-.10	1.0	-.07	-.07	-.07	-.01	-.09	.41	.01	-.04	.21	.76
PbFeO	-.05	-.10	.47	-.10	-.07	-.07	1.0	-.05	1.0	-.06	.98	.08	-.04	-.07	-.07	.15
PbMO	-.06	-.10	.19	-.20	-.08	-.07	-.05	1.0	-.05	-.07	-.06	-.03	-.02	-.09	-.09	-.13
PbO	-.05	-.10	.47	-.10	-.07	-.07	1.0	-.05	1.0	-.06	.98	.08	-.04	-.07	-.07	.15
PbSbO	-.08	-.12	.13	.05	.62	-.01	-.06	-.07	-.06	1.0	-.08	-.20	-.06	-.12	-.12	-.18
PbSiO4	-.07	-.14	.47	-.07	-.09	-.09	.98	-.06	.98	-.08	1.0	.03	-.04	-.11	-.10	.10
Phos	.41	.23	.09	.02	-.29	.41	.08	-.03	.08	-.20	.03	1.0	.67	.01	.06	.64
Slag	-.05	-.09	-.02	-.04	-.07	.01	-.04	-.02	-.04	-.06	-.04	.67	1.0	-.04	-.07	.14
Paint	-.04	-.10	-.19	-.19	-.15	-.04	-.07	-.09	-.07	-.12	-.11	.01	-.04	1.0	-.05	.03
Mixed	.27	.09	-.22	-.20	-.10	.21	-.07	-.09	-.07	-.12	-.10	.06	-.07	-.05	1.0	.39
Bulk Pb	.88	.66	.05	.05	-.14	.76	.15	-.13	.15	-.18	.10	.64	.14	.03	.39	1.0

Table 7. ASARCO Plant Correlation Summary.

	Ang	Cer	FeOOH	MnOOH	PbAsO	PbCl2	PbFeO	PbMO	PbO	PbS	PbSiO4	SbMO	Slag	ZnMO	Bulk
Ang	1.0	.03	.97	-.90	.66	-.34		-.10		.87		1.0	.99		.83
Cer	.03	1.0	.06	-.27	.23	.32		.25	.37	.29	.87	-.29	-.10		.61
FeOO	.97	.06	1.0	.89	.38	.37	1.0	.40	.48	.33	.09	.49	.79	-.49	.31
MnOO	-.90	-.27	.89	1.0	.84	.50		.01	.63	.30		.97	-.07		.45
PbAsO	.66	.23	.38	.84	1.0	.72	.10	.84	.35	.80	1.0	-.23	.25		.76
PbCl2	-.34	.32	.37	.50	.72	1.0		.38	.22	.16	1.0	.53	.00	-.48	.35
PbFeO			1.0		.10		1.0	.96		.93			1.0		.47
PbMO	-.10	.25	.40	.01	.84	.38	.96	1.0	.34	.64	.96	-.09	.30	-.46	.71
PbO		.37	.48	.63	.35	.22		.34	1.0	.44	.77	.40	-.10		.88
PbS	.87	.29	.33	.30	.80	.16	.93	.64	.44	1.0	1.0	-.20	.50		.66
PbSiO4-		.87	.09		1.0	1.0		.96	.77	1.0	1.0	-.49	.28		.97
SbMO	1.00	-.29	.49	.97	-.23	.53		-.09	.40	-.20	-.49	1.0	.02		.09
Slag	.99	-.10	.79	-.07	.25	0.0	1.0	.30	-.10	.50	.28	.02	1.0	1.0	-.01
ZnMO			-.49			-.48							.99	1.0	-.48
Bulk	.83	.61	.31	.45	.76	.35	.47	.47	.88	.66	.97	.09	.01	-.48	1.0

Table 7. Gould Site Correlation Summary.

	Ang	Cer	FeOOH	PbMO	PbO	PbS	PbSbO	Phos	Slag	Bulk Pb
Ang	1.0	.66	-.08		.10		-.54	.54	-.75	.33
Cer	.66	1.0	-.20	.25	-.46	-.33	-.13	1.0	-.24	.26
FeOOH	-.08	-.20	1.0	.79	-.35	.98	.46	.93	.92	-.46
PbMO		.25	.79	1.0			.41		.36	-.38
PbO	.10	-.46	-.35		1.0		-.32	-.88	-.31	.93
PbS		-.33	.98			1.0	.99		.99	.06
PbSbO	-.54	-.13	.46	.41	-.32	.99	1.0	.10	.82	-.31
Phos	.54	1.0	.93		-.88		.10	1.0	.15	-.77
Slag	-.75	-.24	.92	.36	-.31	.99	.82	.15	1.0	-.21
Bulk Pb	.33	.26	-.46	-.38	.93	.06	-.31	-.77	-.21	1.0

5.0 BIOAVAILABILITY

The relative bioavailability for both potential source and community samples was determined using the RBLP Relative Bioavailability Leaching Procedure developed at the University of Colorado, Drexler et. al., 2003. The procedure predicts gasrointestinal adsorbtive bioavailabity of lead. It has been calibrated to the USEPA Region VIII swine model and has been independently validated. A complete SOP is provided in the Appendix..

Results of the test are provided in Table 8 and graphically presented in Figure 9. Data are generally consistent with the speciation results presented in this report averaging 82% relative bioavailability (RBA) for all media. Community soils have RBA values that would normally not be predicted based on the fact that phosphates (37%) represent such large portion of the relative lead mass. However, this may be do to the very small partice-size (2 micron average) of the phosphates. RBA's for the community soils average (84% +/- 6) and those at the ASARCO plant (80% +/- 11) are most similar, while those soils from the GOULD plant average (72% +/- 10) are slightly lower. These lower RBA's are likely related to the increased occurrence of native lead found at the Gould facility. These RBA's are consistent with the presence of highly soluble lead forms (PbO, $PbCO_3$ and $PbCl_x$), and are significantly higher than the IEUBK (Integrated Exposure Uptake Biokinetic Model) default value of 60%.

Figure 9. Omaha Smelter Site- Bioavailability.

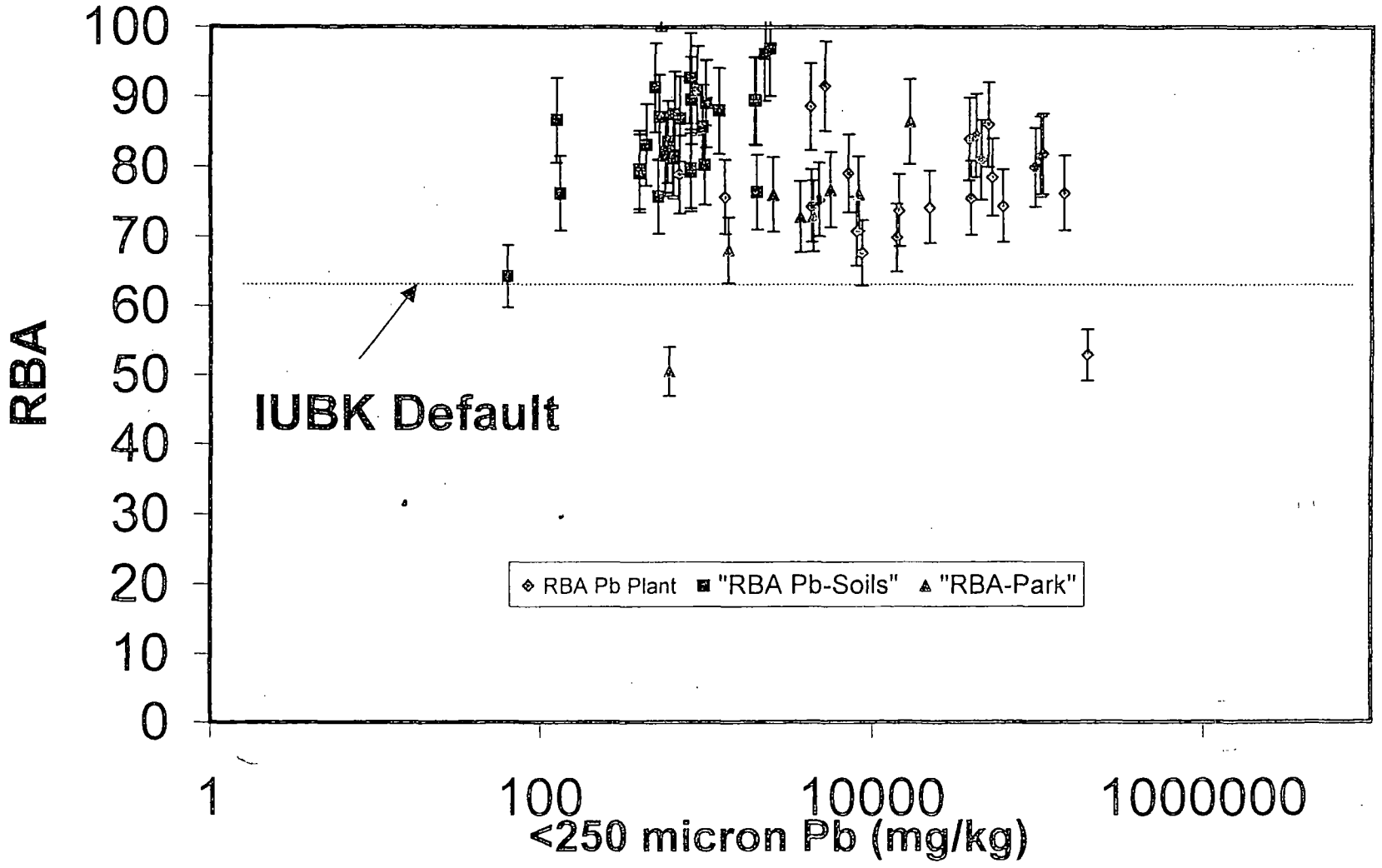


Table 8. Relative Bioavailability Estimates for Omaha Samples.

Run at 1.5pH for 1 hr @ 39*c

Lab ID.	Sample ID	Pb in bulk soil (mg/kg)	mass soil (g)	calc Pb #1	ICP Pb (mg/l)	solution amt (l)	%Pb RBA
Plant							
OM-1	AZZSGPZA12565	1287	1.00513	1.29	9.747	0.1	75
OM-2	AZZSGPZA12566	144079	1.0046	144.74	1100.08	0.1	76
0M-3	AZZSGPZA12568	4273	1.00384	4.29	31.829	0.1	74
OM-4	AZASGPZZ12553	45337	1.00731	45.67	367.6	0.1	80
OM-5	ASASGPZZ12544	50036	1.00747	50.41	430.68	0.1	85
OM-6	AZCESGPZZ12552	13970	1.00634	14.06	97.67	0.1	69
OM-7	AZZSGPZA12569	4733	0.98423	4.66	35.664	0.1	77
OM-8	AZASGPZZ12557	103509	1.00971	104.51	844.12	0.1	81
OM-9	AZZSGPZA12563	38260	0.99034	37.89	321.42	0.1	85
OM-10	AZCESPGZZ12551	7129	1.00357	7.15	56.409	0.1	79
OM-11	AZCESGPZZ12550	61268	1.00783	61.75	456.42	0.1	74
OM-12	AZZSGPZA12582	106665	1.00207	106.89	874.02	0.1	82
OM-13	AZZSGPZA12564	691	1.00543	0.69	5.455	0.1	79
0M-14	AZCESGPZZ12548	14407	1.00486	14.48	106.40	0.1	73
OM-15	AZDSGPZZ12547	22088	1.00384	22.17	164.16	0.1	74
OM-16	AZZSGPZA12581	39190	1.00333	39.32	296.36	0.1	75
OM-17	AZZSGPZA12574	197206	1.0062	198.43	1043.7	0.1	53
OM-18	AZZSGPZA12573	96181	1.00832	96.98	769.88	0.1	79
OM-19	AZZSGPZA12571	5109	1.00265	5.12	46.78	0.1	91
OM-20	AZCSGPZZ12544	7958	1.00558	8.00	56.38	0.1	70
OM-21	AZZSGPZA12576	4201	1.00644	4.23	37.24	0.1	88
OM-22	AZZSGPZA12575	42220	1.00736	42.53	356.84	0.1	84
OM-23	AZCSSGPZZ12543	8601	1.0089	8.68	58.245	0.1	67
OM-24	AZDSGPZZ12541	528	1.00782	0.53	5.647	0.1	106
OM-25	AZCNSGPZZ12542	52961	1.00557	53.26	416.267	0.1	78
Community soils							
5083DZ		2389	1.00242	2.39	23.199	0.1	97
5083 B1		2220	1.00089	2.22	21.358	0.1	96
5082 B1		808	1.00187	0.81	7.251	0.1	90
5080 B2		567	1.00576	0.57	4.65	0.1	82
5048 B2		514	1.00657	0.52	3.921	0.1	76
5079 B2		2010	1.0033	2.02	15.405	0.1	76
5081 F2		693	1.0002	0.69	6.024	0.1	87

Table 8. Relative Bioavailability Estimates for Omaha Samples.

Run at 1.5pH for 1 hr @ 39*c

Lab ID.	Sample ID	Pb in bulk soil (mg/kg)	mass soil (g)	calc Pb #1	ICP Pb (mg/l)	solution amt (l)	%Pb RBA
5046 DZ		1973.74	1.00357	1.98	17.71	0.1	89
5046 B1		394.231	1.0022	0.40	3.124	0.1	79
5063 F2		1184.44	1.0014	1.19	10.44	0.1	88
5061 F2		568.394	1.0058	0.57	4.69	0.1	82
5058 F2		586.062	1.0012	0.59	4.90	0.1	84
5044 B1		432.964	1.0048	0.44	3.62	0.1	83
5055 F1		630.973	1.0037	0.63	5.17	0.1	82
5088 F2		636.876	1.0011	0.64	5.18	0.1	81
5034 B1		490.734	1.0036	0.49	4.50	0.1	91
5017 F1		944.562	1.0002	0.94	8.10	0.1	86
5086 B1		986	1.0017	0.99	8.80	0.1	89
5087 G		978.313	1.0065	0.98	7.91	0.1	80
5060 B2		1939.6	1.0002	1.94	17.36	0.1	89
5020 B2		805.852	1.0073	0.81	6.44	0.1	79
5098 B2		62.7078	1.0062	0.06	0.41	0.1	64
5008 B1		647.108	1.0040	0.65	5.69	0.1	88
5056 F2		878.717	0.9988	0.88	7.98	0.1	91
5030 B1		131.193	1.0065	0.13	1.01	0.1	76
5007 F2		520.622	1.0007	0.52	4.54	0.1	87
5059 B1		793.972	1.0064	0.80	7.4	0.1	93
5041 B1		124.742	1.0068	0.13	1.1	0.1	87
Gould "Park"							
	Loc#1	5546	1.0000	5.55	42.6	0.1	77
	Loc#2	8219	1.0028	8.24	62.8	0.1	76
	Loc#3 6-9"	3645	1.0051	3.66	26.7	0.1	73
	Loc#3 10-15'	599	1.0038	0.60	3.0	0.1	51
	Loc#4	2508	1.0018	2.51	19.1	0.1	76
	Loc#5 10-12'	16636	1.0057	16.73	144.7	0.1	86
	Loc#7 5-8'	4368	1.00	4.38	32.0	0.1	73
	Loc#7 9-11'	1353	1.00157	1.36	9.2	0.1	68
QA/QC							
BLANK					0.082		
BLANK					0.029		
BLANK					0.022		
BLANK					0.006		

Table 8. Relative Bioavailability Estimates for Omaha Samples.

Run at 1.5pH for 1 hr @ 39*c

Lab ID.	Sample ID	Pb in bulk soil (mg/kg)	mass soil (g)	calc Pb #1	ICP Pb (mg/l)	solution amt (l)	%Pb RBA
BLANK					0.048		
BLANK					0.038		
BLANK					0.014		
OM-4-AD		45337	1.00731	45.67	377.12	0.1	83
5007 F2-AD		520.622	1.0007	0.52	4.51	0.1	87
OM-6-DUP		13970	1.00457	14.03	105.112	0.1	75
OM-24-DUP		528	1.00392	0.53	5.522	0.1	104
5020 B2-DUP		805.852	1.0013	0.81	6.59	0.1	82
5020 B2-DUP		805.852	1.0013	0.81	6.44	0.1	80
5046 B1-DUP		394.231	1.00501	0.40	3.154	0.1	80
5046 B1-DUP		394.231	1.00501	0.40	3.29	0.1	83
5020 B2-DUP-spike-20ppm					27.30		
5046 B1-DUP-spike-10ppm					13.79		
BLANK-spike-10ppm					11.301		

AD= Analytical duplicate

6.0 LEAD ISOTOPIC CHARACTERIZATION

As anticipated, the community soils in the central Omaha area have a considerable fraction of their bulk lead associated with the soil forming phases (phosphates, MnOOH and FeOOH). These phase are "non-source specific" in their lead concentration, and represent a mixture of all soluble lead forms historically associated with the soil. Therefore, a new methodology, using ICP/MS/LA to determine lead isotopic values for a single soil particle was conducted in order to provide insight into lead sources for these important and often abundant lead forms.

Both bulk and single particle isotopic lead values were determined on a VARIAN Ultramass inductive coupled plasma mass spectrometer (ICPMS) equipped with a CETAC LS200 laser ablation unit. Bulk samples were prepared following USEPA 3050/6010 while single particles were analyzed from identified lead particles in EMPA pucks. A complete SOP for ICP/MS/LA is provided in the Appendix. Both sample sets were standardized using NIST 982 and/or 3128.

The isotopes of lead Pb^{207}, Pb^{206}, and Pb^{208} are produced by the radioactive decay of U^{235}, U^{238} and Th ^{232} respectively, while Pb^{204} has no radiogenic source. Variations are a function of the initial uranium and thorium concentrations and age of the ore.

Lead isotopic compositions have been previously used in apportionment studies with some limited success (Hurst et.al., 1996, Gulson et. Al., 1995, 1996, Robinowitz and Wetherill, 1972, and Sturges and Barrie, 1987, 1989). The major difficulty with these studies was in the sole use of bulk sample analyses. This isotopic signature represents a mixture of all lead sources, therefore apportionment is complicated when more than two sources are involved. With the improvements made in quadrupole

ICP/MS systems and the advancements in laser technology, we can now combine EMPA studies (identification of lead-bearing phases) with single particle isotopic lead analysis.

