TA-16 Attachment A MDA-P

Los Alamos

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ENVIRONMENTAL PROTECTION GROUP (ESH-8)
WATER QUALITY AND HYDROLOGY SECTION
FAX TRANSMITTAL SHEET

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DATE: 8/3/94 LOG NO: WQ&H-FAX-94-

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TO: _____ FAX #: (___) _____ VERIFY PHONE # (___) _____

GRP/ORG: _____

TO: _____ FAX #: (___) _____ VERIFY PHONE # (___) _____

GRP/ORG: _____

MESSAGE: Attached is summary sheet which verifies the sampling of EPA-05A-056, at TA-16-260. If you have any questions or need more information please call me. Thanks,

NUMBER OF PAGES TO FOLLOW: 1

Cy: WQ&H Fax File
CRM-4, MS A150

SECTION LEADER

GROUP OR DEPUTY GROUP LEADER

January 6, 1994

5944

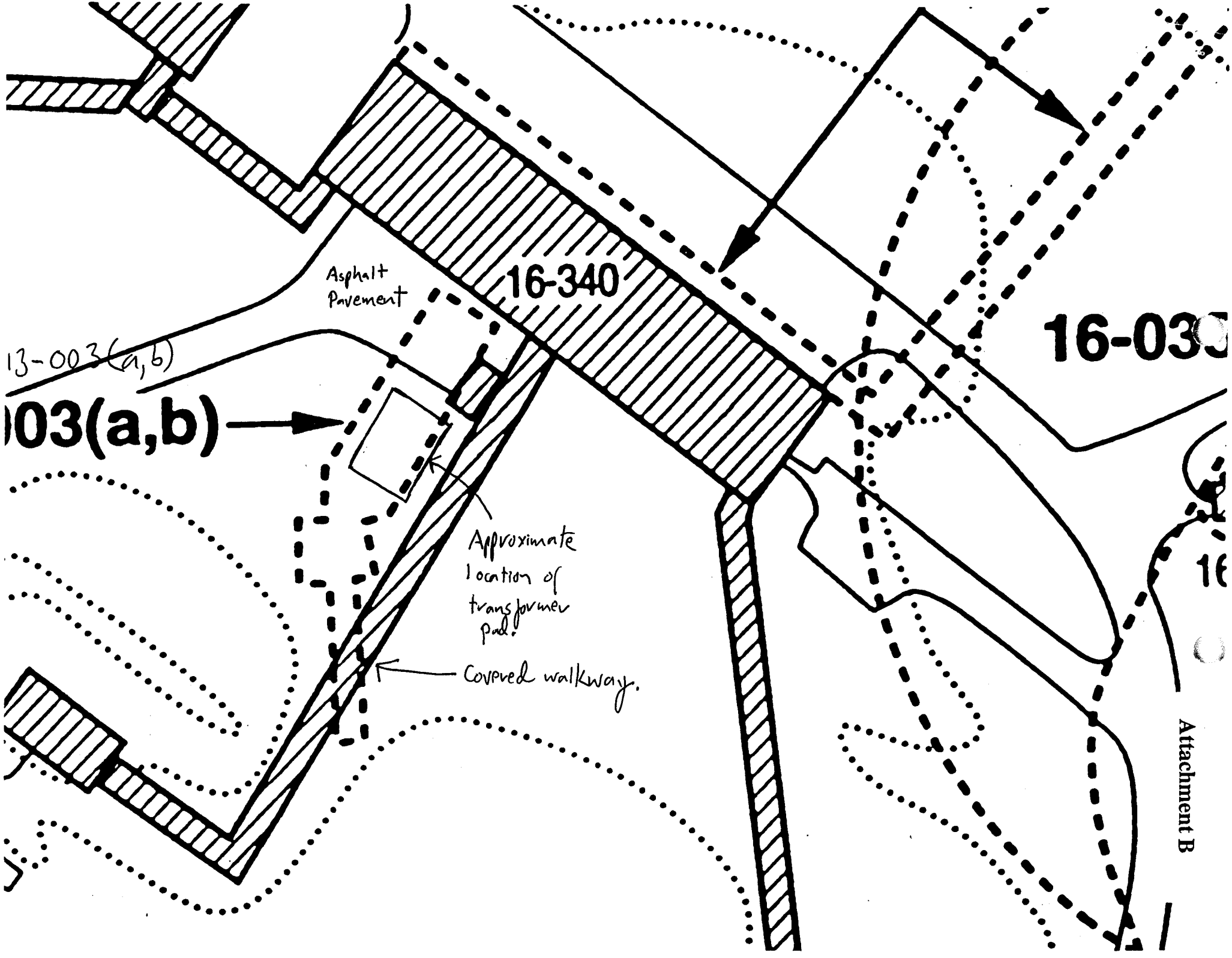
SPECIAL SAMPLING OF OUTFALL EPA-05A-056
TA-16-260 ON AUGUST 3, 1994