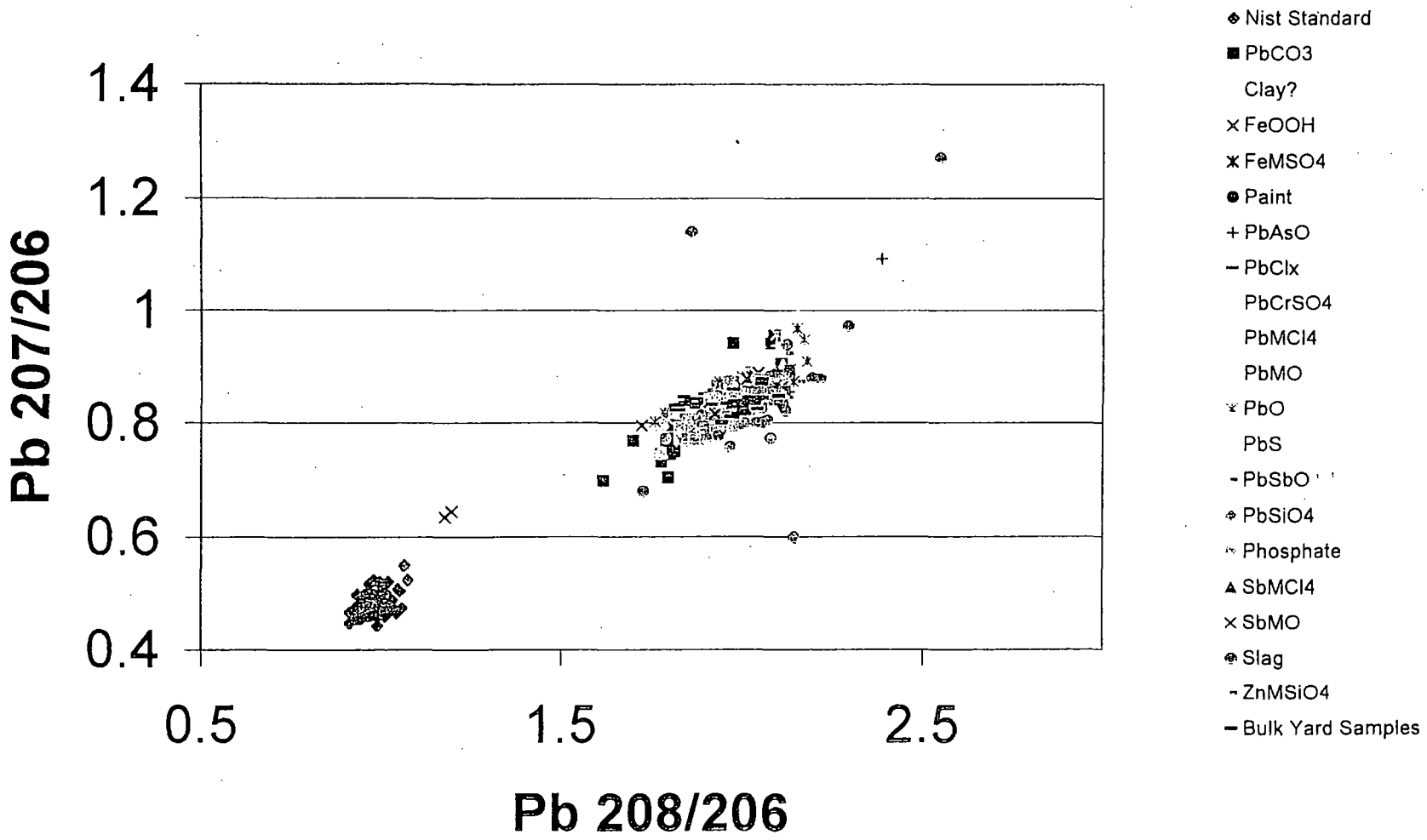
Isotopic results on site samples along with those from the NIST 928 standard are presented in Figure 10. The absolute value and variations about the NIST standard, although not equivalent to a magnetic sector mass spectrometer, provides a good estimate of the precision (2%) and accuracy (3%) at a 95% confidence level for quadrupole ICP/MS/LA.

The three most abundant radiogenic isotopes of lead Pb^{208}, Pb^{206} and Pb^{207} (54%, 24%, and 22%, respectively) are the most useful for source characterization. Figure 11, a plot of $Pb^{207/206}$ vs $Pb^{208/206}$ (a more sanative ratio than Figure 10), illustrates some of the most important characteristics of the data set. It is clear that the ASARCO plant soils have a very wide range in isotopic composition which is likely the result of its more extensive operational history and numerous lead-ore sources. Only the $PbCl_x$ from the plant shows a tight isotopic signature. Preliminary review of the data would support multiple primary lead sources for the plant. The Gould soils on the other hand have a relatively tight isotopic pattern, with a significant enrichment in Pb^{206}.

Data from the community soils was much more difficult to obtain. Single-phase laser analyses were limited to two phases, paint and phosphate primarily do to the size limitations in finding a single particle of lead using the low-power microscope on the laser. Therefore, bulk isotopic lead analyses were included for characterization. Although there are two populations for paint, most of the analyses are similar to lead from the Gould site, ie. enriched in Pb^{206}. The analyzed phosphates also have two populations, one similar to the ASARCO site and the others similar to the Gould/paint samples. The bulk isotopic lead samples however are represented by a rather tight cluster, falling between the main ASARCO population and the Gould/paint population, Figure 12A. Figure 12B is a simplified $Pb^{206/208}$

vs Pb $^{206/207}$ plot, using only average values for all potential sources, residential soils, and US mining districts. In this plot it becomes more apparent that the community soils are isotopically more similar to the ASARCO soils and that neither paint, Gould, nor gasoline could have a significant contribution to their isotopic character.

Figure 10. Lead Isotoipic Summary.



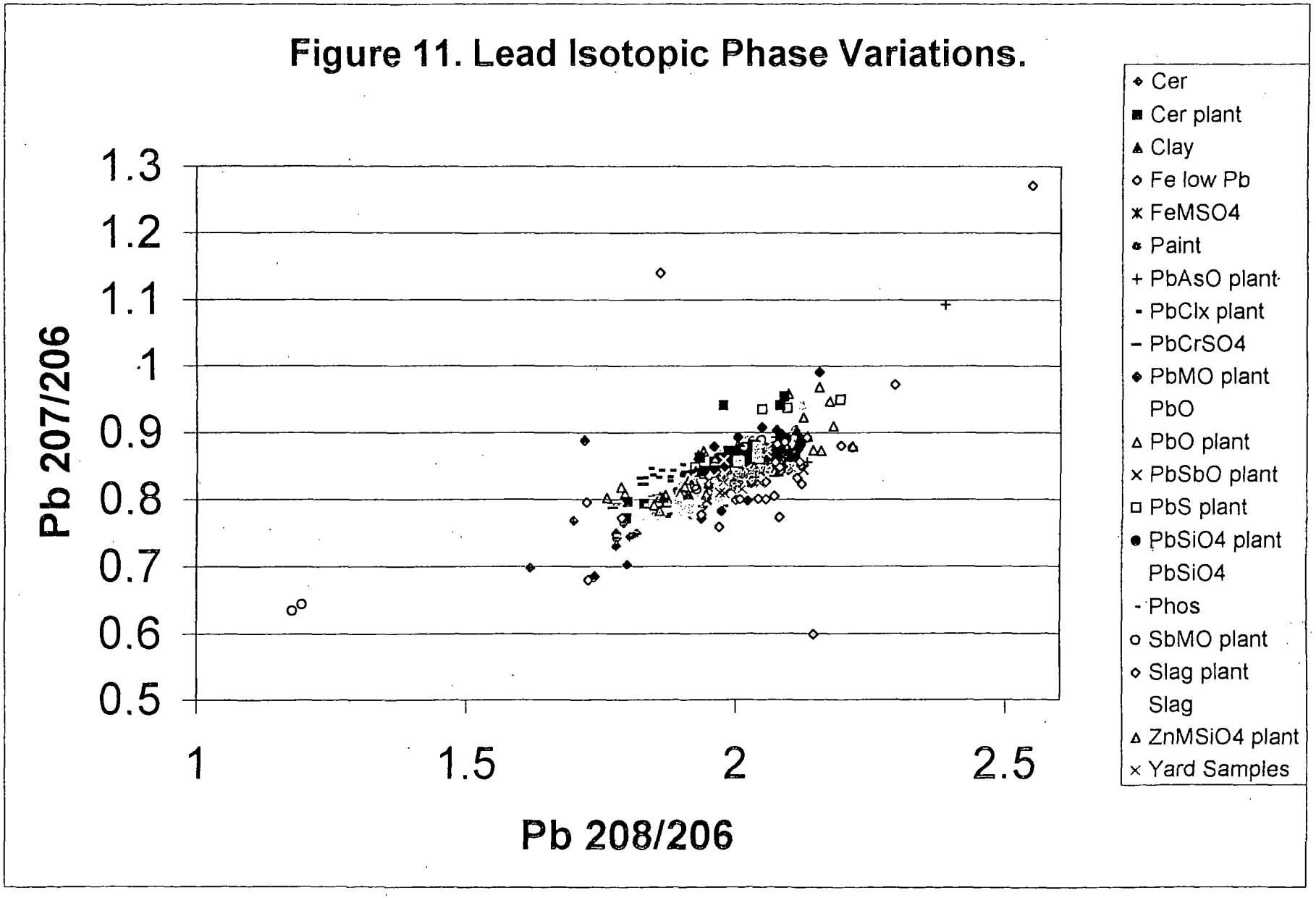


Figure 11. Lead Isotopic Phase Variations.
Pb 207/206
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
1
1.5
2
2.5
Pb 208/206
Cer
Cer plant
Clay
Fe low Pb
FeMSO4
Paint
PbAsO plant
PbClx plant
PbCrSO4
PbMO plant
PbO
PbO plant
PbSbO plant
PbS plant
PbSiO4 plant
PbSiO4
Phos
SbMO plant
Slag plant
Slag
ZnMSiO4 plant
Yard Samples

Figure 12a. Isotopic Sourcing (legend symbols are mean ratio values, other points are from ASARCO site).

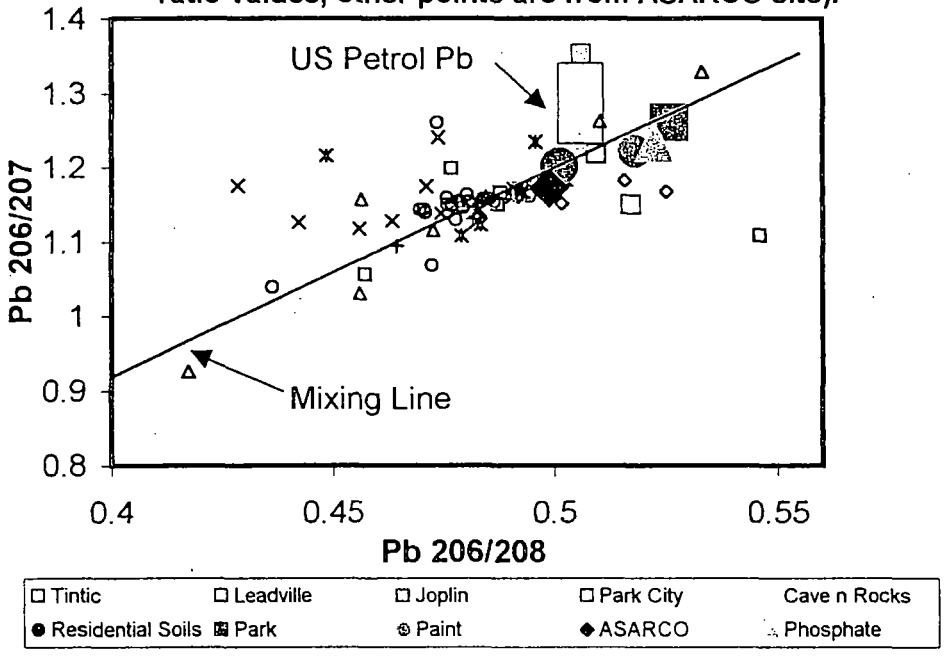
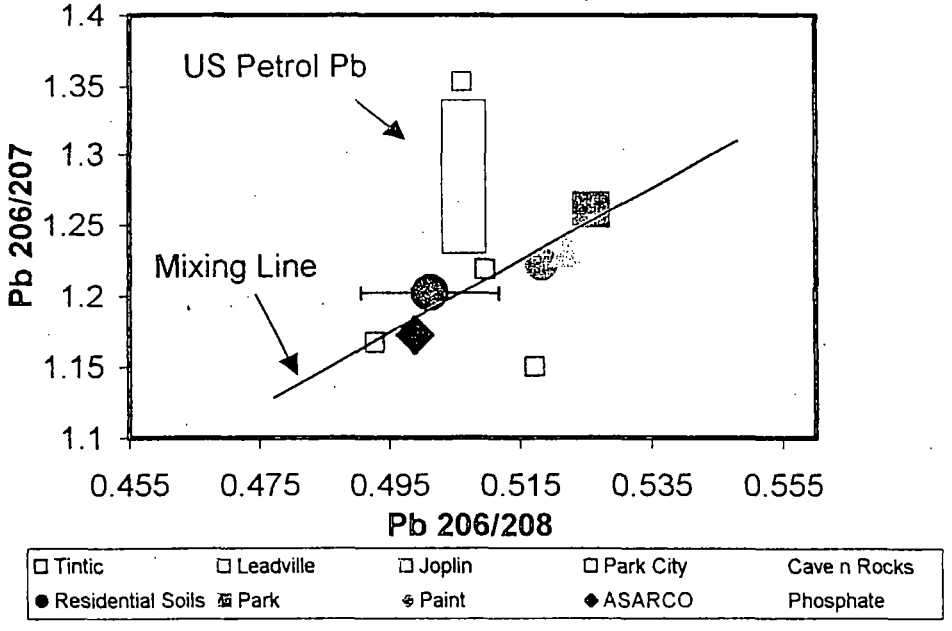


Figure 12b. Isotopic Sourcing (symbols are mean ratio values).



7.0 APPORTIONMENT

Based on the results from the lead speciation study an attempt to apportion the total soil lead to most probable sources was made using the Min-Pb values (Table 6). The Min-Pb value (defined on page 13) is simply a proportional representation of bulk lead concentration to lead mineralogy (%RM-Pb). Three specific categories for the apportionment were made: pyrometallurgical lead, non-specific soil- forming lead, and anthropogenic. Criteria for each of these categories were as follows:

Pyrometallurgical Lead: Slag, PbAsO, PbFeO, PbMO,PbO, $PbCl_x$, $PbCO_3$ and $PbSiO_4$

Soil-Forming Lead: FeOOH, MnOOH, phosphate, and clays

Anthropogenic: Paint, Solder, Pb-Glass and Brass

Min-Pb from each of the lead phases identified in these categories are mathematically added together and compared to the total bulk lead. Pyrometallurgical and anthropogenic species were chosen based on data from site-specific, ASARCO plant and Gould park samples, metallurgical literature (Fergusson, 1990), and previous studies (Drexler, 1995,1997; Thorton 1995). The soil-forming lead phases are most likely the result of solublized lead, released from the other two populations that are now sequestered (by sorption) in common, soil-forming mineral phases. Since at least some of the bulk lead found in this category may have come from pyrometallurgical processes, a percentage of the "non-source specific" category (based on the percentage of pyrometallurgical lead identified in each sample) has been assigned to this source. Results of the apportionment are summarized in Table 9. **(For more detail**

information on the calculation the reader is incoraged to review the spreadsheet for Table 9, which has been included on CD with this report and follow through a single calculation.)No adjustments to final Pb_{Min} were made for "background" concentrations of lead. The author has assumed that background levels would be the same for all samples because of their close proximity and similar soil environment. The apportionment calculation, based only on speciation results, indicates that a range of between 0 and 97% with an average of 38% of the bulk lead concentration in community yards would have had a pyrometallurgical lead source. This proportion could exceed 60% on average if only half of the "non-specific source" lead is attributed to pyrometallurgical activity, as the lead isotopic data suggests. More than 80% of the community soils studied contained pyrometallugical lead.

TABLE 9. Omaha Lead Apportionment.

	Bulk Pb	567	567	693	808	2220	2389	986	978	63	1289	5788	1129	1080	637
		5080B-2	5080B-2-Dup	5081F-2	5082B-1	5083B-1	5083DZ	5086B-1	5087G	5098B-2	1683	11509	1584	1627	5088F-2
Pyrometallurgical															
	Barite	0		0	0	0	0	0	0	0					
	Cerussite	0	8	257	0	442	1364	103	6	0	822	1056	0	79	
	PbAsO	104		0	0	0	0	0	0	0	94	0	0	0	
	Pb Vanidate	0		0	0	0	0	0	0	0					
	PbCl4	0		22	0	0	0	8	0	0	3	66	19	0	
	PbFeOOH	0		0	0	0	0	0	0	0					
	PbMO	0		0	0	0	0	9	0	0					
	PbO	0		0	0	0	0	0	0	0					
	PbSbO	39	4	12	0	0	0	0	0	0					
	Slag	0		0	0	0	0	0	0	0					
	PbSiO4	0	13	0	52	0	0	1	0	61					
	Mixed Lead	0		0	0	0	0	0	692	0	82	526	0	0	
	Anglesite	0		2	0	205	370	0	0	0	35	2691	7	0	
		143	25	293	52	647	1734	121	698	61	1036	4339	26	79	0
Less Paint Factor (~50% of Paint Min-Pb)				30		150	1	8	4		4	18	62	14	
		0.252	0.044	0.423	0.065	0.291	0.726	0.123	0.714	0.968	0.804	0.750	0.023	0.073	0.000
Pyrometallurgical contribution to Non-Source Specific Lead		107	24	144	49	371	474	104	194	0	196	1050	22	67	0
Total Pyrometallurical		250	49	407	102	868	2208	218	889	61	1229	5371	-14	131	0
% Pyrometallurgical of Total Pb		44%	9%	59%	13%	39%	92%	22%	91%	97%	95%	93%	-1%	12%	0%
Non-Source Specific															
	Clay	0		0	0	6	0	0	0	0	0	9	0	0	
	FeSO4	0		0	0	0	0	0	0	0	0	0	0	0	18.8
	Fe Oxide	54	16	22	70	11	21	74	5	0	7	33	48	41	29.8
	Mn Oxide	220	218	38	446	170	78	191	14	0	69	163	307	146	26.8
	Organics	0		0	0	0	0	0	0	0					
	Phosphate	149	303	281	239	1089	555	585	254	0	169	1196	618	729	561
Total Non-Source Specific		423	537	340	756	1275	653	850	272	0	244	1401	972	916	636
Anthropegentic															
	Pb Glass	0		0	0	0	0	0	0	0					
	Paint	0		59	0	298	1	15	8	0	8	35	124	27	
	Solder	0	3	1	0	0	0	0	0	0	0	13	7	59	
	Brass	1		0	0	0	0	0	0	1					
Total Anthropegentic		1	3	60	0	298	1	15	8	1	8	48	131	86	0

TABLE 9. Omaha Lead Apportionment.

	Bulk Pb	647	944	805	490	125	433	1974	514	630	879	794	1939	568	1184	2010
		5008B-1	5017F-1	5020B-2	5034B-1	5041B-1	5044B-1	5046DZ	5048B-2	5055F-1	5056F-2	5059B-1	5060B-2	5061F-2	5063F-2	5079B-2
Pyrometallurgical																
	Barite	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Cerussite	0	508	0	12	23	34	26	28	9	0	4	95	0	148	5
	PbAsO	0	0	0	0	0	88	0	0	0	0	0	0	0	0	0
	Pb Vanidate	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2
	PbCl4	0	0	0	0	0	0	5	0	0	0	0	0	0	0	0
	PbFeOOH	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2
	PbMO	0	0	0	0	0	0	2	84	6	0	0	0	0	0	0
	PbO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	147
	PbSbO	0	0	0	8	0	6	0	0	0	0	0	0	0	0	0
	Slag	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	PbSiO4	0	2	0	11	0	7	4	0	10	0	5	0	0	0	400
	Mixed Lead	0	0	0	0	0	0	0	0	0	0	0	1290	0	372	0
	Anglesite	0	45	0	0	0	0	0	0	0	0	0	0	0	62	4
		0	555	0	31	23	136	37	111	26	0	9	1386	0	583	561
.ess Paint Factor (~50% of Paint Min-Pb)				0				20	4				46		7	6
		0.000	0.588	0.000	0.064	0.187	0.313	0.019	0.217	0.041	0.000	0.011	0.715	0.000	0.492	0.279
Pyrometallurgical contribution to Non-Source Specific Lead		0	229	0	28	19	93	35	86	24	0	9	328	0	289	213
Total Pyrometallurical		0	784	0	59	42	228	52	193	50	0	18	1668	0	865	768
% Pyrometallurgical of Total Pb		0%	83%	0%	12%	34%	53%	3%	38%	8%	0%	2%	86%	0%	73%	38%
Non-Source Specific																
	Clay	0	1	0	2	0	2	8	0	0	0	12	1	0	0	0
	FeSO4	0	0	0	0	0	1	0	0	0	0	0	0	0	0	1
	Fe Oxide	0	5	24	15	7	36	28	54	3	5	63	14	75	10	95
	Mn Oxide	0	258	18	29	0	167	112	0	252	74	356	22	251	241	73
	Organics	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Phosphate	647	125	119	390	94	91	1744	342	344	309	353	423	238	337	596
Total Non-Source Specific		647	389	161	437	102	296	1892	395	599	389	784	459	565	588	765
Anthropegentic																
	Pb Glass	0	0	0	0	0	0	0	0	0	0	0	0	0	0	672
	Paint	0	0	644	0	0	0	40	7	0	489	0	93	0	13	12
	Solder	0	0	0	22	0	0	5	0	0	0	0	0	0	0	0
	Brass	0	0	0	0	0	0	0	0	5	0	0	0	3	0	0
Total Anthropegentic		0	0	644	22	0	0	45	7	5	489	0	94	3	13	685

8.0 FURTHER STUDIES

The conclusions reached in this report are based on review of available data, which was primarily collected to protect the public health and not to determine the specific source(s) of a particular metal. Therefore, additional data should be collected that could aid in the final identification of the source(s) of lead within the Omaha area soils. These data include:

1. Look at more park samples
2. Improve the precision and accuracy of the ICP/MS/LA technique.
3. Develop a means of analyzing smaller particles by ICP/MS/LA
4. Analyze more paint samples

9.0 CONCLUSIONS

Based on the data presented in this report the following observations...conclusions can be reached with respect to the occurrences of lead found in residential soils from the Omaha area.