At 10:18 AM on August 3, 1994 outfall EPA-05A-056 was sampled per request of the Environmental Protection Agency. The outfall was sampled for the following parameters: COD, oil & grease, TSS, TNT, HMX, acetone, methyl ethyl ketone, n-butyl acetate and toluene. The analysis will be done by three laboratories due to the variety of parameters which are to be analyzed and to keep in compliance with the Laboratory's NPDES Permit. The following table summarizes where the samples were submitted for analysis.

CST-9, TA-59	M-1, TA-9	CST-9, TA-50
acetone, toluene, methyl ethyl ketone	TNT, RDX, HMX, n-butyl acetate	NPDES Parameters: COD, TSS, oil & grease

All samples were identified by the name **"EPA-05A-056"**. All laboratory correspondence and analytical results will be sent to Mike Saladen of ESH-8.

The samples were submitted under the program code provided by Brad Martin(CST-6) and Donald Hickmott(EES-1) in their memo to Mike Saladen dated July 28, 1994.



Attachment B

Attachment C

THE TOXICITY OF SPENT PHOTOGRAPHIC SOLUTIONS AND OTHER SILVER COMPOUNDS AND THEIR MIGRATION IN SOIL

by

Claudine Ann Kasunic

A Thesis Submitted to the Faculty of the

COMMITTEE ON TOXICOLOGY (GRADUATE)

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 8 2

APPENDIX C

SILVER CONTENT OF SAMPLES COLLECTED IN CAÑON DE VALLE AND CONTROL CANYON

All data represent one sample. Blanks indicate that sample material was not present at sample location. Numbers in parenthesis represent distance (m) that samples were collected from the center of the stream channel. Numbers in parenthesis for water samples indicate pH.

Table C.1. Silver content of samples collected in Canon de Valle and control canyon.

Location from outfall (m)	Water (ppb)	Sediment (ppm)	Soil (ppm)	Grass (ppm)
Control	-0 ± 0.5 (6.8)	0.48 ± 0.29	1.60 ± 0.40	0.29 ± 0.11
		2.60 ± 0.70	2.00 ± 1.00	0.52 ± 0.08
0	0.7 ± 0.5 (7.4)	14500 ± 1100		12 ± 1 (1.0)
10	0.7 ± 0.5 (7.3)	22300 ± 1800	14000 ± 1100 (0.8)	8.80 ± 0.85 (2.0)
20	-0 ± 0.5 (7.0)	22400 ± 1800	1860 ± 150 (1.2)	8.00 ± 0.90 (2.4)
30	-0 ± 0.5 (6.6)	10500 ± 800	654 ± 52 (1.6)	5.80 ± 0.60 (1.7)
60	6.7 ± 0.5 (4.8)	13700 ± 1100	3520 ± 280 (0.6)	3.00 ± 0.30 (1.9)
* main 90		14100 ± 1100	278 ± 23 (0.7)	1.70 ± 0.30 (1.2)
trib 90		1280 ± 100	686 ± 56 (0.7)	9.40 ± 0.80 (1.3)
120		4660 ± 380	2160 ± 170 (0.4)	4.00 ± 0.40 (0.1)
150		542 ± 44	78 ± 6 (0.6)	2.30 ± 0.30 (0.5)
180		600 ± 48	19 ± 2 (0.8)	2.20 ± 0.20 (0.6)
** 210		81 ± 7	97 ± 8 (1.0)	1.20 ± 0.10 (0.4)
240		51 ± 4	20 ± 2 (0.6)	1.30 ± 0.10 (0.4)
270		109 ± 9	15 ± 1 (1.2)	0.95 ± 0.09 (0.2)
*** 300	0.9 ± 0.5 (5.8)	4.80 ± 0.90	14 ± 1 (1.6)	1.10 ± 0.10 (1.7)
330	1.8 ± 0.5 (6.4)	12 ± 1	21 ± 2 (1.2)	0.53 ± 0.10 (0.9)
360		9.60 ± 1.10	1.60 ± 0.70 (0.1)	0.60 ± 0.15 (1.4)
390		7.60 ± 0.90	8.00 ± 0.90 (0.7)	2.30 ± 0.20 (0.5)
420		9.70 ± 1.10	12 ± 2 (0.9)	0.47 ± 0.15 (0.9)
450		3.80 ± 0.80	0.76 ± 0.38 (0.7)	0.40 ± 0.15 (1.5)

Table C.1. Silver content--Continued.

Location outfall (m)	Shrub Oak (ppm)	Ponderosa Pine (ppm)	Douglas-fir (ppm)
Control	0.22 ± 0.13		
	0.96 ± 0.09		
0			
10			
20		4.80 ± 0.50 (3.9)	
30		2.10 ± 0.20 (3.1)	
60	3.60 ± 0.40 (5.4)	1.10 ± 0.20 (5.4)	
*main 90		0.53 ± 0.18 (3.2)	
trib 90			
120	9.10 ± 0.80 (1.9)	1.40 ± 0.20 (1.8)	
150			
** 180	1.90 ± 0.30 (1.1)		
210	4.10 ± 0.40 (1.1)		
240	2.30 ± 0.30 (0.8)		
270	1.40 ± 0.20 (2.9)	1.40 ± 0.10 (3.1)	
*** 300	1.80 ± 0.40 (2.9)	0.40 ± 0.15 (1.5)	
330	0.79 ± 0.10 (2.3)	0.29 ± 0.11 (2.8)	0.46 ± 0.15 (2.0)
360	0.16 ± 0.08 (1.7)		0.24 ± 0.11 (1.4)
390	0.86 ± 0.09 (2.4)		0.38 ± 0.11 (0.6)
420	0.82 ± 0.08 (1.7)	0.39 ± 0.11 (2.8)	
450	1.10 ± 0.10 (2.1)		

* Waste outflow converges with main stream channel of Cañon de Valle at approximately 90 m.

** Land and soil type changes at approximately 195 m

*** Side canyon converges with Cañon de Valle at approximately 300 m.

Table C.1. Silver content--continued.

Depth from Surface (in)	Soil 10 m from outfall (ppm)	Soil 20 m from outfall (ppm)
0- 6	14000 ± 1100 (0.8)	1860 ± 150 (1.2)
6-12	4480 ± 285	824 ± 66
12-18	1250 ± 75	
18-24	770 ± 50	
24-30	138 ± 9	
30-36	182 ± 12	