- A strong isotopic correlation between community soils and ASARCO plant soils.
- Yards have "fingerprinting" phases (PbMO, $PbCl_x$, Slag, PbFeO, $PbSiO_4$, and PbAsO).... **PYROMETALLURGICAL SOURCE** many of these are more common to the ASARCO plant.
- At least 38% of the bulk lead concentration in community soils is from a pyrometallurical source.
- More than 80% of yards speciated have pyrometallurgically apportioned lead .....**SMELTER MAINTAINS RESPONSIBILITY**

Based on the data reviewed in this report it is my opinion that the lead in residential soils from the Omaha area are the result of both smelter-stack and fugitive emissions and lead-bearing paint. Further, it is my opinion that the primary non-anthropogenic source is the ASARCO smelter facility.

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Appendix

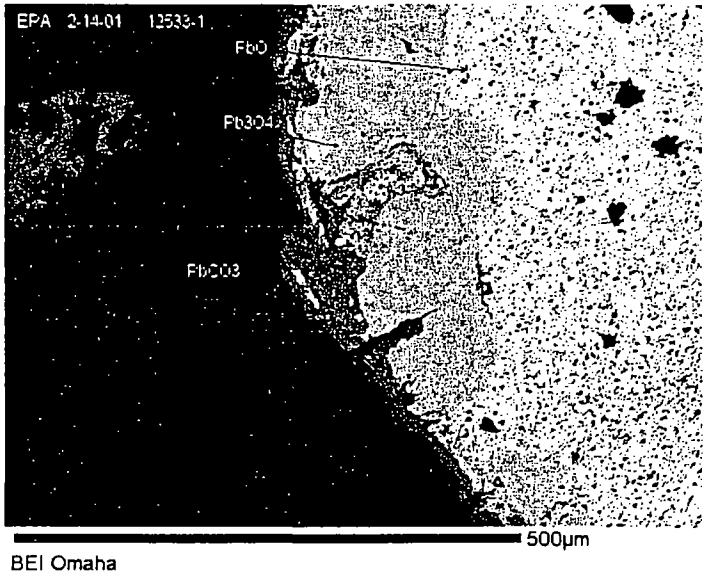
70

SPECIATION SOP

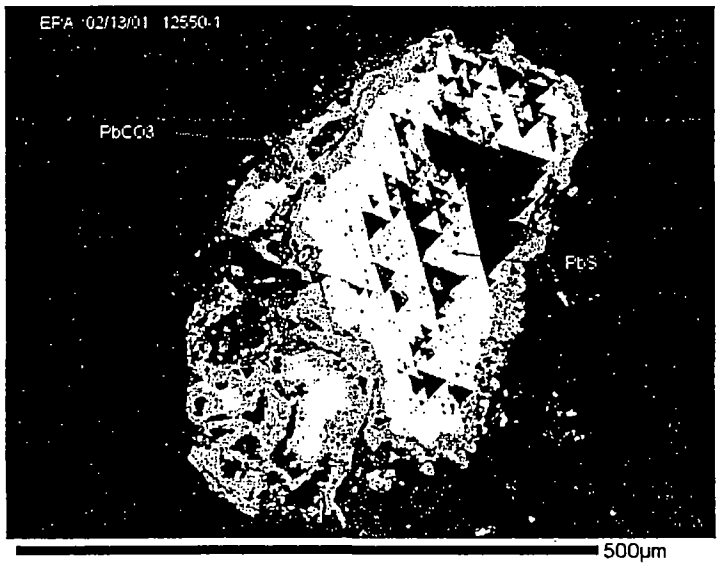
ICP/MS/LA SOP

Chain of Custody Forms

PHOTO 1.

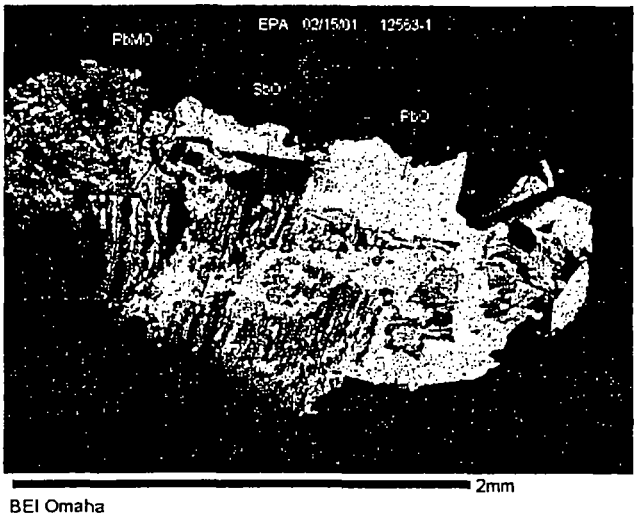


BEI Omaha



BEI Exponent

PHOTO 2.



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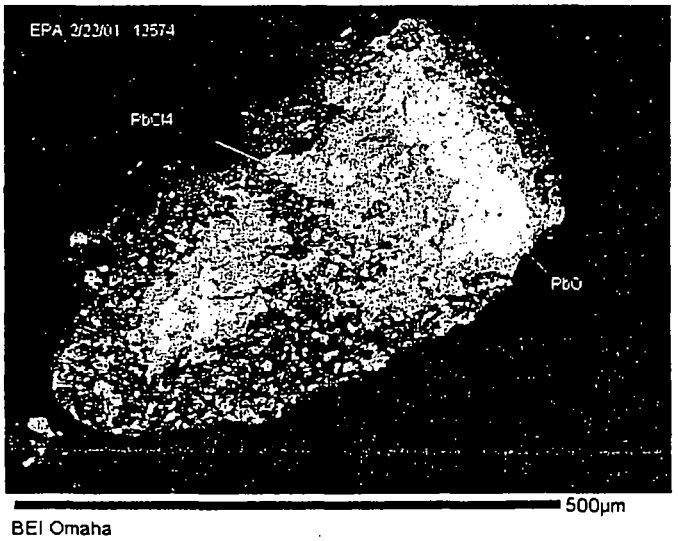
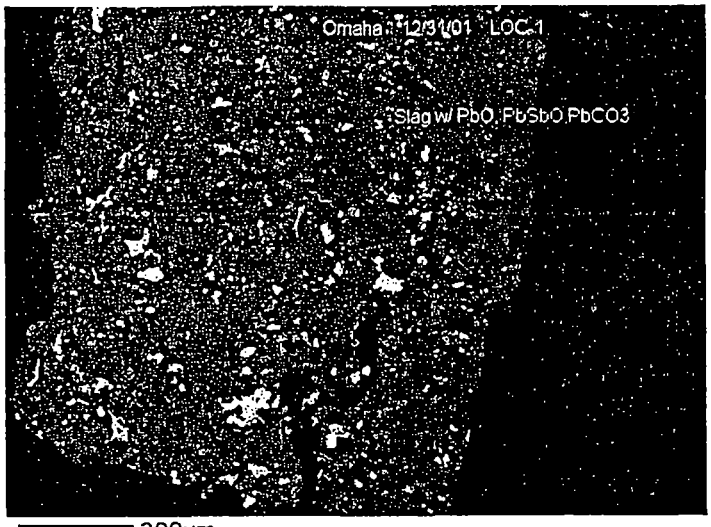
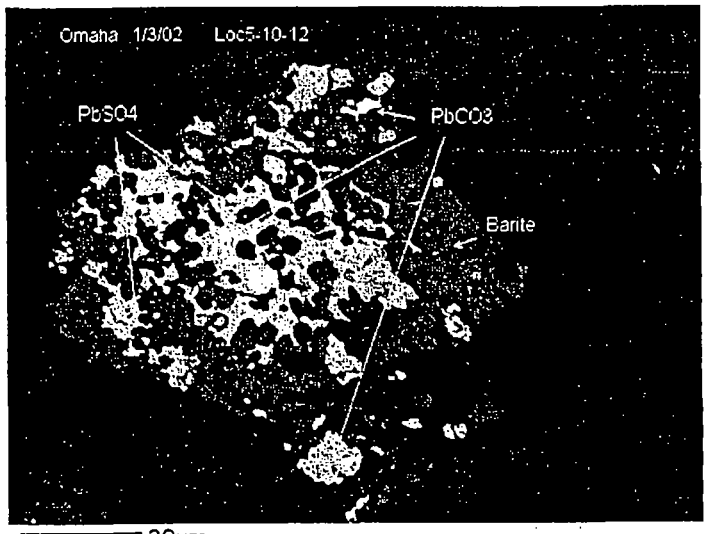


BEI Omaha

PHOTO 3.

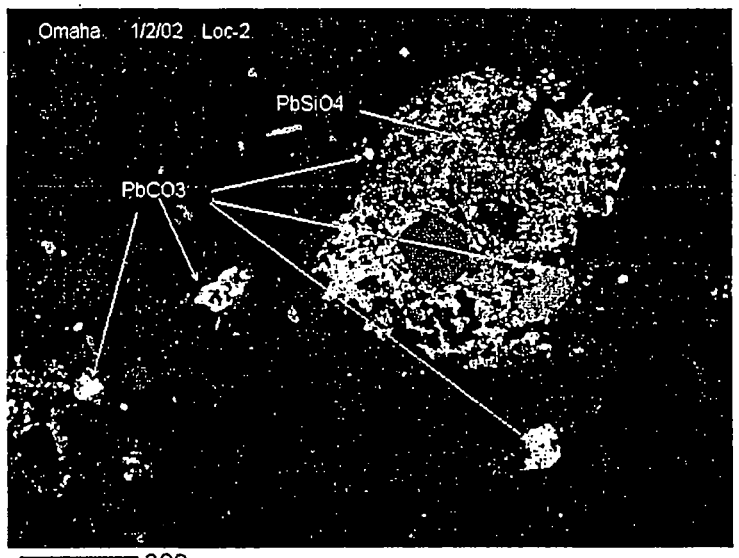


300µm
BEI Omaha



30µm
BEI Omaha

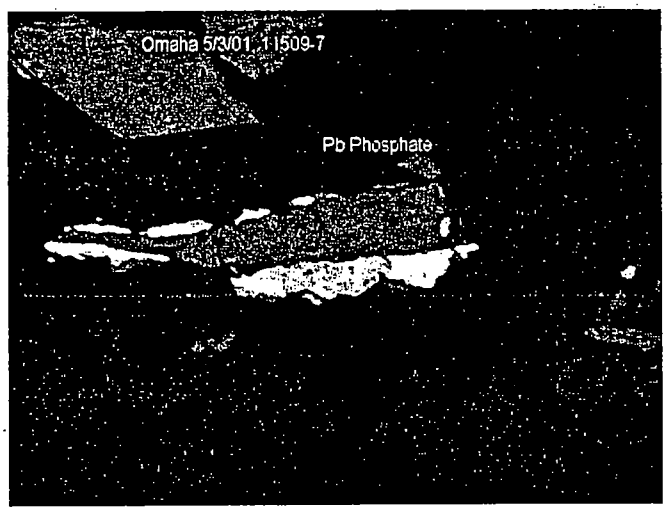
PHOTO 4.



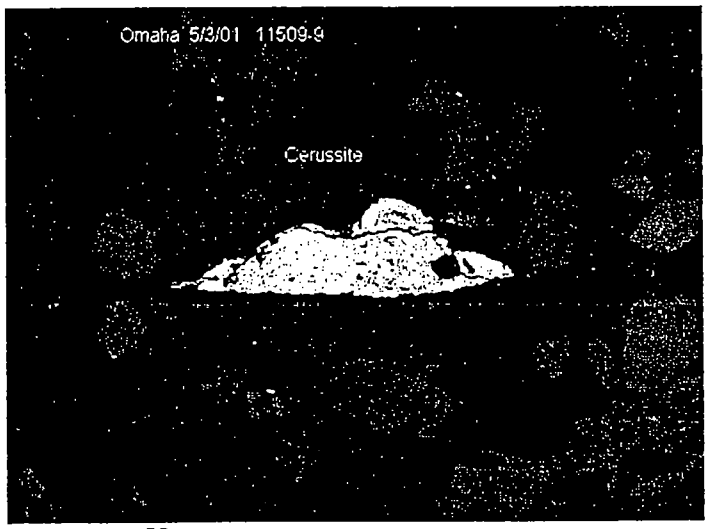
300μm

BEI Omaha

PHOTO 5.

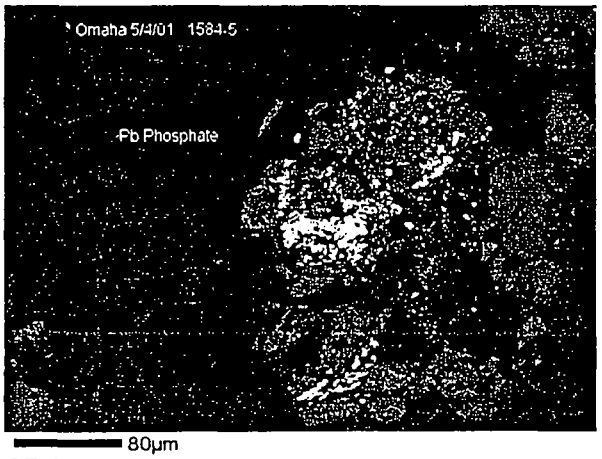


20μm
BEI Omaha

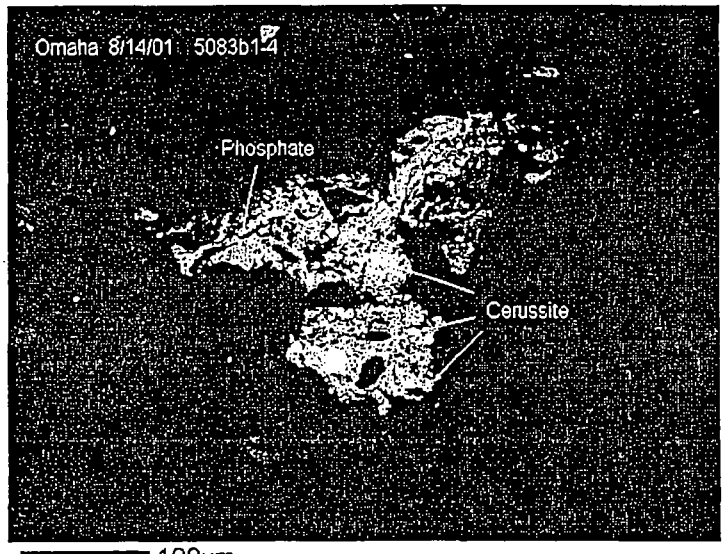


50μm
BEI Omaha

PHOTO 6.

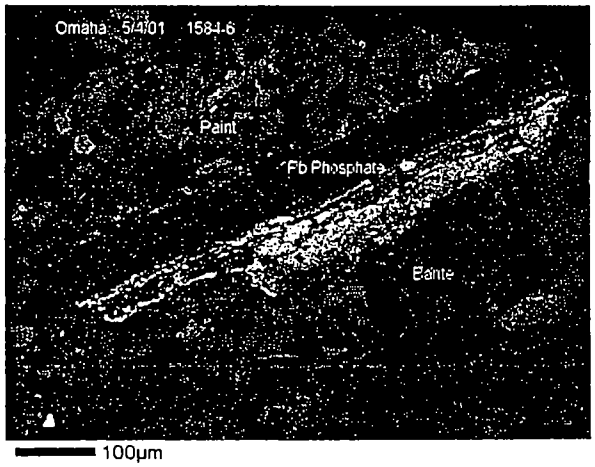


80μm
BEI Omaha

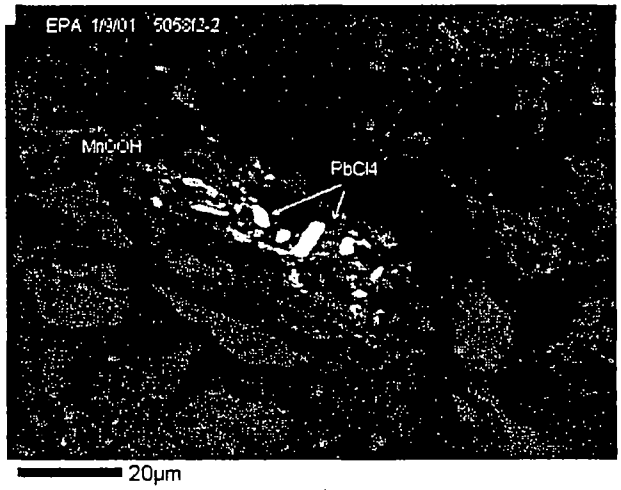


100μm
BEI Omaha

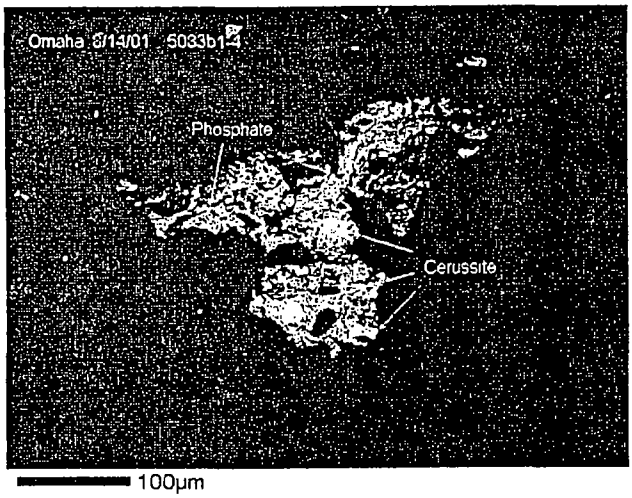
PHOTO 7.



100µm
BEI Omaha

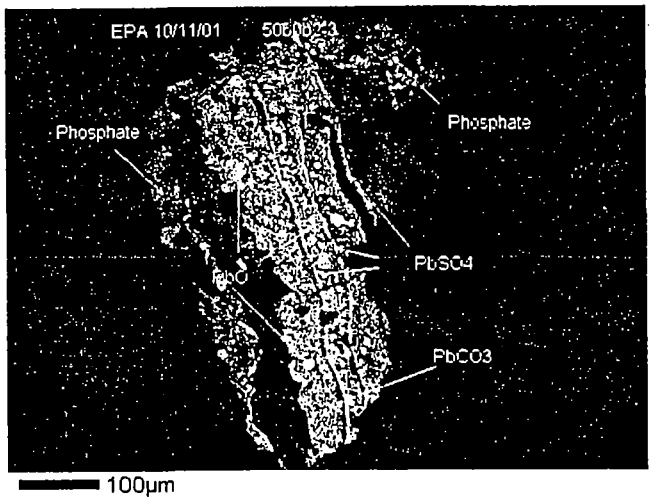


20µm
BEI Omaha



100µm
BEI Omaha

PHOTO 7.



100µm

BEI EPA

Appendix

67

SPECIATION SOP

ICP/MS/LA SOP

Chain of Custody Forms

TABLE 1A. Summary of Non-Stoichimetric,Site-Specific phase parameters.

Phase	pecific Gravit	Compositions (ppm) Pb	As
AsFeO	5	40826	195773
AsMO	5	11800	150000
AsMSO4	6	584000	100000
Barite	5	4000	0
BiMO	7	117000	3000
Brass	7	1700	0
Calcite	4	57000	0
Clay	3	57000	0
CaSiO4	3	32000	0
Fe Oxide	4	55000	4500
Fe Sulfate	4	12000	56000
FePbOOH	5	124000	4500
Organic	2	17000	0
Mn Oxide	5	132000	750
Mixed Lead	6	720000	0
PbAsO	8	449608	96535
PbMO	7	490000	32000
PbMS	7	400000	0
PbSiO4	6	244326	5154
Phosphate	5	388000	75
SbMO	4	85000	32000
Slag	4	7400	630
PbCrO4	6	300000	
PbMSO4	6	584000	100000
Solder	7	100000	500
ZnMO	5	9400	370
ZnMSiO4	4	29000	1500

Table 2.0A Site Specific Phase Analyses.

		Pb	As
	alsi	0.162669	0.041039
	clay	0.091876	0.005202
	clay	0.105213	
Average		0.119919	0.023121
ZAF		0.100372	0.005965
ppm		**100000**	**6000**
	asmo	0.125046	0.402953
	asmo	0.040184	0.049337
	asmo	0.25711	0.522637
Average		0.14078	0.324976
ZAF		0.117833	0.083844
			0.150919
ppm		**117000**	**150000**
	bimo	0.139771	0.007178
		0.116988	0.001852
ppm		**117000**	**3400**
	casio4	0.038455	0
	cc	0.010424	0
	cc	0.108004	0
Average		0.052294	0
ZAF		0.04377	0
ppm		**44000**	
	fe	0.034797	0.000176
	fe	0.331099	0.01243
	fe	0.036488	0.001728
	fe	0.144187	0.027706
	fe	0.100514	0.04938
	fe	0.012645	0.000849
	fe	0.37534	0.008582
	fe	0.016847	0.001755
	fe	0.041366	0.000913
	fe	0.09014	0.008124
	fe	0.021318	0.05376
	fe	0.025164	0.007481
	fe	0.015446	
	fe	0.025467	
	fesi	0.012767	0.00748
	fesi	0.14132	0.029631
Average		0.089057	0.015
ZAF		0.07454	0.00387
			0.006966
ppm		**74000**	**7000**
	mn	0.164764	0.019759
	mn	0.316898	0.00468
	mn	0.196195	0.004553
	mn	0.128839	0
	mn	0.093755	
	mn	0.045858	
	mn	0.131186	
Average		0.153928	0.007248
ZAF		0.128838	0.00187
			0.003366
ppm		**128000**	**3300**
	nacapbclo	0.078869	0.037754

Table 2.0A Site Specific Phase Analyses.

		Pb	As
	pbmo	0.507431	0.212664
	pbmo	0.461319	0.159264
	pbmo	0.743699	0.000353
	pbmo	1.079165	0.003511
	pbmo	0.465353	0.01176
	pbmo	0.379737	0.015277
	pbms	0.478251	0
Average		0.587851	0.057547
ZAF		0.492031	0.014847
			0.026725
ppm		**490000**	**26000**
	phos	0.289149	
	phos	0.499461	
	phos	0.442787	
	phos	0.652259	
	phos	0.620489	
	phos	0.525586	
	phos	0.535332	
	phos	0.632263	
Average		0.524666	
ZAF		0.439145	0
ppm		**439000**	
	sbmo	0.183983	0.013558
	sbmo	0.123642	0.01883
	sbmo	0.190178	0.021782
	sbmo	0.026965	0.296835
	sbo	0.028312	0.056572
Average		0.110616	0.081515
ZAF		0.092586	0.021031
ppm		**92000**	**21000**
	slag	0.028312	0.013094
	slag	0.004668	0
	slag	0.000361	
	slag	0.000846	0
	slag	0.026664	0.000545
	slag	0.00062	0
	slag	0.005023	0
	slag	0.003808	0
	slag	0.007205	0
	slag	0.012195	0
	slag	0.015626	0
Average		0.009575	0.001364
ZAF		0.008015	0.000352
			0.000633
ppm		**8000**	**600**
	snsb	0.060718	0.014263
	sold	0.112219	
	sulf	0.197009	0.10474
	sulf	0.089964	0.137833
Average		0.143487	0.121287
ZAF		0.120098	0.031292
			0.056325
ppm		**120000**	**56000**
	znmo	0.01127	0.000792
	znmsio4	0.034786	0.003297
Average		0.023028	0.002045
ZAF		0.019274	0.000527
ppm		**19000**	**500**

1.0 OBJECTIVES

The objectives of this Standard Operating Procedure (SOP) are to specify the proper methodologies and protocols to be used during metal speciation of various solid samples (including tailings, slags, sediments, dross, bag house dusts, and paint), residential soils and dusts for metals. The metal speciation data generated from this SOP may be used to assess the solid samples as each phase relates to risk. Parameters to be characterized during the speciation analyses include particle size, associations, stoichiometry, frequency of occurrence of metal-bearing forms and relative mass of metal-bearing forms. In addition, aliquots of solid samples can be analyzed separately for perlite, using the same methodology. Perlite particles are counted and sized based on the elemental constituents of each particle. This electron microprobe (EMP) technique, instrument operation protocols and sample preparation to be used during implementation of the Metals Speciation SOP are discussed in the following sections.

2.0 BACKGROUND

To date, numerous forms (phases) of metal-bearing particles have been identified in soils from various environments within western mining districts (Table 2-1) (Emmons et al., 1927; Drexler, 1992; Davis et al., 1993; Ruby et al., 1994; CDM, 1994; WESTON, 1995). This listing does not preclude the identification of other metal-bearing forms, but only serves as an initial point of reference. Many of these forms are minerals with varying metal concentrations (e.g., lead phosphate, iron-lead oxide, and slag). Since limited thermodynamic information is available for many of these phases and equilibrium conditions are rarely found in soil environments, the identity of the mineral class (e.g., lead phosphate) will be sufficient and exact stoichiometry is not necessary.

It may be important to know the particle-size distribution of metal-bearing forms in order to assess potential risk. It is believed that particles less than 250 microns (μm) are most available for human ingestion and/or inhalation (Bornschein, et al., 1987). For this study, the largest dimension of any one metal-bearing form will be measured and the frequency of occurrence weighted by that dimension. Although not routinely performed, particle area can be determined. It has been shown (CDM, 1994) that data collected on particle area produces similar results. These measurements add a considerable amount of time to the procedure and limit the total number of particles or samples that can be observed in a study.

Mineral association may have profound effects on the ability for solubilization. For example, if a lead-bearing form in one sample is predominantly found within quartz grains while in another sample it is free in the sample matrix, the two samples are likely

to pose significantly different risk levels to human health. Therefore, associations of concern include the following:

1) free or liberated
2) inclusions within a second phase
3) cementing
4) alteration rims

3.0 SAMPLE SELECTION

Samples will be selected and handled according to the procedure described in the Project Plan.

4.0 SCHEDULE

A schedule for completion of projects performed under this Metals Speciation SOP will be provided in writing or verbally to the contractor along with monthly reporting requirements if large projects are performed. These schedules are based on an aggressive analytical program designed to ensure that the metals speciation analyses are completed in a timely period. Monthly reports are expected to reflect schedule status.

5.0 INSTRUMENTATION

Metal Speciation

Speciation analyses will be conducted at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado, Boulder or other comparable facilities. Primary equipment used for this work will include:

Electron Microprobe (*JEOL 8600*) equipped with four wavelength spectrometers, energy dispersive spectrometer (EDS), BEI detector and the TN-5600 data processing system. RJ Lee ZEPPELIN and DATALINK hardware may be used for image storage and processing. An LEDC spectrometer crystal for carbon and LDE-1 crystal for oxygen analyses will be used.

Qualitative Perlite Analysis

Identification of perlite morphology will be performed with an optical microscope that utilizes polarized transmitted light.

6.0 PRECISION AND ACCURACY

6.1 Precision

Metal Speciation

The precision of the data generated by the manual particle light microscopy (PLM) particle count and by the "EMP point count" will be evaluated by preparing a graph that compares the original result with the duplicate result.

In general, detectable concentrations for these variable, metal-bearing forms will be determined by performing "peak counts" on the appropriate wavelength spectrometer. Average concentrations will then be used for further calculations. Data on specific gravity will be collected from referenced databases or estimated based on similar compounds. A minimum of two peak counts per sample will be performed on non-stoichiometric phases, as appropriate (that is, if they exist in that sample).

The precision of quantitative elemental analysis will be evaluated based on sample duplicates analyzed at a frequency of 10%.

Perlite

The precision of the data generated by the manual particle light microscopy (PLM) particle count will be evaluated based on sample duplicates analyzed at a frequency of 10%.

6.2 Accuracy

The accuracy of the analyses will be estimated based on a number of methods, depending on the source of the data. Data generated by the "EMP point count" will be evaluated statistically based on the methods of Mosimann (1965) at the 95% confidence level on the frequency data following Equation 1.

$$E_{0.95} = 2P(100-P)/N \qquad \text{(Eq. 1)}$$

Where: $E_{0.95}$ = Probable error at the 95% confidence level

P = Percentage of N of an individual metal-bearing phase based on percent length frequency

N = Total number of metal-bearing grains counted

7.0 PERSONNEL RESPONSIBILITY

The analyst(s) will carefully read this SOP prior to any sample examination.

It is the responsibility of the laboratory supervisor and designates to ensure that these procedures are followed, to examine quality assurance (QA) samples and replicate standards, and to check EDS and WDS calibrations. The laboratory supervisor will collect results, ensure they are in proper format, and deliver them to the contractor.

Monthly reports summarizing all progress, with a list of samples speciated to date with data analyses sheets (DAS), will be submitted each month.

It is also the responsibility of the laboratory supervisor to notify the contractor representative of any problems encountered in the sample analysis process.

8.0 SAMPLE PREPARATION

Grain mounts (1.5 inches in diameter) or polished sections of each sample will be prepared using air-cured epoxy. This grain mounting technique is appropriate for both the electron microprobe (EMP) and polarized light microscopy (PLM) analyses. However, separate splits for the two analyses must be prepared. The grain mounting is performed as follows:

1) Log the samples for which polished mounts will be prepared.

2) Inspect all disposable plastic cups, making sure each is clean and dry.

3) Label each "mold" with its corresponding sample number.

4) All samples will be split to produce a homogeneous 1-4 gram sample.

5) Mix epoxy resin and hardener according to manufacturer's directions.

6) Pour 1 gram of sample into mold. Double check to make sure sample numbers on mold and the original sample container match. Pour epoxy into mold to just cover sample grains.

7) Using a new wood stirring stick with each sample, carefully blend epoxy and grains so as to coat all grains with epoxy.

8) Set molds to cure at ROOM TEMPERATURE in a clean, restricted area. Add labels with sample numbers and cover with more epoxy resin. Leave to cure completely at room temperature.

9) One at a time remove each sample from its mold and grind flat the back side of the mount.

10) Use 600 grit wet abrasive paper stretched across a grinding wheel to remove the bottom layer and expose as many mineral grains as possible. Follow with 1000 grit paper.

11) Polish with 15 um oil-based diamond paste on a polishing paper fixed to a lap. Do not use cloth, as the use of paper will minimize relief.

12) Next use 6um diamond polish on a similar lap.

13) Finally, polish the sample with 1um oil-based diamond paste on polishing paper, followed by 0.05 um alumina in water suspension. The quality will be checked after each step. Typical polishing times are 30 minutes for 15 um, 20 minutes for 6 um, 15 minutes for 1 um, and 10 minutes for 0.05 um.

NOTE: use low speed on the polishing laps to avoid "plucking" of sample grains.

14) Samples will be completely cleaned in an ultrasonic cleaner with isopropyl alcohol or similar solvent to remove oil and fingerprints.

15) To ensure that no particles of any metal are being cross-contaminated during sample preparation procedures, a blank (epoxy only) mold will be made every 20th sample (5% of samples) following all of the above procedures. This mold will then be speciated along with the other samples.

16) Each sample must be carbon coated. Once coated, the samples will be stored in a clean, dry environment with the carbon surface protected from scratches or handling.

9.0 PERLITE ANALYSIS USING POLARIZED LIGHT MICROSCOPY

Optical microscopy will be employed to determine the morphology of perlite particles, if present, in each investigative sample. The perlite samples will be mounted on glass thin sections prior to polishing. Perlite particles will be counted under polarized transmitted light in the magnification range of 45-400X. Any particle that appears to be perlite (based on morphology) will be counted, and the number of the perlite particles will be documented on the Perlite DAS (Figure 9-1). The visual identification of perlite particles will be confirmed by EMP, as discussed below.

10.0 GEOCHEMICAL SPECIATION USING ELECTRON MICROPROBE

All investigative samples will also be characterized using EMP analysis to determine the chemical speciation, particle size distribution and frequency for several target metals. These are arsenic, lead, cadmium, zinc, thallium, selenium, indium, antimony, and mercury. Additionally, chemical speciation and particle size distribution for perlite will also be determined. The perlite speciation will be performed to confirm the morphological results obtained using the PLM.

10.1 Instrument Calibration and Standardization

The WDS will have spectrometers calibrated for the metals of concern (As, Pb, Cd, Zn, Tl, Se, Sb, Hg and In), carbon, oxygen and sulfur on the appropriate crystals using mineral standards. The EDS will have a multi-channel analyzer (MCA) calibrated for known peak energy centroids. Calibration will be performed so as to have both low (1.0-3.0 KeV) and high (6.0-9.0 KeV) energy peaks fall within 0.05 KeV of its known centroid.

The magnification marker on the instrument will be checked once a week. This will be performed by following manufacturer instructions or by measurement of commercially available grids or leucite spheres. Size measurements must be within 4 microns of certified values.

Initial calibration verification standards (ICVs) must be analyzed at the beginning of each sample delivery group or once every 48 hours, whichever is more frequent. A set of mineral or glass standards will be run quantitatively for the metals of concern (As, Pb, Cd, Zn, Tl, Se, Sb, Hg and In), sulfur, oxygen and carbon. If elemental quantities of the ICVs do not fall within 5% of certified values for each element, the instrument must be recalibrated prior to analysis of investigative samples.

The metal-bearing forms in these samples will be identified using a combination of EDS, WDS and BEI detection. Once a particle is isolated with the backscatter detector, a 5-second EDS spectra is collected and peaks identified. The count rates for the metals of concern, sulfur, carbon and oxygen can be either visually observed on the wavelength spectrometers or K-ratios calculated.

10.2 Analytical Procedure

A brief visual examination of each sample will be made prior to EMP examination. This examination may help the operator by noting the occurrence of slag and/or organic matter. Standard operating conditions for quantitative and qualitative analyses of metal-bearing forms are given in Table 10-1. However, it is the responsibility of the operator to select the appropriate analytical line (crystal/KeV range) to eliminate peak overlaps and ensure proper identification/quantification of each analyte. Quality control will be maintained by analyzing duplicates at regular intervals (Section 6.1).

The backscattered electron threshold will be adjusted so that all particles containing the element of interest (i.e., both those with low content and high content) can be seen. For particles that have generally high content (i.e., those that are especially bright), it may be necessary to lower the threshold in order to identify sub-regions of the particle that may contain different phases. This procedure will minimize the possibility that metal-bearing minerals may be overlooked during the scanning of the polished grain mount. The scanning will be done manually in a manner similar to that depicted in Figure 10-1. Typically, the magnification used for scanning all samples except for airborne samples will be 40-100X and 300-600X. The last setting will allow the smallest identifiable (1-2 um) phases to be found. Once a candidate particle is identified, then the backscatter image will be optimized to discriminate any different phases that may be making up the particle or defining its association. Identification of the metal-bearing phases will be done using both EDS and WDS on an EMP, with spectrometers peaked at sulfur, oxygen, carbon and the metal of concern (M). The size of each metal-bearing phase will be determined by measuring the longest dimension (in microns).

10.3 Point Counting

Counts are made by traversing each sample from left-to-right and top-to-bottom as illustrated in Figure 10-1. The amount of vertical movement for each traverse would depend on magnification and CRT (cathode-ray tube) size. This movement will be minimized so that NO portion of the sample is missed when the end of a traverse is reached. Two magnification settings generally are used. One ranging from 40-100X and a second from 300-600X. The last setting will allow one to find the smallest identifiable (1-2 micron) phases.

The portion of the sample examined in the second pass, under the higher magnification, will depend on the time available, the number of metal-bearing particles, and the complexity of metal mineralogy. Eight hours will be spent on each sample.

The particle counting goal for the As, Pb, Cd, Sb, Tl, In, Hg and Se analysis is to count the number of particles for each metal type until 8 hours has expired. Zinc particles will also be counted during this 8-hour period. However, only particles having a zinc composition of greater than 2% (mass/mass) will be scanned and analyzed.

Perlite

Particles that are tentatively identified as perlite using PLM will be examined by EPM to identify the major elemental constituents. A particle will be identified as perlite if the elemental composition contains silica, aluminum and potassium in relative amounts such that a spectrum is produced that is similar to the example provided in Figure 10-2.

10.4 Quantitative Analyses

Quantitative analyses are required to establish the elemental stoichiometry (and hence the elemental mass fraction) of the metal-bearing minerals. Quantitative analyses of representative phases will be performed for each of the target elements (As, Pb, Cd, Sb, Tl, In, Se, Zn and Hg).

Results for each phase will be averaged across several representative grains to establish mean values. The range of values may also be depicted as histograms to show the range of metal concentrations measured as well as the presence of one or more populations in terms of metal content. In the latter case, non-parametric statistics may have to be used or the median value has to be established. Photomicrographs and EDS spectra will be printed, as described in Section 11.2. Example EDS spectra for common or important phases are provided as an attachment (Attachment A).

10.5 Associations

The association of the metal-bearing forms will be established from the backscattered electron images. Particular attention will be paid in establishing whether the grains are totally enclosed, encapsulated or liberated. The rinds of metal-bearing grains will be identified. Representative photomicrographs of backscatter electron images establishing the association of the principal metal-bearing forms will be obtained for illustration purposes.

10.6 Source Material Dilutions

In the case where test materials are highly enriched with target metals (e.g., PAX, flue dust), it may be necessary to dilute the sample to facilitate sample characterization. This will be performed at the discretion of the analyst. For samples that are determined to require dilution, clean quartz sand (SiO_2) will be mixed with the sample material. The sand will be certified to be free of target analytes. The quartz sand will be added to an aliquot of the investigative sample, then mixed by turning the sample for a minimum of one hour, or until the sample is fully homogenized. The initial mass of the investigative sample aliquot, and the mass of the quartz addition must be recorded on the Data Analysis Sheet (Figure 10-3).

11.0 DATA RECORDING AND DOCUMENTATION

11.1 Analysis Results

Analysts will record information on the initial calibration for each metal, and the results for each sample (in counts observed for each 8-hr period) on the Analysis Logsheet (Figure 11-1).

Analysts will electronically record data as they are acquired from each sample using the LEGS Microsoft Access® software, which places all data in a spreadsheet file format. An example of the data entry screen is provided in Figure 11-2. An example of the spreadsheet format is provided in Figure 10-3. Data entry fields have been established for numbering the metal-bearing phase particles, their identity, size of longest dimension in microns, along with their association (L = liberated, C= cementing, R = rimming, I = included). The analyst will also summarize his/her observations in the formatted data summary files.