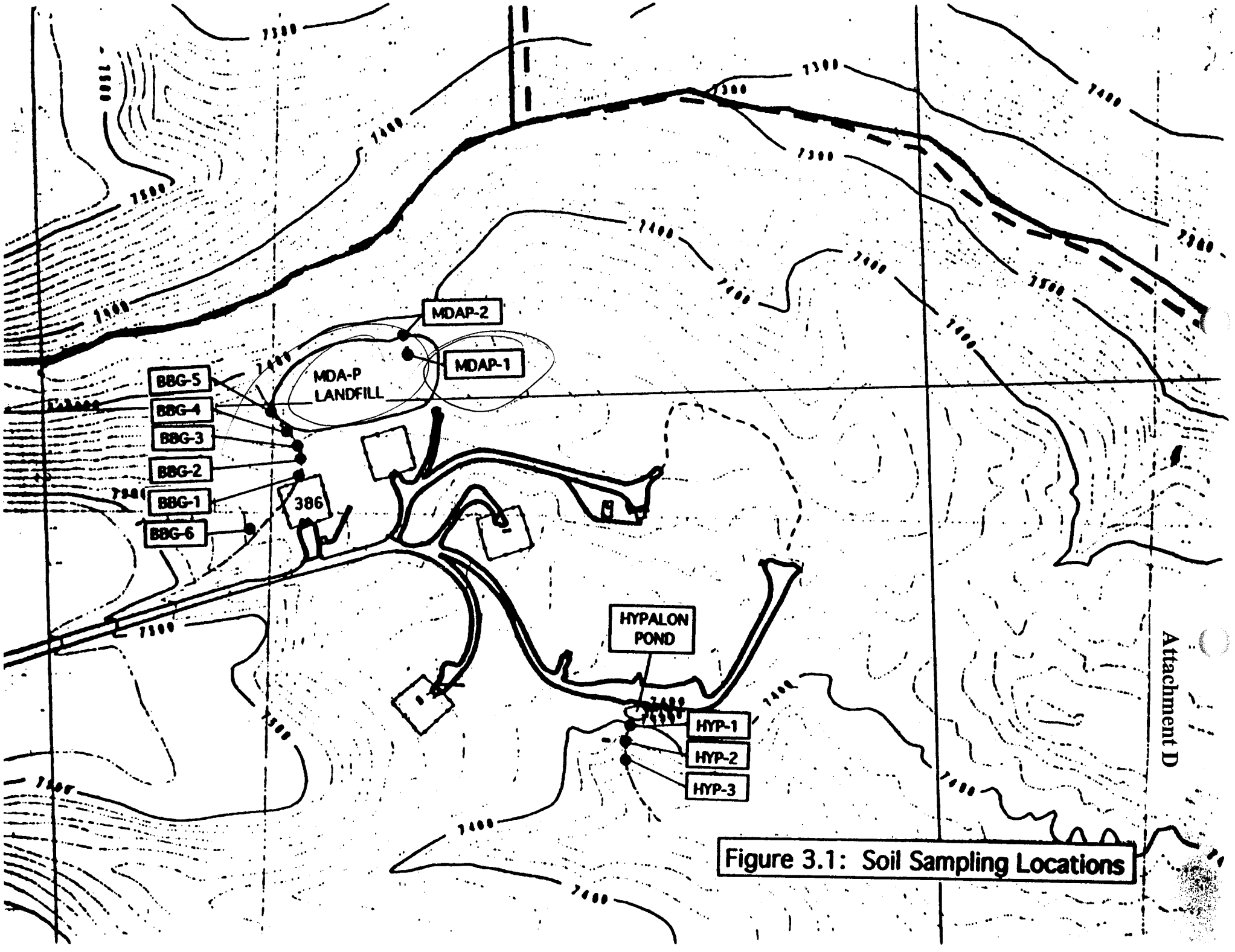


Figure 3.1: Soil Sampling Locations

Attachment D

TABLE 3.1

Soil Sampling Results

Sample	Na2O %	MgO %	Al2O3 %	SiO2 %	P2O5 %	K2O %	CaO %	TiO2 %	MnO %	Fe2O3 %
BBG-1	4.69	0.36	12.99	72.52	0.02	3.69	0.81	0.40	0.07	2.67
BBG-2	4.70	0.37	13.23	69.51	0.01	3.84	0.73	0.60	0.09	3.79
BBG-3	4.44	0.35	13.41	70.63	0.03	3.92	0.71	0.36	0.07	2.76
BBG-4	4.32	0.40	13.91	68.02	0.03	4.09	0.65	0.41	0.05	2.94
BBG-5	4.55	0.37	13.51	70.17	0.03	3.86	0.71	0.37	0.06	2.72
BBG-6	3.23	0.44	12.17	71.30	0.03	3.48	0.86	0.44	0.06	2.08
MDA-P-2	4.07	0.30	12.76	69.08	0.05	4.25	0.60	0.30	0.06	2.22
HYP-1	3.28	0.32	10.50	76.75	0.04	3.33	0.80	0.31	0.05	2.32
HYP-2	4.09	0.39	11.90	74.51	0.05	3.49	0.88	0.31	0.06	2.59
HYP-3	4.39	0.42	13.51	70.14	0.05	4.11	1.24	0.30	0.07	2.58

Sample	V ppm	Cr ppm	Ni ppm	Zn ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Nb ppm	Ba ppm
BBG-1	40	8	15	157	56	152	16	373	34	1750
BBG-2	47	10	16	102	61	142	17	534	38	2351
BBG-3	43	8	16	70	71	135	19	320	38	2658
BBG-4	42	7	16	61	88	128	31	412	46	6253
BBG-5	44	8	14	58	73	129	20	326	37	2823
BBG-6	42	14	13	39	93	132	31	406	41	620
MDA-P-2	41	3	19	80	98	134	32	324	49	10026
HYP-1	39	7	15	61	84	143	19	268	32	1430
HYP-2	38	6	14	73	78	137	23	275	38	941
HYP-3	36	7	16	73	103	130	30	304	44	1180

FIELD SCREENING OF INORGANIC CONTAMINANTS IN SOIL BY ENERGY DISPERSIVE XRF ANALYSIS

INTRODUCTION

In the characterization and remediation of contaminated soil sites, a need exists for quick and reliable in-situ assays of course soils to provide guidance toward areas of significant contamination. Accuracy and precision limitations due to the course and inhomogeneous nature of the in-situ measurement may or may not be considered an important factor in field screening of soils. The site specific action levels of contaminants would determine the usefulness of a field portable in-situ instrument. In many cases, integrating the ability of in-situ screening to characterize the extent of soil contamination with Contract Laboratory Program sampling assays can allow very cost-effective site remediation.