11.2 Photomicrographs and EDS Spectra

Photomicrographs must be taken for each sample, at a rate of 5% (1 photograph per 20 particles counted) for a maximum of 10 photographs per sample, and submitted with the sample results. Particles selected for photography must be recorded on the EMP graph, as well as in the Photomicrograph Logbook (Figure 11-3). Each photo will be assigned a number, starting with 1 and increasing until the project is complete. Any additional photographs will be labeled as "opportunistic" and must be accompanied by a brief explanation of the reason for taking the picture. For each photomicrograph that is taken, an EDS spectrum of each target chemical present in the sample will also be printed. Each spectrum will be assigned a number as follows:

- The same integer used for the corresponding photomicrograph will also be used for the EDS spectrum.
- Each photo will also be assigned a letter ID. Therefore, if 3 spectra are generated for photo #3, the spectrum IDs would be 3A, 3B, and 3C, respectively.

A positive black and white film (Polaroid 52) will be used, and a 128x128 (minimum) binary image in ".tif" format will be developed and stored, using a high resolution scanner. Recorded on each photomicrograph will be a scale bar, magnification, sample identification, date and phase identification. Abbreviations for the identified phases can be used. Examples are listed in Table 10-2. A final list must be submitted with the laboratory report, along with printouts of the corresponding EDS spectra for each particle that was photographed. An example photomicrograph is provided in Figure 11-4.

11.3 Data Storage and Archival

For each day of data acquisition, all electronic files (DAS forms and other sample logbook sheets) will be saved on the hard drives of the local instrument computer and the general laboratory computer. All files will be saved under a directory reserved for the VBI70 project. The files for each analytical batch (each day's run) will be stored in a unique subdirectory. The subdirectories will be named as the analysis data (e.g., 12-01-99). Additionally, the files for each analysis data will be stored on a floppy disk. Floppy disks will be maintained in a single location with limited access.

11.4 Data Reduction and Reporting

The frequency of occurrence and relative metal mass of each metal-bearing form as it is distributed in each sample will be depicted graphically as a frequency bar graph. The particle size distribution of metal-bearing forms will be depicted in a histogram. Size-histograms of each metal-bearing form can be constructed from data in the file.

Data from EMP will be summarized using two methods. The first method is the determination of FREQUENCY OF OCCURRENCE. This is calculated by summing the longest dimension of all the metal-bearing phases observed and then dividing each phase by the total.

Equation 2 will serve as an example of the calculation.

$$F_M \text{ in phase-1} = \frac{\Sigma\,(PLD)_{\text{phase 1}}}{\Sigma\,(PLD)_{\text{phase-1}} + \Sigma(PLD)_{\text{phase-2}} + \Sigma\,(PLD)_{\text{phase-n}}} \qquad \text{(Eq. 2)}$$

Where:
F_M = Frequency of occurrence of metal in a single phase.
PLD = An individual particle's longest dimension
$\%F_M$ in phase-1 = F_M in phase-1 * 100

These data thus illustrate which metal-bearing phase(s) are the most commonly observed in the sample or relative volume percent.

The second calculation used in this report is the determination of RELATIVE METAL MASS. These data are calculated by substituting the PLD term in the equation above with the value of M_M. This term is calculated as defined below.

$$M_M = FM * SG * ppm_M \qquad \text{(Eq. 3)}$$

Where:
M_M = Mass of metal in a phase
SG = Specific Gravity of a phase
ppm_M = Concentration in ppm of metal in a phase

The advantage in reviewing the RELATIVE METAL MASS determination is that it gives one information as to which metal-bearing phase(s) in a sample are likely to control the total bulk concentration for a metal of interest. For example, PHASE-1 may comprise

98% relative volume of the sample; however, it has a low specific gravity and contains only 1,000 parts per million (ppm) arsenic. PHASE-2 comprised 2% of the sample, has a high specific gravity, and contains 850,000 ppm of arsenic. In this example it is PHASE-2 that is the dominant source of arsenic to the sample.

Finally, a concentration for each phase is calculated. This quantifies the concentration of each metal-bearing phase. This term is calculated as defined below (Eq. 4).

$$ppm_M = M_M * \text{Bulk metal concentration in ppm} \qquad \text{(Eq. 4)}$$

12.0 PERSONAL HEALTH AND SAFETY

Each individual operating the KEVEX x-ray fluorescence or electron microprobe instruments will have read the "Radiation Safety Handbook" prepared by the University and follow all State guidelines for operation of X-ray equipment.

Latex gloves and particulate masks will be worn during preparation of sample cups. All material that comes in contact with the samples or used to clean work surface areas will be placed in poly-bags for disposal.

13.0 SAMPLE HANDLING, CUSTODY AND ARCHIVAL

13.1 Sample Handling and Custody

All raw sample material, pucks and thin mounts will be clearly labeled and handled to avoid cross-contamination and damage. These samples and associated chain-of-custody forms will be stored in a location such as a lockable file cabinet having limited access.

13.2 Unused Sample

All raw, unused sample will be returned to the Contractor under chain-of-custody at the completion of the study.

14.0 FINAL REPORT AND DELIVERABLES

14.1 Final Report

A final laboratory report will be prepared for the Contractor. The report will include all EMP data including speciation results, summary tables and figures, EDS spectra, and photomicrographs. A narrative that describes any deviations to this SOP or the

associated Project Plan(s), and the reason for the deviation will be included in the case narrative.

Speciation results will include: 1) a series of tables summarizing frequency of occurrence for each metal phase identified along with a confidence limit; 2) summary histograms of metal phases identified for each waste type; 3) a summary histogram of particle size distribution in each waste type; and 4) a summary of metal phase associations.

14.2 Deliverables

The following deliverables will be submitted to the contractor at the completion of the study:

- Final Laboratory Report
- EDS Spectra
- Photomicrographs
- CD-ROM of all electronic files generated throughout the study (including raw data files, figures, tables, and the final report file) as follows:
  - Sample.geo
  - Sample.xls
  - Sample.wb3
  - Photo#.tif
  - Size.xls
  - Ass.xls
  - Sam.xls
  - Probe.xls

15.0 REFERENCES

Bornschein, R.L., P.A. Succop, K.M. Kraft, and C.S. Clark. 1987. Exterior surface lead dust, interior lead house dust and childhood lead exposure in an urban environment. In D.D. Hemphil, Ed., Trace Substances in Environmental Health XX Proceedings of the University of Missouri's 20th Annual Conference. June 1986, pp 322-332. University of Missouri, Columbia, MO.

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Drexler, J.W. 1992. Speciation Report on the Smuggler Mine, Aspen CO., Prepared for EPA.

Emmons, S.F., J.D. Irving, and G.F. Loughlin. 1927. Geology and Ore Deposits of the Leadville Mining District, Colorado. USGS Professional Paper 148.

Davis, A., J.W. Drexler, M.V. Ruby, and A. Nicholson. 1993. The micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. *Environ. Sci. Technol.* (In Press).

Mosimann, J.E. 1965. Statistical methods for the Pollen Analyst. In: B. Kummel and D. Raup (EDS.). *Handbook of Paleontological Techniques.* Freeman and Co., San Francisco, pp. 636-673.

Ruby, M.V., A. Davis, J.H. Kempton, J.W. Drexler, and P.D. Bergstrom. 1992. Lead bioavailability: Dissolution kinetics under simulated gastric conditions. *Environ. Sci. Technol.* 26(6): pp 1242-1248.

WESTON (Roy F. Weston, Inc.). 1995. Metal Speciation Interpretive Report, Leadville, CO. CERCLA Site. March, 1995.

Table 2-1

Metal-Bearing Forms Found Within Western Mining and Smelting Districts

OXIDES

Lead Oxide
Manganese (metal) oxide
Iron (metal) oxide
Lead (metal) oxide
Lead molybdenum oxide
Arsenic (metal) oxide
Cadmium Oxide
Copper Oxides
Zinc Oxide
Lead Arsenate
Arsenic Trioxide
Calcium (metal) oxide

SILICATES

Slag
Lead silicate
Arsenic silicate
Zinc silicate
Clays

SULFATES

Iron (metal) sulfate
Lead sulfate
Lead barite
Zinc Sulfate
Arsenic sulfate
Copper sulfate

CARBONATES

Lead Carbonate
Zinc Carbonate

PHOSPHATES

(metal) phosphates

SULFIDES

Lead sulfide
Sulfur-containing salts
Iron-arsenic sulfide
Zinc sulfide
Copper sulfides
Copper-iron sulfide
Cadmium Sulfide

OTHER

Native: Lead, Copper, Cadmium, Mercury, Indium, Thallium, Selenium

Lead/Arsenic/Cadmium/Mercury Chlorides
Lead paint
Solder
Organic lead
Lead vanadate
Minor telluride, and bismuth-lead phases

Figure 9-1. Perlite Data Analysis Sheet

Polarized Transmitted Light Microscopy

Date: _____ Analyst: _____

Analytical Sequence #	Sample ID	Magnification	Qualitative Perlite Count (# of particles)	Notes *

* Indicate any required dilutions: initial sample mass plus SiO_2 addition

Logbook Page Reviewed By: _____

Date: _____

Figure 10-1

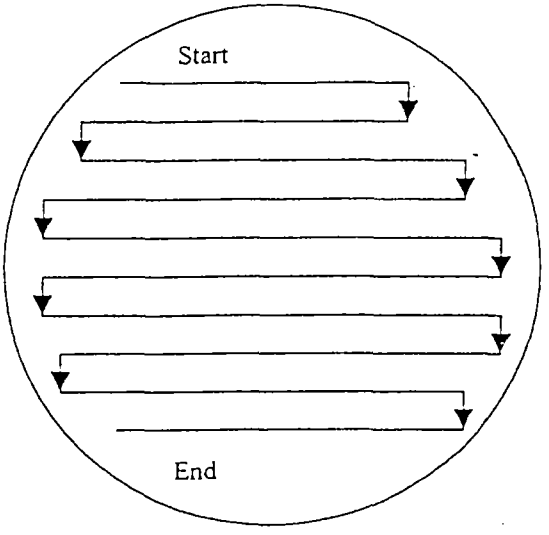


Figure 10-2. Example of Perlite Spectrum

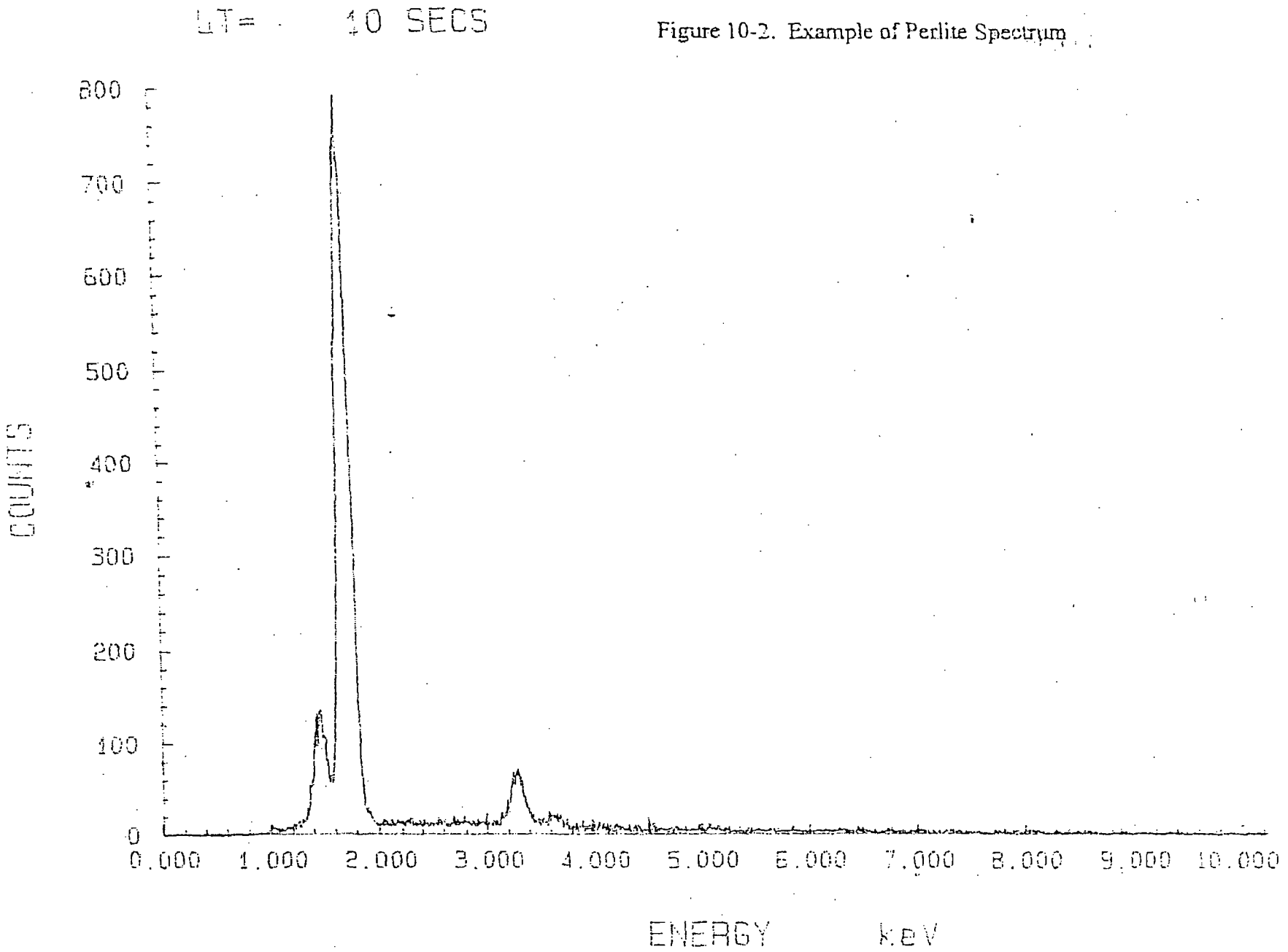


Figure 10-3. Geochemical Speciation Data Analysis Sheet

Analytical Sequence #	Notes *	Sample ID	Size		Liberated	Inclusions	Cemented	Rim
			Length (um)	Area (um)				

* Indicate any required dilutions: initial sample mass plus SiO_2 addition

Logbook Page Reviewed By: _____

Date: _____

Table 10-1

EMP Standard Operating Conditions

	WDS	EDS
Accelerating Voltage	15 KV	15-20 KV
Beam Size	1-2 microns	1-2 microns
Cup Current	10-30 NanoAmps	10-30 NanoAmps
Ev/Channel	NA	10 or 20
Stage Tilt	NA	Fixed
Working Distance	NA	Fixed
MCA time Constant	NA	7.5-12 microseconds
X-ray lines	S K-alpha PET O K-alpha LDE1 C K-alpha LDEC Zn K-alpha PET As L-alpha TAP Cu K-alpha LIF Cd L-alpha PET Pb M-alpha PET Pb L-alpha LIF In L-alpha PET Tl L-alpha LIF Hg L-alpha LIF Se L-alpha LIF Sb L-alpha PET	S K-alpha 2.31 KeV O K-alpha 0.52 KeV C K-alpha 0.28 KeV Pb M-alpha 2.34 KeV Pb L-alpha 10.5 KeV Zn K-alpha 8.63 KeV Cu K-alpha 8.04 KeV As K-alpha 10.5 KeV As L-alpha 1.28 KeV Cd L-alpha 3.13 KeV In L-alpha 3.28 KeV Tl M-alpha 2.27 KeV Tl L-alpha 10.26 KeV Hg L-alpha 9.98 KeV Hg M-alpha 2.19 KeV Se L-alpha 1.37 KeV Sb L-alpha 3.60 KeV

Table 10-2

Suggested Abbreviation for Photomicrographs

Metal-bearing Phase	Abbreviation
In	In
Tl	Tl
Hg	Hg
Se	Se
Sb	Sb
Lead Sulfide	Ga
Lead Sulfate	Ang
Lead Carbonate	Cer
Mn-(M) Oxide	Mn(M)
Fe-(M) Oxide	Fe(M)
(M)Phosphate	(M)Phos
Fe-(M) Sulfate	Fe(M)Sul
Metal Oxide	(M)O
Pb-Mo Oxide	Wulf
Slag	Slag
Metallic Phase	(M)
Metal Silicate	(M)Si
Solder	Sold
Paint	Pnt
Metal-bearing Organic	(M)(Org)
(M) barite	(M)Bar
Pb arsenate	PbAsO
Pb vanadate	PbVan
As-Sb Oxide	AsSbO
Chalcopyrite	Cp
Sphalerite	Sph
Arsenopyrite	Apy

Figure 11-1. Analysis Logsheet

Analyst: _____ Logbook Page Reviewed By: _____

Magnification Marker [a] _____ Date: _____

Standard ID [b]	Analytical Sequence #	Date/Time[c]	K-ratio	Result[d]	Acceptance Limits	Comments
As	As-1		1		0.95 - 1.05	
Pb	Pb-1		1		0.95 - 1.05	
Cd	Cd-1		1		0.95 - 1.05	
Zn	Zn-1		1		0.95 - 1.05	
Tl	Tl-1		1		0.95 - 1.05	
Se	Se-1		1		0.95 - 1.05	
Sb	Sb-1		1		0.95 - 1.05	
Hg	Hg-1		1		0.95 - 1.05	
In	In-1		1		0.95 - 1.05	
O	O-1		1		0.95 - 1.05	
C	C-1		1		0.95 - 1.05	
S	S-1		1		0.95 - 1.05	

Standard ID [b]	Analytical Sequence #	Date/Time[c]	Sample ID	Phase	Result	Comments

[a] - The magnification marker on the instrument must be checked once a week. If less than one week has elapsed since the last time the magnification marker was calibrated, enter "N/A"

[b] - *Initial calibration verification must be performed once every 48 hours.*

[c] - Enter time in 24-hour format

[d] - The calibration standards must be within 5% of the concentration factor to be acceptable.