As a field instrument, energy dispersive X-ray fluorescence (EDXRF) analyzers make very efficient use of time and resources as they are able to simultaneously detect most inorganic pollutants present in a soil with little or no sample preparation. In the past, inconveniences of field protable EDXRF analyzers have been either poor resolution as a result of gas proportional detection (around 800 eV for Mn K-alpha) or extra size and weight of instruments using a cryogenically cooled detector. The development of the solid state mercuric iodide (HgI2) detector provides high resolution X-ray detection (around 270 eV for Mn K-alpha) at near ambient temperature.

The purpose of this report is to study the ability of the Spectrace 9000 to measure inorganic contaminants in soil and compare it's results with certified standards and AA/ICP characterized standards. The precision of intensity measurements will also be calculated for several analytes at various concentrations with a fixed counting time. The report will also describe the Spectrace 9000 and discuss it's capabilities involving in-situ soil analysis. The results of the experimental precision and crossover data will be tabulated along with lower limits of detection for various inorganic contaminants in silica based samples.

INSTRUMENTATION

The Spectrace 9000 combines radioactive source excitation with solid state mercuric iodide detection to provide field portable EDXRF analysis. The analyzer consists of two main components: an analysis probe and supporting electronics unit.

The probe unit consists of a sealed aluminum enclosure containing a mercuric iodide (HgI2) semiconductor detector and three radioisotope X-ray excitation sources. The radioisotope sources, Fe-55, Cd-109, and Am-241 are seperately shielded within the probe and are rotated into position for measurement of independent source spectra. Each source emits a different radiation energy which provides efficient excitation over specific ranges of elements as listed in Table 1.

TABLE 1

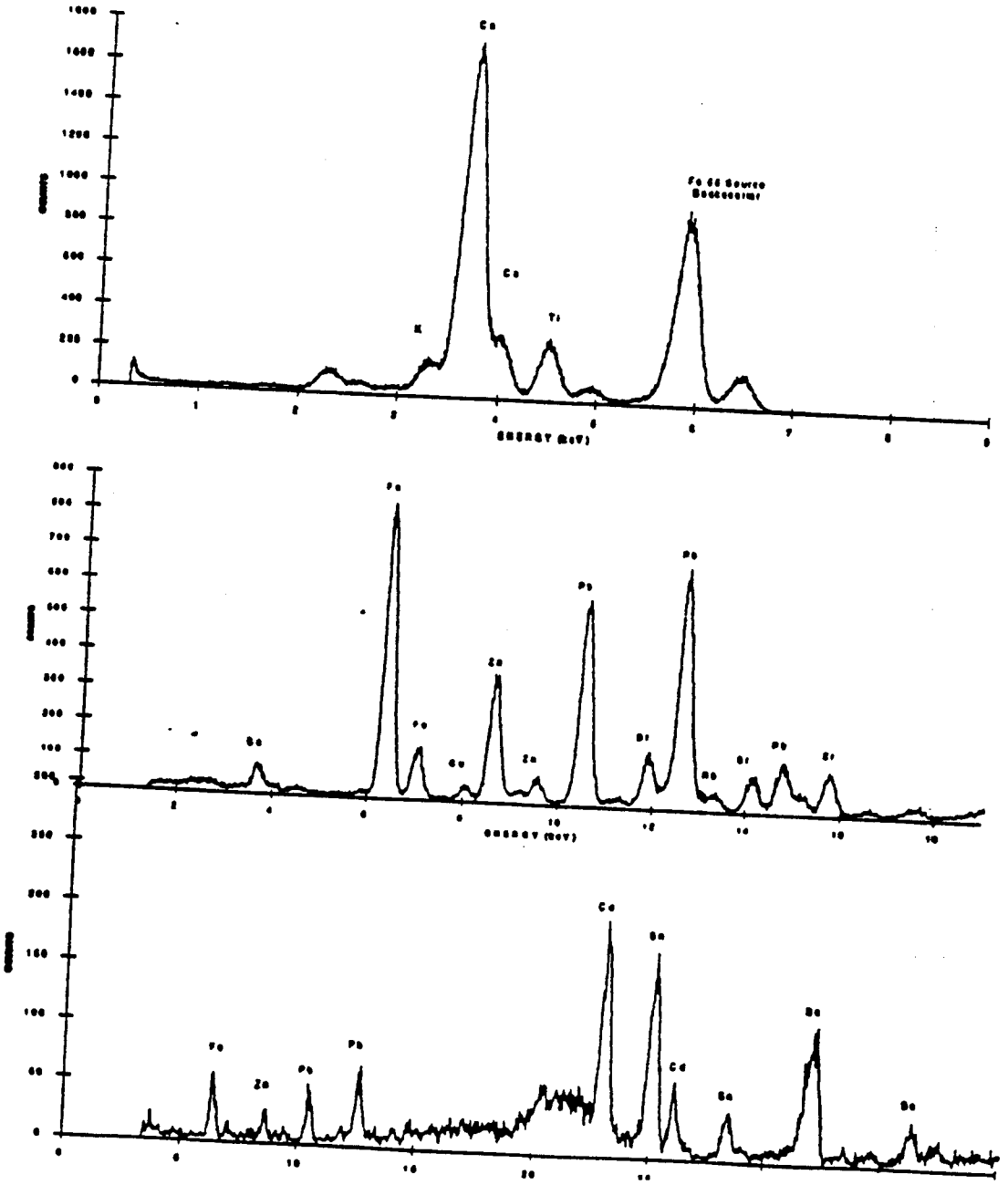
Source	Element Range	
Fe-55	S to Cr	(K X-rays)
	Mo to Ba	(L X-rays)
Cd-109	Ca to Rh	(K X-rays)
	Ta to Pb	(K X-rays)
	Ba to U	(L X-rays)
Am-241	Cu to Tm	(K X-rays)
	W to U	(L X-rays)