Figure 11-2

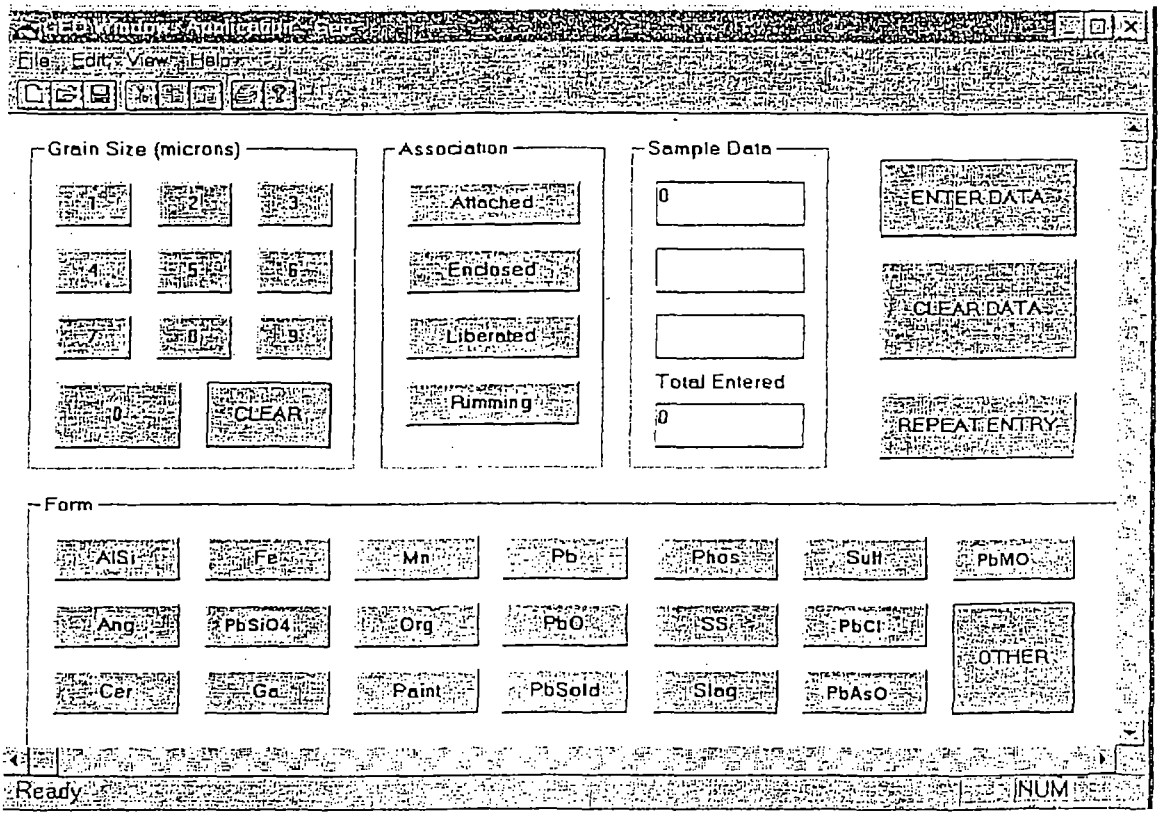

File Edit View Help
Grain Size (microns)
1
2
3
4
5
6
7
8
9
0
CLEAR
Association
Attached
Enclosed
Liberated
Rimming
Sample Data
0
Total Entered
0
ENTER DATA
CLEAR DATA
REPEAT ENTRY
Form
AlSi
Fe
Mn
Pb
Phos
Sulf
PbMO
Ang
PbSiO4
Org
PbO
SS
PbCl
OTHER
Cer
Ga
Paint
PbSold
Slag
PbAsO
Ready
NUM

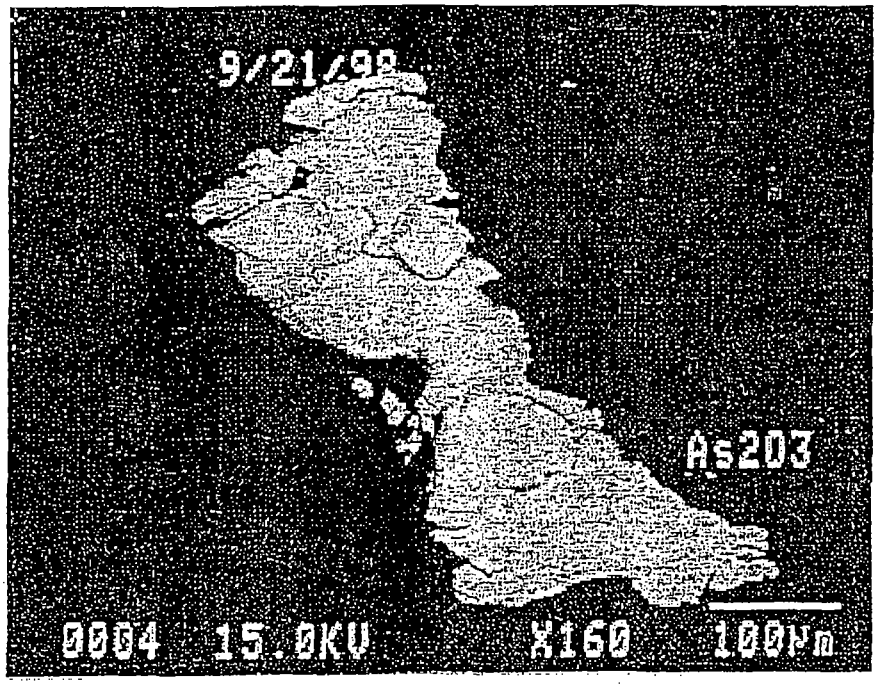
Figure 11-3

Photo Micrograph Logbook				
Sample No.	Particle No. (20, 40, 60, etc.)	Photograph ID	EDS Spectra ID	Comments[a]

a - If discretionary or opportunistic photographs are collected, indicate this and the reason for collection.

Logbook Page Reviewed By: _____ Date: _____

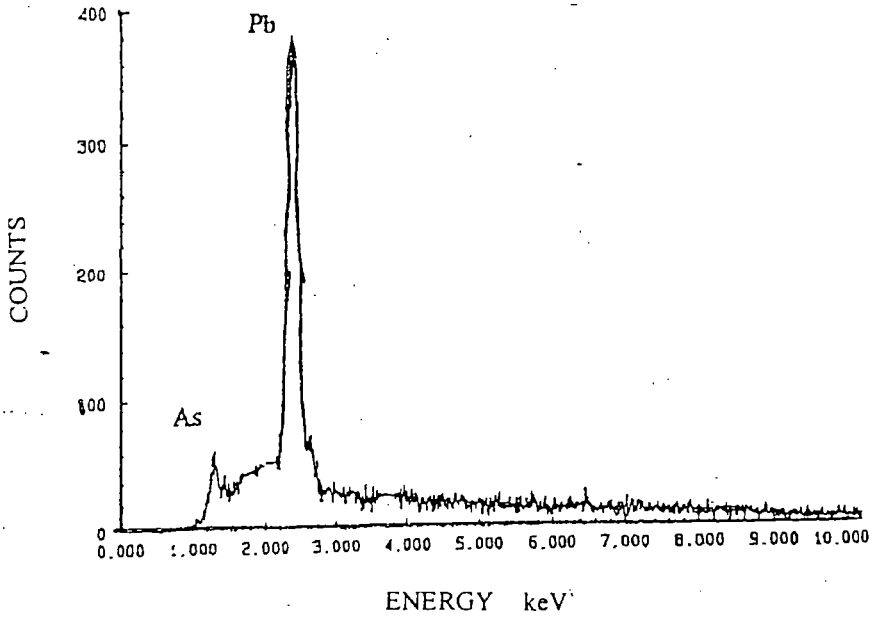
Figure 11-4. Example Photomicrograph



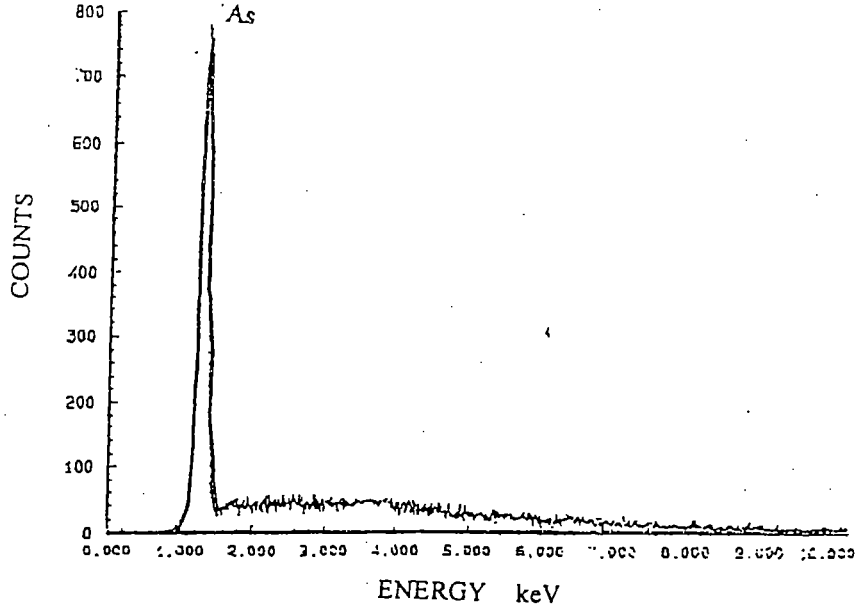
Attachment A

Example Spectra

Example Spectrum: Lead Arsenic Oxide



Example Spectrum: Arsenic Trioxide



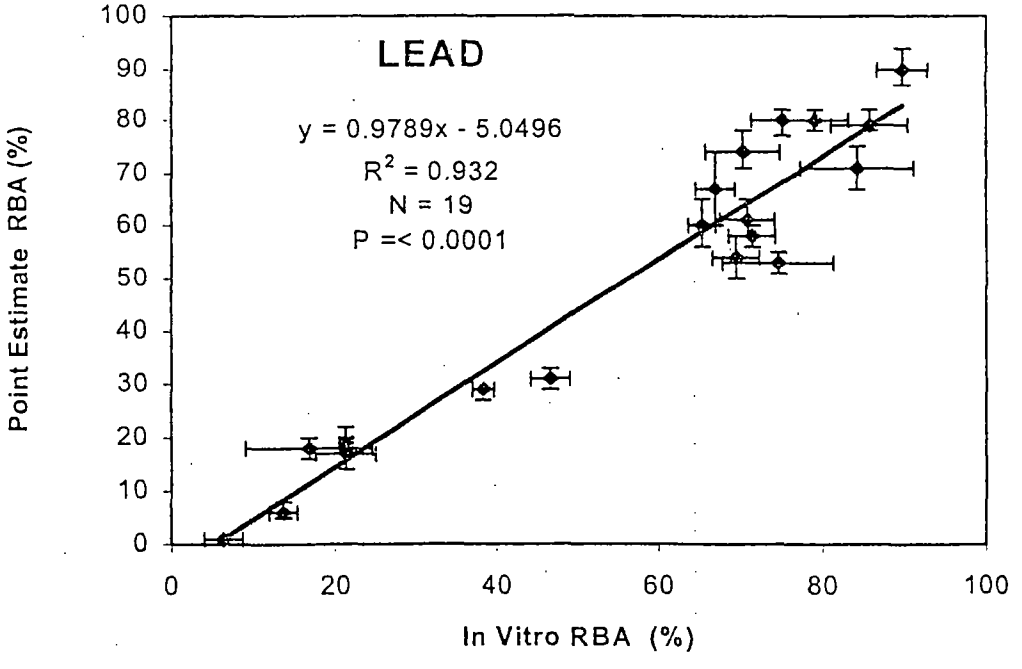
University of Colorado
Relative Bioavailability Leaching Procedure (RBLP)

Standard Operating Procedure

1.0 Purpose

An increasingly important property of contaminated media found at environmental sites is the bioavailabilty of individual contaminants. Bioavailability is the fraction of a contaminant that is absorbed by an organism via a specific exposure route. Many animal studies have been conducted to experimentally determine oral bioavailability of individual metals, particularly lead and arsenic. During the period 1989-97, a juvenile swine model developed by USEPA Region VIII was used to predict the relative bioavailability of lead and arsenic in approximately 20 substrates (Weis and LaVelle 1991; Weis et al. 1994). The bioavailability determined was relative to that of a soluble salt (i.e. lead acetate trihydrate or sodium arsenate). The tested media had a wide range of mineralogy, and produced a range of lead and arsenic bioavailabilty values. In addition to the swine studies, other animal models (e.g. rats and monkeys) have been used for measuring the bioavailabilty of lead and arsenic from soils.

Several researchers have developed in vitro tests to measure the fraction of a chemical solubilized from a soil sample under simulated gastrointestinal conditions. The in vitro tests consist of an aqueous fluid, into which the contaminant is introduced. The solution than solubilizes the media under simulated gastric conditions. Once this procedure is complete, the solution is analyzed for lead and/or arsenic concentrations. The mass of the lead and/or arsenic found in the filtered extract is compared to the mass introduced into the test. The fraction liberated into the aqueous phase is defined as the bioavailable fraction of lead or arsenic in that media. To date, for lead-bearing materials tested in the USEPA swine studies, this in vitro assay has correlated well ($R^2 = 0.93$, $p = .0001$) with relative bioavailability. Arsenic has yet to be fully validated but shows a promising correlation with in vivo results.



Standard Operating Procedure for the Determination of Lead Isotopes with the ICP-MS-LA.

After starting the plasma and letting the Varian Ultra-Mass 700 warm up for at least 1 hour the settings were adjusted to maximize the detection of lead and thallium. These setting were then saved as part of the method file and have been used for all subsequent analyses. The Cetac LSX-200 laser ablation unit (Figure 1) is plumbed in series with the argon gas line that feeds the K-Type nebulizer. During operation a 100 ppb solution of thallium in a 1% nitric acid solution is nebulized as an internal standard. About once per week the Varian Ultra-Mass 700 is mass calibrated. During the calibration the kilocounts for beryllium, cobalt and lead are recorded. When the kilocounts for beryllium drop below ~20, the cones, torch and nebulizer are cleaned and the peristaltic pump tubing replaced.

Samples are first prepared for EMPA in order to identify and locate lead-bearing particles of interest. A series of Backscatter electron images (BEI) are collected to aid in locating the particles once placed in the laser. Since the laser is limited to 400X magnification the BEI's are essential. In general, it has been found that locating individual lead-bearing particles less than 80 microns is very difficult.

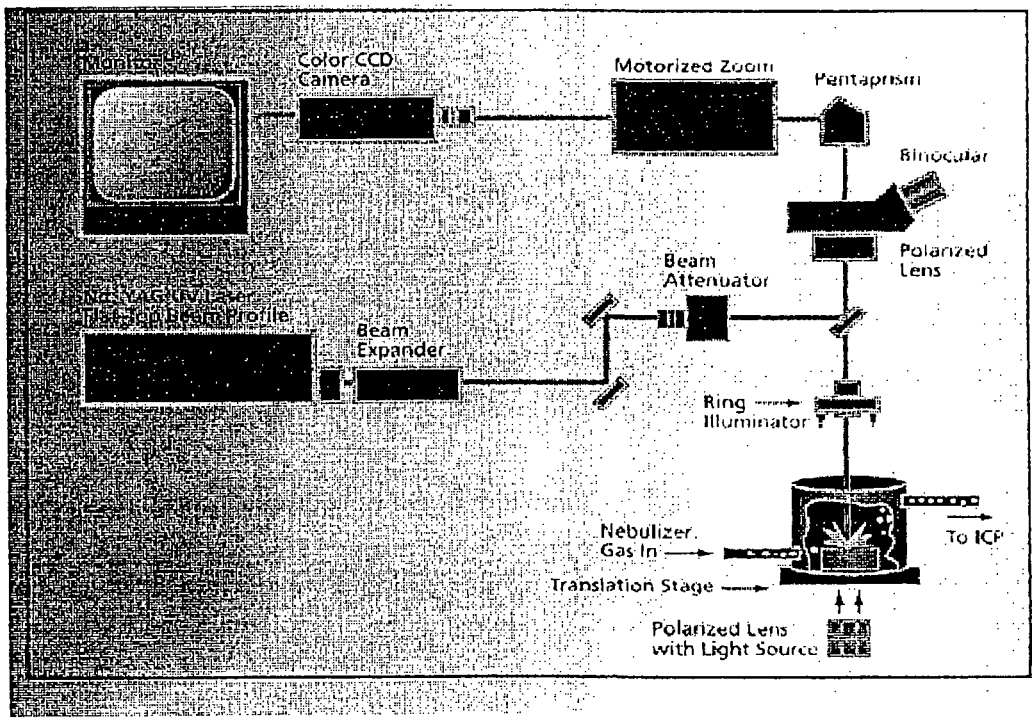
A sample, which contains lead bearing particles, is then loaded into the laser ablation chamber along with the NIST lead standard (SRM 982). The laser ablation chamber is then purged with argon and then placed in line with the argon gas feed to the nebulizer on the ICP-MS. One or two blanks (the laser is off) are run to ascertain that the thallium internal standard is nebulizing properly and that there is no or a very low lead background signal. After the blanks are run the NIST lead standard is run three times. Most of the particles were abladed using the scanning mode. Less frequently, a segmented line mode was used on rinds or long, narrow particles. The laser was set at 35% power, 5 pulses per second, and a 50-micron spot size. These settings were maintained for all samples and standards, expect on a very few samples where the laser power may have been as high as 60% because the particle being analyzed contained low lead concentrations.

The analysis would begin with activating the laser and letting it run for about 30 seconds to allow the argon gas to travel to the nebulizer and for the flow to stabilize. Then the ICP-MS is activated and the kilocounts for Hg^{202}, Tl^{203}, Tl^{205}, Pb^{204}, Pb^{206}, Pb^{207} and Pb^{208} are measured. In the Varian WinMass software, which is used to control the ICP-MS, the Scan Mode is set to peak hopping, the Spacing is set to 0.025 AMU (Fine), the Acquisition Mode is set to Steady State, and the Acquisition parameters are set to 1 point per peak, 40 scans per replicate and 10 replicates per sample. The dwell times are set to 10000 micro seconds for Hg^{202}, 5000 micro seconds for Tl^{203}, Tl^{205}, Pb^{206}, Pb^{207}, and Pb^{208} and 50000 micro seconds for Pb^{204}. The plasma flow settings are 15 liters per minute, 1.05 liters per minute for the auxiliary flow, 1.1 liters per minute for the nebulizer flow (this is the same as the flow through the laser ablation chamber), 7.0 mm

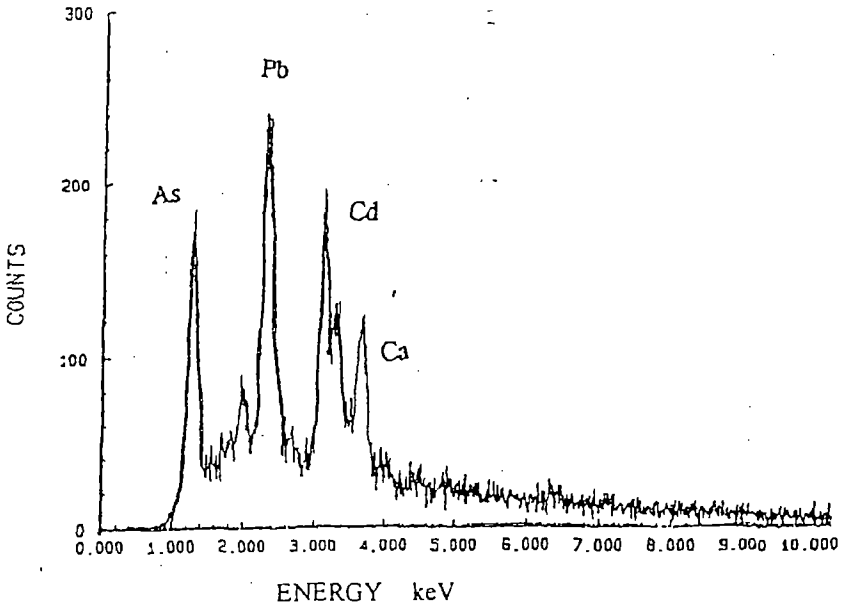
for the sampling depth, 1.2 kilowatts for the RF power, and 5 rpm for the peristaltic pump.

After running about 10 particles the NIST lead standard is re-analyzed 3 times. When all of the particles on a sample are measured the NIST standard is re-analyzed 3 times again just before changing the sample. The results are then exported to an Excel spreadsheet. In the spreadsheet the results are drift corrected and the Tl^{203} and Tl^{205} results are use to correct for isotope drift (Walder and Furuta, 1993). Because many of the particles that are being analyzed are either very small or are not homogeneous the data that is significantly different is excluded from the final ratio and element percentages results.

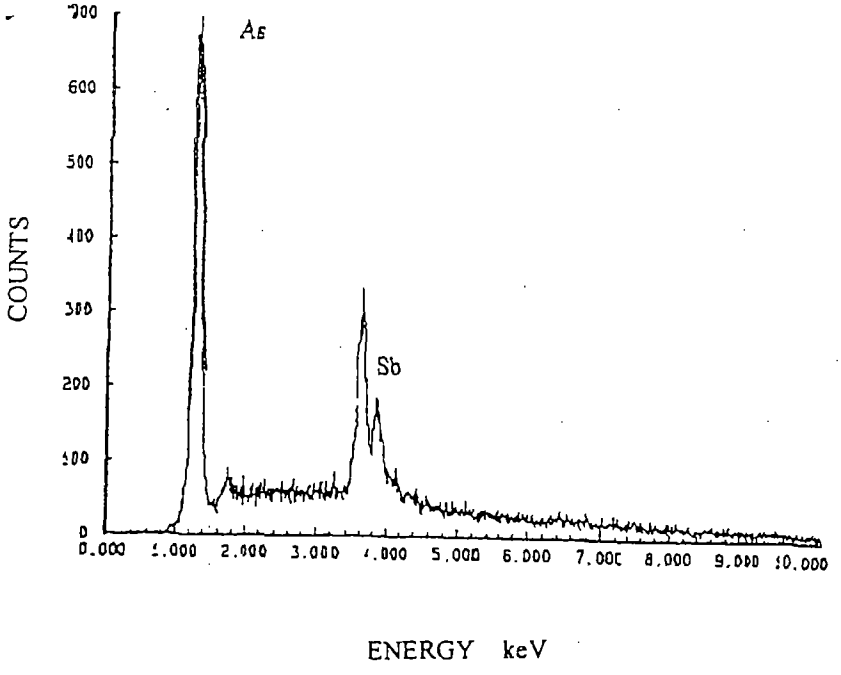
Figure 1. Schematic of laser ablation system.