The analytical range of the Spectrace 9000 is sulfur to uranium with detection limits of 50-100 ppm for most analytes.

The electronics unit provides data acquisition, processing, and display capabilities. The unit contains sufficient memory to store up to 300 sets of analysis results and up to 120 spectra. An RS-232 port allows off-line downloading of results and spectra to a personal computer for additional processing. The system operates off either AC-power or rechargeable NiCd batteries.

For qualitative identification of elements, the on-board 2048 channel MCA spectrum display allows the user to view any of the three spectra that comprise a complete analysis. A number of operations can be performed on a displayed spectrum. A few of these are: element identification lines (K,L,M markers), energy cursor, display keV of cursor, horizontal or vertical magnification of the spectrum, course/fine cursor movement. Following downloading, the three spectra of an analysis can be simultaneously viewed on a PC. An example of this is shown below in Figure 1.

Figure 1



STANDARDIZATION

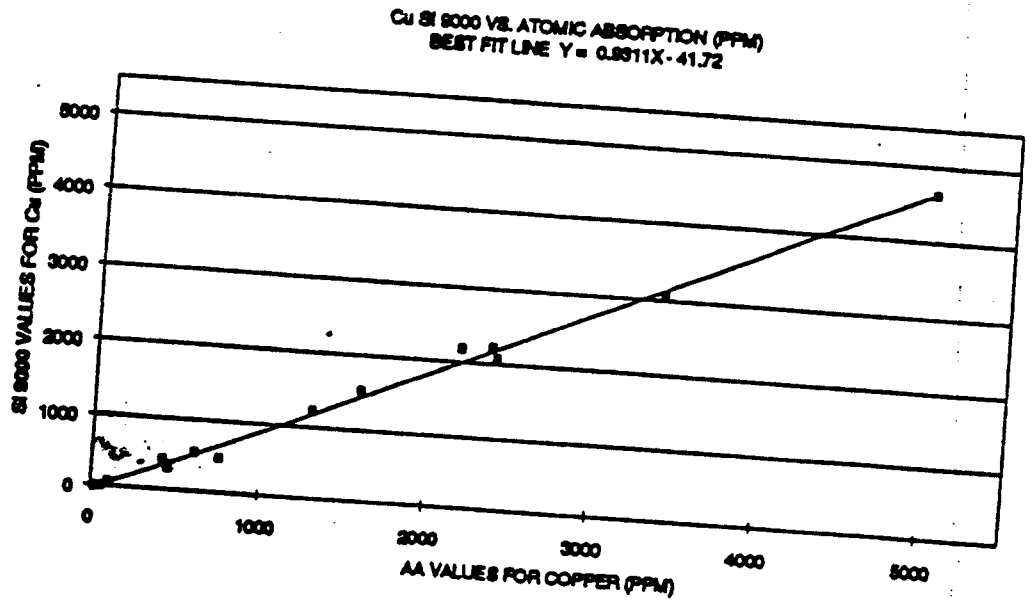
The Spectrace 9000 is equipped with a factory installed fundamental parameters standardization that is stored on board the analyzer. The fundamental parameters algorithm is a method of standardization that is derived from theoretical considerations for calculation of the element concentrations. The three main factors of the calculation are: 1. The measured analyte X-ray intensity relative to the pure element intensity of that analyte. The pure element intensities are instrument specific and are measured and stored on the analyzer at the factory. 2. The fluorescent yield of the analyte, which accounts for electron transitions that may compete with those that produce useful X-rays. These values are known constants and represent a percentage of excited atoms of the same atomic number that will fluoresce to produce X-rays. 3. The sum of many terms that characterize the X-ray absorbing nature of the matrix the analyte is within. This term addresses the probability of an analyte emitted X-ray reaching the detector.