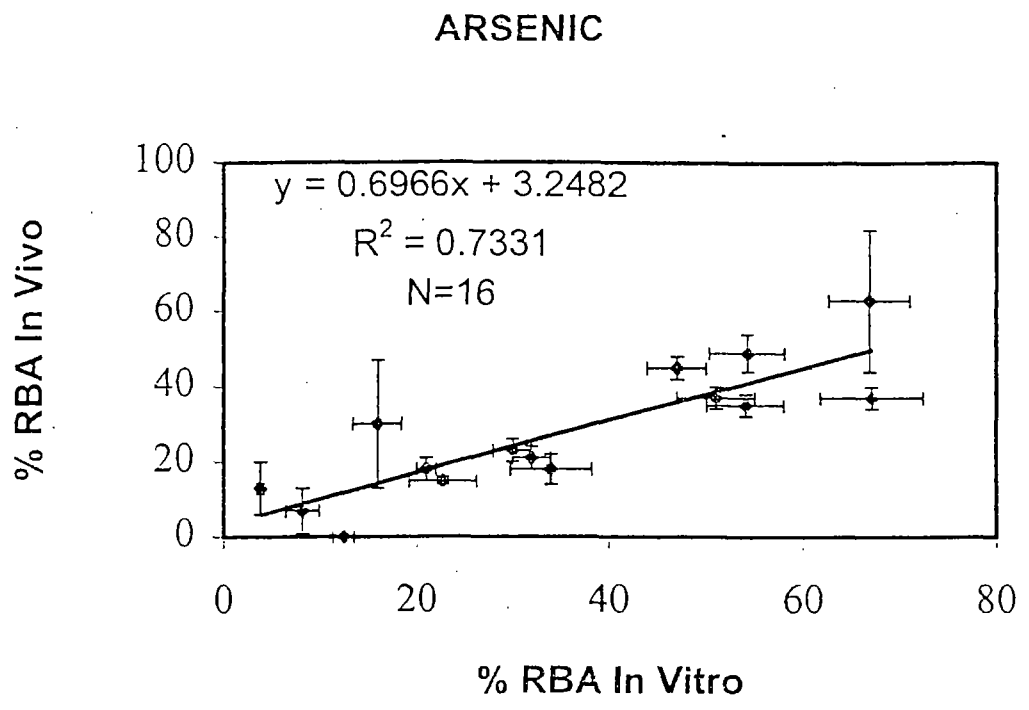


Example Spectrum: Lead/Arsenic Metal Oxide



Example Spectrum: Arsenic Antimony Oxide





It has been postulated that a simplified in vitro method could be used to determine bioavailability of lead and arsenic. The method described in this SOP represents a simplified in vitro method, which is currently being subjected to a formal validation.

2.0 Scope

This procedure has been developed to test contaminated media in animal studies, to determine the correlation between in vitro and in vivo. Only samples from which mineralogy has been fully characterized by EMPA techniques and for which bioavailability results from acceptable animal studies are available have been used for this study. A total of 20 substrates have been tested in validating the relative bioavailability leaching procedure (RBLP).

3.0 Relevant Literature

Background on the development and validation of in vitro test systems for estimating lead and arsenic bioaccessibility can be found in; Ruby et al. (1993, 1996); Medlin (1972); Medlin and Drexler, 1997; Drexler, 1998; and Drexler et al., 2001.

Background information for the USEPA swine studies may be found in (Weis and LaVelle, 1991; Weis et al. 1994; and Casteel et al., 1997) and in the USEPA Region VIII Center in Denver, Colorado.

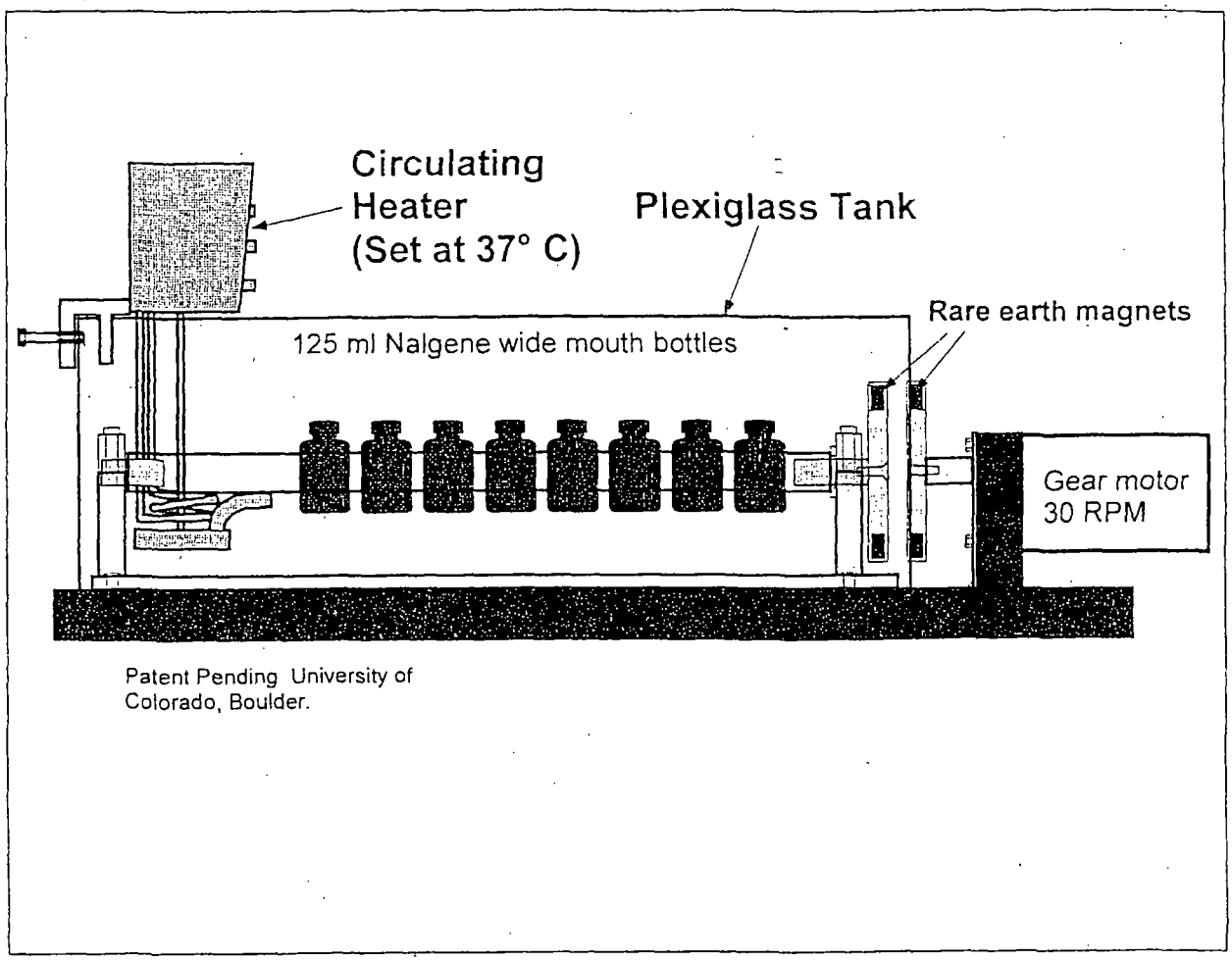
4.0 Sample Preparation

All media are prepared for the in vitro assay by first drying (<40 °C) all samples and then sieving to < 250 m. The <250 micron size fraction was used because this is the particle size is representative of that which adheres to children's hands. Samples were thoroughly mixed prior to use to ensure homogenization. Samples are archived after the study completion and retained for further analysis for a period of six months unless otherwise requested. Prior to obtaining a subsample for testing in this procedure, each sample must be homogenized in its sample container by end-over-end mixing.

5.0 Apparatus and Materials

5.1 Equipment

The main piece of equipment required for this procedure is the extraction device illustrated in Figure 1. The device can be purchased from the Department of Geological Sciences, University of Colorado. For further information contact Dr. John W. Drexler, at (303) 492-5251 or drexlerj@spot.colorado.edu. The device holds ten 125 ml, wide-mouth high-density polyethylene (HDPE) bottles. These are rotated within a Plexiglas tank by a TCLP extractor motor with a modified flywheel. The water bath must be filled such that the extraction bottles remained immersed. Temperature in the water bath is maintained at 37 +/- 2 °C using an immersion circulator heater (Fisher Scientific Model 730).



The 125-ml HDPE bottles must have an airtight screw-cap seal (Fisher Scientific #02-893-5C), and care must be taken to ensure that the bottles do not leak during the extraction procedure.

5.2 Standards and Reagents

The leaching procedure for this method uses an aqueous extraction fluid at a pH value of 1.5. The pH 1.5 fluid is prepared as follows:

Prepare 2 L of aqueous extraction fluid using ASTM Type II demonized (DI) water. The buffer is made up in the following manner. To 1.9 L of DI water, add 60.06 g glycine (free base, reagent grade), and bring the solution

volume to 2 L (0.4M glycine). Place the mixture in the water bath at 37 °C until the extraction fluid reaches 37 °C. Standardize the pH meter (one should use both a 2.0 and a 4.0 pH buffer for standardization) using temperature compensation at 37 °C or buffers maintained at 37 °C in the water bath. Add trace metal grade, concentrated hydrochloric acid (12.1N) until the solution pH reaches a value of 1.50 +/_ 0.05 (approximately 60 mL).

All reagents must be free of lead and arsenic, and the final fluid must be tested to confirm that lead and arsenic concentrations are less than one-fourth the project required detection limits (PRDLs) of 100 and 20 µg/L, respectively (e.g., less than 25 µg/L lead and 5µg/L arsenic in the final fluid.

Cleanliness of all materials used to prepare and/or store the extraction fluid and buffer is essential. All glassware and equipment used to prepare standards and reagents must be properly cleaned, acid washed, and finally, triple-rinsed with demonized water prior to use.

6.0 Leaching Procedure

Measure 100 +/- 0.5 mL of the extraction fluid, using a graduated cylinder, and transfer to a 125 mL wide-mouth HPDE bottle. Add 1.00 +/- 0.5 g of test substrate (<250 m) to the bottle, ensuring that static electricity does not cause soil particles to adhere to the lip or outside threads of the bottle. If necessary, use an antistatic brush to eliminate static electricity prior to adding the media. Record the mass of substrate added to the bottle. Hand-tighten each bottle top and shake/invert to ensure that no leakage occurs, and that no media is caked on the bottom of the bottle.

Place the bottle into the modified TCLP extractor, making sure each bottle is secure and the lid(s) are tightly fastened. Fill the extractor with 125 mL bottles containing test materials or QA samples.

The temperature of the water bath must be 37 +/- 2 °C.

Turn on the extractor and rotate end-over-end at 30 +/- 2 rpm for 1 hour. Record the start time of rotation.

When extraction (rotation) is complete, immediately stop the extractor rotation and remove the bottles. Wipe them dry and place upright on the bench top.

Draw extract directly from the reaction vessel into a disposable 20 cc syringe with a Luer-Lok attachment. Attach a 0.45 µm cellulose acetate disk filter (25 mm diameter) to the syringe, and filter the extract into a clean 15 mL polypropylene centrifuge tube (labeled with sample ID) or other appropriate sample vial for analysis.

Record the time that the extract is filtered (i.e. extraction is stopped). If the total time elapsed is greater than 1 hour 30 minutes, the test must be repeated.

Measure the pH of the remaining fluid in the extraction bottle. If the fluid pH is not within +/_ 0.5 pH units of the starting pH, the test must be discarded and the sample reanalyzed as follows:

If the pH has changed more than 0.5 units, the test will be re-run in an identical fashion. If the second test also results in a decrease in pH of greater than 0.5 s.u. this will be recorded, and the extract filtered for analysis. If the pH has increased by 0.5 s.u. or more, the test must be repeated, but the extractor must be stopped at specific intervals and the pH manually adjusted down to pH of 1.5 with dropwise addition of HCl (adjustments at 5, 10, 15, and 30 minutes into the extraction, and upon final removal from the water bath { *60 min*}). Samples with rising pH values might better be run following the method of Drexler and Medlin, 1999.

Store filtered samples in a refrigerator at 4 °C until the are analyzed. Analysis for lead and arsenic concentrations must occur within 1 week of extraction for each sample.

Extracts are to be analyzed for lead and arsenic, as specified in SOP #2, following EPA methods 6010B, 6020, or 7061A.

6.1 Quality Control/Quality Assurance

Quality Assurance for the extraction procedure will consist of the following quality control samples.

Reagent Blank-extraction fluid analyzed once per batch.

Bottle Blank-extraction fluid only run through the complete procedure at a frequency of 1 in 20 samples.

Duplicate sample-duplicate sample extractions to be performed on 1 in 10 samples.

Matrix Spike-a subsample of each material used will be spiked at concentrations of 10 mg/L lead and 1 mg/L arsenic and run through the extraction procedure (frequency of 1 in 10 samples).

National Institute of Standards and Testing (NIST) Standard Reference Material (SRM) 2711 will be used as a control soil. The SRM will be analyzed at a frequency of 1 in 25 samples.

Control limits and corrective actions are listed in Table 1.

	Analysis Frequency	Control Limits
Reagent Blank	once per batch	< 25 μg/L lead
Bottle blank	5%	<50 μg/L lead
Blank spike*	5%	85-115% recovery
Matrix spike*	10%	75-125% recovery
Duplicate sample	10%	+/- 20% RPD**
Control soil***	5%	+/- 10% RPD

* Spikes contained 10 mg/L lead. ** RPD= relative percent difference. *** The National Institute of Standards and Technology (NIST) Standard Reference Material (SRM)

7.0 Chain-of-Custody Procedures

All media once received by the Laboratory must be maintained under standard chain-of-custody.

8.0 Data Handling and Verification

All sample and fluid preparation calculations and operations must be recorded on data sheets, Figure 3. Finally all key data will be entered into the attached EXCEL spreadsheet for final delivery and calculation of Bioavailability.

9.0 References

Casteel, S.W., R.P. Cowart, C.P. Weis, G.M.,Henningsen, E.Hoffman and J.W. Drexler, 1997. Bioavailability of lead in soil from the Smuggler Mountain site of Aspen Colorado. Fund. Appl. Toxicol. 36: 177-187.

Drexler, J.W., 1998. An in vitro method that works! A simple, rapid and accurate method for determination of lead bioavailability. EPA Workshop, Durham, NC..

Drexler, J.W., Weis, C,P., W. Brattin, G.M. Henningsen, and M.Goldade. 2001. Lead Bioavailability: A Validated in vitro method. Fund. Appl. Toxicol.
(In Press).

Medlin, E., and Drexler, J.W., 1995. Development of an in vitro technique for the determination of bioavalability from metal-bearing solids., International Conference on the Biogeochemistry of Trace Elements, Paris, France.

Medlin, E.A., 1997, An In Vitro method for estimating the relative bioavailability of lead in humans. Masters thesis. Department of Geological Sciences, University of Colorado, Boulder.

Ruby, M.W., A. Davis, T.E. Link, R. Schoof, R.L. Chaney, G.B. Freeman, and P. Bergstrom. 1993. Development of an in vitro screening test to evaluate the in vivo bioaccessability of ingested mine-waste lead. Environ. Sci. Technol. 27(13): 2870-2877.

Ruby, M.W., A. Davis, R. Schoof, S. Eberle. And C.M. Sellstone. 1996 Estimation of lead and arsenic bioavailbilty using a physiologically based extraction test. Environ. Sci. Technol. 30(2): 422-430.

Weis, C.P., and J.M. LaVelle. 1991. Characteristics to consider when choosing an animal model for the study of lead bioavailability. In: Proceedings of the International Symposium on the Bioavailability and Dietary Uptake of Lead. Sci. Technol. Let. 3:113-119.

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Chain of Custody Record

PDP Analytical Services
1680 Lake Front Circle, Suite B ▪ The Woodlands, Texas 77380 ▪ Phone (281) 363-2233 ▪ Fax (281) 298-5784

CM115-

Client Name / Address: Jacobs Federal Operations

Send Report to:

Project Number:

Project Name: Omaha Lead SI

Samplers (Signature):

P.O. Number

Sta. No.	Date	Time	Comp.	Grab	Station Location	Number of Containers	Matrix	Lead Spectrometry						Remarks
OM-8	4/20/00	1550		X	AZASGPZZ 12557	1	Soil	X						Dead Man Trench (3 ft)
	4/20/00	1607			AZASGPZZ 12558									Chicago Street Pump Station (3.5 ft)
	4/20/00	1615			AZCESGPZZ 12559									Pump Station Near South Bay House (3 ft)
	4/20/00	1621			AZBSGPZZ 12560									Douglas St. Pump Station (2.5 ft)
	4/20/00	1640			AZASGPZZ 12561									Floodgate near Chicago St. Pump Station (3 ft)
	4/20/00													

4-21-00

Relinquished by (Signature)	Date / Time	Received by (Signature)	Date / Time
	04/21/00 11:00		
Laura A Roland	10/29/00 12:00	William T. Dudley	06/29/00 12:00
William T Dudley	10/20/00 09:40	Don Bahnke	10/20/00 19:40

Remarks:

Method of Shipment:

PDP Quote Number:

Distribution: Original accompanies shipment; Copy to coordinator and field files

Om 112

Chain of Custody Record

PDP Analytical Services
1680 Lake Front Circle, Suite B ▪ The Woodlands, Texas 77380 ▪ Phone (281) 363-2233 ▪ Fax (281) 298-5784

Client Name / Address: Jacobs Federal Operations (Sverdrup Env)

Send Report to:

Project Number:

Project Name

Samplers (Signature): Jeff Higgs, Todd Tomster

P.O. Number

Lab ~~Sta. No.~~	Date	Time	Comp.	Grab	Station Location	Number of Containers	Matrix	Lead Applicable						Remarks
	4/20/00	1742		X	AZZSGPZA12562	1	Soil	X						TH-10 0-2'
Om-9		1557			AZZSGPZA12563									MW-9D 0-2'
Om-13		1744			AZZSGPZA12564									TH-5 0-2'
Om-1		1745			AZZSGPZA12565									TH-23 0-2'
Om-2		1414			AZZSGPZA12566									MW-16 0-2'
		1545			AZZSGPZA12567									MW-17 0-2'
Om-3		1757			AZZSGPZA12568									TH-26 0-2'
Om-7		1759			AZZSGPZA12569									TH-22 0-2'
		1554			AZZSGPZA12570									MW-19 0-2'
Om-19		1811			AZZSGPZA12571									MW-200G 0-2'
		1801			AZZSGPZA12572									TH-33 0-2'
Om-18		1802			AZZSGPZA12573									TH-13 0-2'
Om-17		1803			AZZSGPZA12574									TH-9 0-2'
Om-22		1804			AZZSGPZA12575									TH-1 0-2'
Om-21		1805			AZZSGPZA12576									TH-21 0-2'