SAMPLE MEASUREMENTS

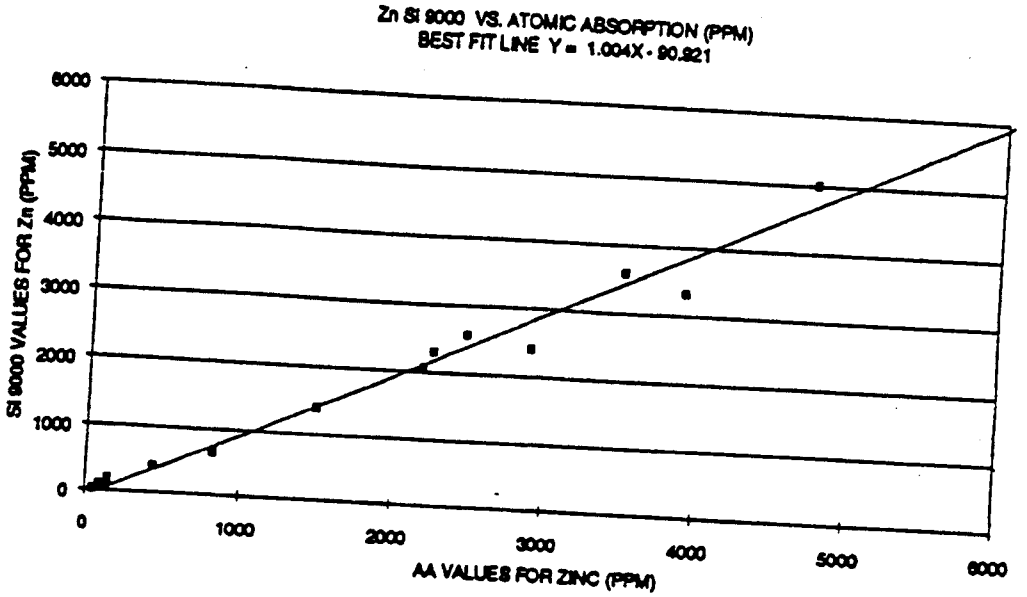
All of the sample measurements taken by the Spectrace 9000 were 200 seconds for each of the three sources. The samples ranged from finely ground soils to relatively large particle soils. For convenience, the soils were placed in 32 mm sample cups, sealed with a 4 micrometer polypropylene X-ray film window and analyzed with the Spectrace 9000 probe in the lab stand base.

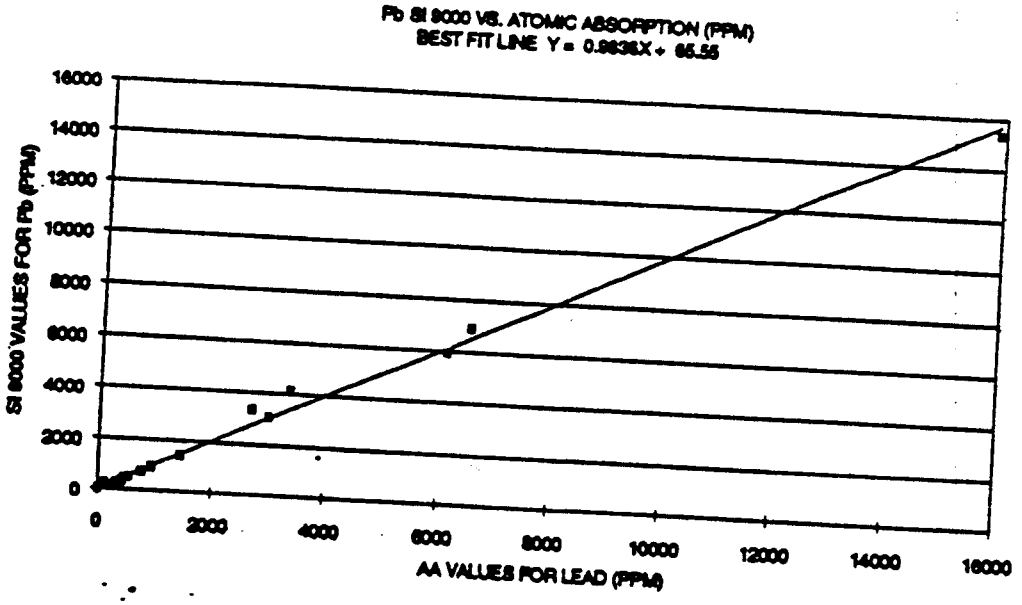
RESULTS

Crossover Study: Results of measured values from the Spectrace 9000 vs. Atomic Absorption values for Cu, Zn, Pb, Cr, and As.