Relinquished by (Signature)	Date / Time	Received by (Signature)	Date / Time
[signature]	04/21/00 11:00		
Relinquished by (Signature)	Date / Time	Received by (Signature)	Date / Time
Laura C Roland	6/29/00 12:00	William T. Dudley	06/29/00 12:00
Relinquished by (Signature)	Date / Time	Received for Laboratory by (Signature)	Date / Time
William T Dudley	10/20/00 0940	Don Barker	10/20/00 9:40

Remarks:

Method of Shipment:

PDP Quote Number

Distribution: Original accompanies shipment; Copy to coordinator and field files

Chain of Custody Record

PDP Analytical Services
1680 Lake Front Circle, Suite B ▪ The Woodlands, Texas 77380 ▪ Phone (281) 363-2233 ▪ Fax (281) 298-5784

Client Name / Address: Jacobs Federal Operations

Send Report to:

Project Number:

Project Name

Samplers (Signature)

P.O. Number

Sta No.	Date	Time	Comp.	Grab	Station Location	Number of Containers	Matrix	Field appearance							Remarks
C.M-24	4/19/00	1120		X	AZDSGPZZ12541	1	Soil	X							BH-1 (3 to 4 ft)
C.M-25	4/19/00	1152			AZCNSGPZZ12542										BH-2 (3 to 4 ft)
C.M-23	4/19/00	1359			AZCSSGPZZ12543										BH-3 (5 to 6.5 ft)
C.M-20	4/19/00	1450			AZCSGPZZ12544										BH-4 (5 to 5.5 ft)
	4/20/00	0835			AZCWSGPZZ12546										BH-7 (5.5 to 6 ft)
C.M-15	4/20/00	0946			AZDSGPZZ12547										BH-9 (3 to 3.5 ft)
C.M-14	4/20/00	1020			AZCESGPZZ12548										BH-10 (3 to 3.5 ft)
	4/20/00	1052			AZCESGPZZ12549										BH-11 (3.5 to 4 ft)
C.M-11	4/20/00	1115			AZCESGPZZ12550										BH-12 (3.5 to 4 ft)
C.M-10	4/20/00	1253			AZCESGPZZ12551										BH-13 (2.5 to 3 ft)
C.M-6	4/20/00	1315			AZCESGPZZ12552										BH-14 (2.75 to 3 ft)
C.M-4	4/20/00	1418			AZASGPZZ12553										BH-15 (3 to 3.5 ft)
C.M-5	4/20/00	1430			ASASGPZZ12554										BH-16 (3 to 3.5 ft) ~~(4 to 4.5 ft)~~ +T
	4/20/00	1503			AZDSGPZZ12555										BH-17 (4 to 4.5 ft)
	4/20/00	1545			AZCESGPZZ12556										Dark Man Trench (3 ft)

Relinquished by (Signature)	Date / Time	Received by (Signature)	Date / Time
[signature]	04/20/00 11:00		
Laura A. Roland	6/29/00 12:00	William T. Dudley	06/29/00 12:00
William Dudley	10/20/00 0940	Received for Laboratory by (Signature): Don Bahner	10/20/00 9:40

Remarks:

Method of Shipment:

PDP Quote Number

Distribution: Original accompanies shipment; Copy to coordinator and field files

Chain of Custody Record

PDP Analytical Services
1680 Lake Front Circle, Suite B ▪ The Woodlands, Texas 77380 ▪ Phone (281) 363-2233 ▪ Fax (281) 298-5784

Client Name / Address: Jacobs Federal Operations (Sunshine Park)

Send Report to:

Project Number:

Project Name

Samplers (Signature): Jeff Hogan, Todd Tramelor

P.O. Number

Sta. No.	Date	Time	Comp.	Grab	Station Location	Number of Containers	Matrix	Lead approximate						Remarks
	4/20/00	1807		X	AZZSGPZA12578	1	Soil	X						TH-16 0-2'
		1604			AZZSGPZA 12579									TH-7 0-2'
		1620			AZZSGPZA 12580									TH-8 0-2'
CM-16		1631			AZZSGPZA 12581									TH-18 0-2'
CM-12		1814			AZZSGPZA 12582									TH-34 0-2'
		1627			AZZSGPZA 12577									TH-3 0-2'

4/21/00

Relinquished by (Signature)	Date / Time	Received by (Signature)	Date / Time	Remarks
Todd Tramelor	04/21/00 11:00			
Relinquished by (Signature): Laura A Roland	Date / Time: 6/29/00 12:00	Received by (Signature): William T Dudley	Date / Time: 06/27/00 12:00	
Relinquished by (Signature): William T Dudley	Date / Time: 10/20/00 0940	Received for Laboratory by (Signature): Don Barker	Date / Time: 10/20/00 0940	

Method of Shipment:

PDP Quote Number:

Distribution: Original accompanies shipment; Copy to coordinator and field files

BLACK & VEATCH
SPECIAL PROJECTS CORP.

CHAIN OF CUSTODY RECORD

PROJ. NO.: 41904781
PROJECT NAME: Omaha Lead
SAMPLERS: (Signature) [illegible]

STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS							REMARKS XRF Result (ppm)
	11/7/01	1010			HPA-1	2							2390 ± 110
		1030			HPA-2								2590 ± 120
		1110			HPA-3								420 ± 84
		1110			HPA-3/10-15'								149 ± 51
		1230			HPA-4/7-10'								1590 ± 86
		1318			HPA-5-/10-12'								6170 ± 280
		1500			HPA-7/9-11'								843 ± 61
		1500			HPA-7/5-8'								1280 ± 89

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Relinquished by: (Signature)	**Date/Time**	**Received by: (Signature)**	**Relinquished by: (Signature)**	**Date/Time**	**Received by: (Signature)**
Relinquished by: (Signature)	**Date/Time**	**Received for Laboratory by: (Signature)**	**Date/Time**	**Remarks**	

Distribution: White and Yellow Accompanies Shipment; Pink copy to Field Files

CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME
46904.783	Omaha Lead Site Investigation

SAMPLERS: (Signature) Sverdrup / Jacobs Engineering

STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS	Lead Apportionment Study						REMARKS
277	5/13/99	11:11	X		1627 1722 South 8th	1	X						
741	5/12/99	16:52	X		1504 2620 Grant	1	X						
845	1/19/00	15:09	X		11509 2861 Browne St	1	X						
1448	12/1/99	14:38	X		10437 5384 N. 27th Ave	1	X						
1594	5/14/99	14:48	X		1683 8195. 38th Ave	1	X						

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
William Dudley	04/02/01 15:00				
Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Relinquished by: (Signature)	Date/Time	Received for Laboratory by: (Signature)	Date/Time	Remarks	

Distribution: White and Yellow Accompanies Shipment; Pink copy to Field Files

BLACK & VEATCH
SPECIAL PROJECTS CORP.

CHAIN OF CUSTODY RECORD

PROJ. NO.: 411901.783
PROJECT NAME: Omaha Lead Site
SAMPLERS: (Signature)

STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS	REMARKS
	10/4/01	1605	✓		SD80-B	1	
		1610			SD87-G		
		1700			SD88-FD		
	10/5/01	1315			SD58-FD		
	10/6/01	1700			SD17-F1		
	10/5/01	1245			SD61-FD		
	10/6/01	1630			SD44-B1		
	10/5/01	1400			SD55-F1		
	10/7/01	1414			SD34-B1		
		1735	✓		SD03-FD		

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
	10/8/01 1645	FedEX 838934054313			
Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Relinquished by: (Signature)	Date/Time	Received for Laboratory by: (Signature)	Date/Time	Remarks	

Distribution: White and Yellow Accompanies Shipment; Pink copy to Field Files

BLACK & VEATCH
SPECIAL PROJECTS CORP.

CHAIN OF CUSTODY RECORD

PROJ. NO.: 41.9C1.7A1
PROJECT NAME: Omaha Lead
SAMPLERS: (Signature) [illegible]

STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS							REMARKS
	5/23/91	0915	X		SD48-B0	1							
		1100			SD79-B0								
		1335			SD80-B0								
		1410			SD81-B0								
		1515			SD80-B1								
		1100			SD83-B1								
		1100			SD83-D2								
	5/24/91	1501			SD41-B1								
		1501			SD41-D2								

Relinquished by: (Signature)	Date/Time	Received by (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
[illegible]	5/31/91 1500				
Relinquished by: (Signature) Fed Ex Air-bill # 8[illegible]1234546[illegible]	Date/Time	Received by. (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Relinquished by: (Signature)	Date/Time	Received for Laboratory by (Signature)	Date/Time	Remarks	

Distribution: White and Yellow Accompanies Shipment, Pink copy to Field Files

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SPECIAL PROJECTS CORP.

CHAIN OF CUSTODY RECORD

PROJ. NO.	PROJECT NAME
	Omaha Lead Site

SAMPLERS: (Signature)

STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS	REMARKS
	6/21/01				SD20B2	1	
					SD56F2		
					SD59B1		
					SD57F2		
					SD08B1		
					SD00B2		
					SD41B1		
					SD98B2		
					SD30B1		
					SD41B1		
					SD98B2		
					SD30B1		

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
	6/21/01 1445	Fed Ex 808 934 54335			
Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Relinquished by: (Signature)	Date/Time	Received for Laboratory by: (Signature)	Date/Time	Remarks	

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John William Drexler
Director of Analytical Facilities
Associate Professor
Department of Geological Sciences
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University of Colorado
Boulder, Colorado 80309
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Born: November 13, 1954

Nationality: U.S.A.

Education:

B.S., Western Illinois University, 1976 (Geology-Chemistry)
M.S., Michigan Technological University, 1978 (Geology)
Ph.D.,Michigan Technological University, 1982 (Geology)

Environmental Protection Agency's Technical Advisory Committee for the Leadville, Colorado CERCLA site. 1990-1993.

Environmental Protection Agency's Advisor to the Technical Advisory Committee for the Aspen, Colorado CERCLA site. 1992.

Invited speaker:
U.S. EPA Mine, Milling, and Smelter Waste Seminar, August, 1994.

U.S. EPA Lead Risk Assessment and Remediation Large Area Lead Sites Workgroup, April, 1995.

US EPA Workshop on Modeling Lead Exposure and Bioavailability, August, 1998.

NEPI 'Protecting Children's Health: Assessing the Relationship of Soil Lead to Blood Lead' Washington, DC.) October 27-28, 1998.

ITRC Conference 'New Environmental Technologies and Market Opportunities' San Antonio, TX. October, 19, 2000

USEPA Workshop Metals Assessment Issue Papers Washington, D.C., December 16-17, 2002.

USEPA Workshop Bioavailability estimations by in vitro techniques Tampa, Fl., April 14-17, 2003.

Professional Experience:

Since 1989 I have been working extensively with the EPA on Superfund remediation of heavy metal mining, smelting, and milling sites including: Leadville, CO., Aspen, CO. Midvalle, Utah., Sandy City, Utah, Anaconda and Butte, Montana, Omaha, Nebraska, El Paso, Texas, and Kennecott Utah.

1982 to present faculty member in the Department of Geology at University of Colorado. I supervise and maintain the departments analytical facilities, including a JEOL 8600 automated electron microprobe with four wavelength dispersive detectors and energy dispersive capabilities, two Kevex 0700 automated XES x-ray fluorescence system, a PHILIPS PW1730 WDS x-ray fluorescence system, a ISI SX30 SEM with a KEVEX energy dispersive analyzer and image analyzer, VARIAN Ultra Mass Inductive-coupled mass spectrometer with CETAC LSX-200 laser abaltion, a DIONEX 4500i ion chromatography system, a ARL 3410 Inductive-Coupled Plasma, a Hewlett-Packard 5890/5971 GC Mass Spectrometer, VARIAN Ultramass ICP/MS, Perkin Elemer Elan DRC-e ICP/MS and GIS workstation. The laboratories average operating budget is $150,000/yr with management responsibility of 2.4 FTE's.

Recent Publications:

1992
Weiss,C., Hemlin,C., and Drexler,J.W., Collection and characterization of mine waste and lead-based paint for the purpose of determining lead bioavailability, Society of Toxicology, Seattle, Wa.

1992
Hughes, J.M., Marianoo, A.N., and Drexler, J.W., Crystal structures of synthetic Na-REE-Si oxyapatites, synthetic monoclinic britholite. N. Jb. Miner. Mh, V 7, p. 311-319.

1992
Ruby, M.V., Davis, A.O., Kempton, J.H., Drexler, J.W., and Bergstrom, P.D., Lead bioavailability: Dissolution kinetics under simulated gastric conditions. Envir. Sci. Tech., V.26, p.1242-1248.

1993
Billing, P., Howe, B., Drexler, J.W., Olsen, R., and LaVelle, J.M., Bioavailability of mercury in cinnabar ore mine wastes. Society of Toxicology, Cincinnati, OH., March, 1993.

1993
Ruby, M.V., Davis, A. and Drexler, J.W., Induced Paragenesis

of Galena under Environmental Conditions. Environmental Science and Technology, V.27, (7), p.1415-1425.

1993
Davis, A., Drexler, J.W., Ruby, M.V., and Nicholson, A., Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. Environ. Sci. Technol., V. 27, p. 1415-1425.

1994
Broz, J.J., Simske, S.J., Greenberg, A.R., and Drexler, J.W., Determination of Compositional and Material Properties of Cortical Bone Constituent Phases.

1994
Drexler, J.W., Mushak, P., Health risks from extractive industry wastes: An approach to bioavailability of toxic metal and metalloidal contaminants. GSA Abstracts w/ Programs, Seattle, Wa.

1995
Medlin, E., and Drexler, J.W., Development of an IN VITRO technique for the determination of bioavailability from metal-bearing solids., International Conference on the Biogeochemistry of Trace Elements, Paris, France.

1995
Drexler, J.W., Mushak, P., Health risks from extractive industry wastes: Characterization of heavy metal contaminants and quantification of their bioavailability and bioaccessability., International Conference on the Biogeochemistry of Trace Elements, Paris, France.

1997
Casteel, S.W., Cowart, R.P., Weiss, C.P., Henningsen, G.M., Hoffman, E., Brattin, W.J., Guzman, R.E., Starost, M.F., Payne, J., Stockman, S.L., Becker, S.V., Drexler, J.W., and Turk, J.R., Bioavailability of Lead in Soil from the Smuggler Mountain Site of Aspen, Colorado. Fundam. Appl. Toxicol. V.36 (2) p. 177-187.

1997
Kendall, D.S., Mushak, P., and Drexler, J.W., Comment on Mass balance on surface-bound, mineralogic, and total lead concentrations as related to industrial aggregate bioaccessability, Envir. Sci. Toxicol. V. 31, (9), A393.

1997
Medlin, E.A, and Drexler, J.W., Calibration of an vitro Technique for estimating the bioavailability of lead in humans. , 15th Annual European Meeting of the Society of Environmental Geochemistry and Health: Mining and the Environment, Dublin,

Ireland (abstract).

1997
Jones, S.B., Drexler, J.W.,Selstone, C., and Hilts, S., Bench-scale study of phosphate as a potential remediation technique for lead contaminated soils. International Conference on the Biogeochemistry of the Trace Elements, Riverside, CA.

1997
Drexler, J.W., Validation of an In Vitro Method: A tandem Approach to Estimating the Bioavailability of Lead and Arsenic to Humans, IBC Conference on Bioavailability, Scottsdale, Az.

1998
Drexler, J.W., An In Vitro Method that works! A Simple, Rapid and Accurate Method for Determination of Lead Bioavailability. EPA Workshop, Durham, NC., August, 1998.

1998
Drexler, J.W., Evaluating Differences in Bioavailability of Lead in Soils. NEPI Conference, Washington, D.C.,

1998
Maddaloni, M., Lolacono, N.,Manton, W., and Drexler, J.W., Bioavailability of Soilborne Lead in Adults, by Stable Isotope Dilution. Environ. Health Persp. V.106, p.1589-1594.

2003
Drexler, J.W., and Bannon,D. The History, Development and Use of *In Vitro* Techniques for Assessing Lead Bioavailability: A Critical Review. SERDP/ESTCP, 10p.

2004
Brattin,W., Weis, C.,Casteel, S.W., Drexler, J.W., Henningsen, G.M., Estimation of Relative Bioavailability of Lead in Soil and Soil-Like Materials Using *In Vivo* and *In Vitro* Methods. USEPA Technical Document. OSWER 9285.7-77, Office of Solid Waste and Emergency Response, Washington, DC.

2007
Drexler,J. and Brattin,W., An *In Vitro* Procedure for Estimation of Lead Relative Bioavailability: With Validation. Environ. Health Persp.(April, 2007).

Selected Technical Reports for Private Companies:

1982 Silver and Gold concentration in mineral concentrate, U.S. Minerals.

1983 Pyrite concentrations in mineral processing samples, IntraSearch.

1984 Silicate contamination as a cause of hard-disk failure, Amcodyne.

1985 Zinc plating on mass spectrometer walls; a source of contamination, Masstron.

1985 Synthetic glass and its morphology, Tetra Tech Inc.

1985 Characterization of Indian Potery for correlation studies, Gilbert and Commonwealth.

1986 Platnoid mineralization potential of Kennet Mine, Montana, IntraSearch and Au-Ag Resources.

1987 Platnoid mineralization in placer sands, Dallas, Texas, SELCO.

1987 Evaluation of Equity Mine, Colorado for Crown Resourses.

1988 Lead contamination at rock wool plant, Water, Waste and Land Inc.

1988 Gold-silver mineralization from the Manhattan Mine, Echo Bay Minerals Company.

1989 Lead-Arsenic mineralogy from soil-rat studies by PTI Environmental Services.

1989 Lead contamination from Midvalle toxic waste site, Camp Dresser and McKee Inc.

1990 Lead contamination from Midvalle, Utah, Superfund Site, U.S. Environmental Protection Agency.

1990 Lead contamination at Bunker Hill, Idaho,Environmental Services, p. 1-82.

1990 Lead speciation in samples from Bunker Hill, Idaho, XXX Corporation.

1991 Lead speciation in paints, PTI Environmental Services.

1992 Heavy metal speciation in aggregate from vitrification process. Department of Justice

1991 Heavy metal spectioation in soils from residential sites at

Butte, Montana. PTI Environmental Services.

1992 Heavy metal contamination and bioavailability of mine waste from the Smuggler Mine, Aspen, CO. Camp Dresser and McKee and URS Consultants.

1993 Heavy metals (Cr, Pb, Zn)characterization in contaminated soils in and around an industrial plating factory. Camp Dresser and McKee.

1993 Arsenic and lead speciation at Midvale OU2 Superfund site, Midvale, Utah. SVERDRUP.

1993 Arsenic spectiation from smelter contaminated soils, Murray, Utah. Roy F. WESTON.

1994 Metal speciation for the California Gulch CERCLA site, Leadville, CO. Camp Dresser and McKee.

1995 Findings of Metal Speciation Investigation at the California Gulch NPL Site, USEPA-WESTON.

1996 Hazardous Wastes from metal refineries: The use of iron filings as a treatment, long-term effectiveness, environmental factors, and effects on TCLP. Environmental Protection Agency.

1996 Characterization of paint and ink wastes in soils, heavy metal (Cr, Pb) speciation. The Weinberg Group.

1997 Speciation of lead from paint, smelter and tailings sources in residential soils at Tar Creek, Ok. U.S. Bureau of Land Management.

1998 Arsenic and lead speciation of contaminated soils: their sources, smelter(s), paints, insecticides, or auto emissions? Colorado Department of Public Health.

2000 Arsenic and lead speciation of contaminated soils from the Vasquez Boulevard and I70 Site, Denver, Colorado: their source(s); smelter(s), paints, or insecticides? USEPA Region VIII.

2002 Source attribution of lead from contaminated residential soils in central Omaha, Nebraska. A speciation and LA/ICP/MS study. USEPA Region VII.

2002 The history, development and use of in vitro techniques for estimating lead biaavailability: A critical review. USAHPPM.

2003 Source attribution of lead from contaminated residential soils in El Paso, Texas. A speciation and LA/ICP/MS study. USEPA Region VII.