Crossover Results continued





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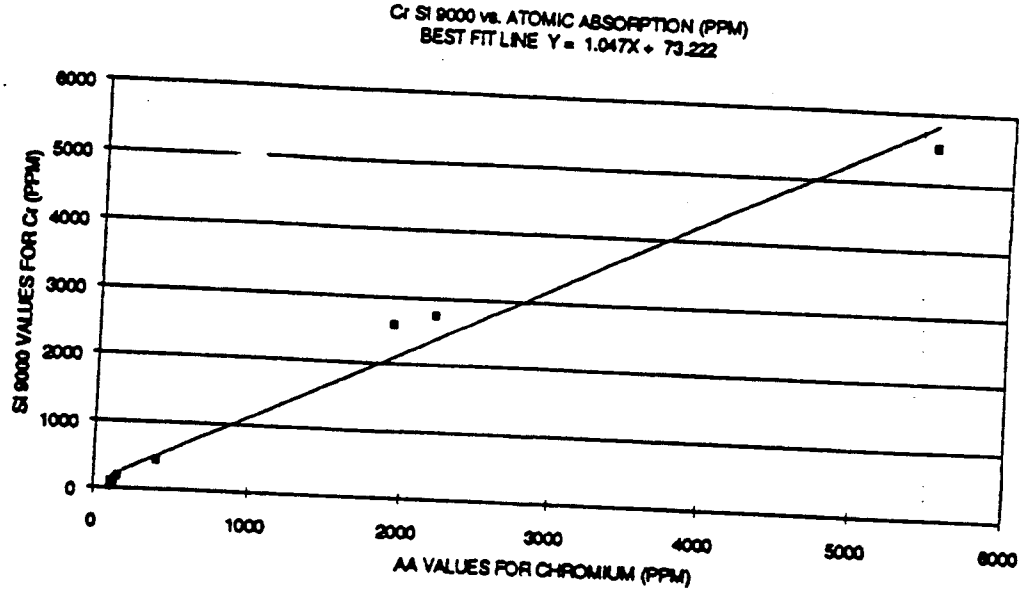

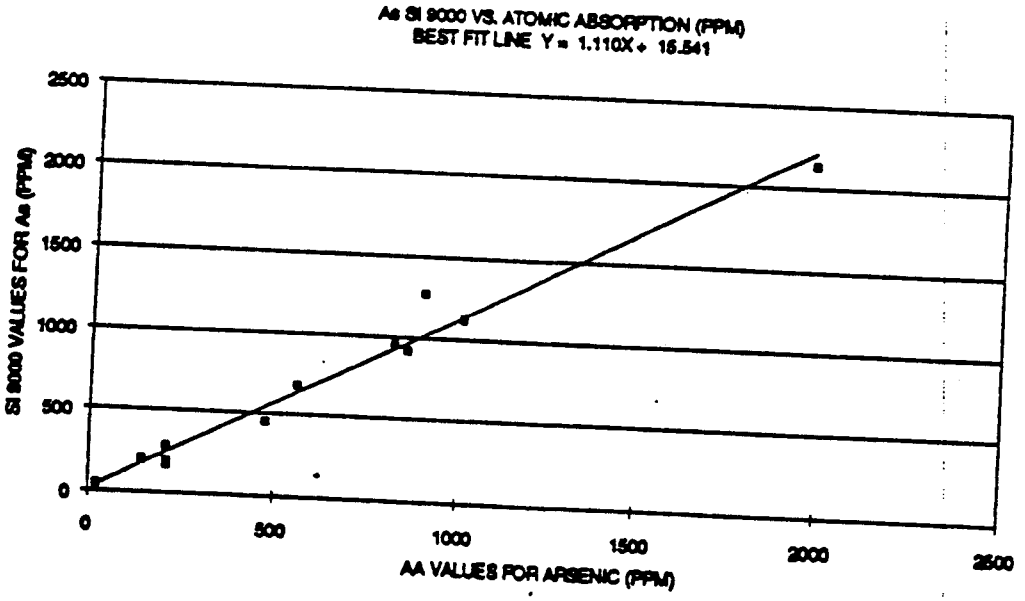

Minimum detection limits for elements in quartz are listed below.

Lower Limits of Detection for the Spectrace 9000 [3 SD (bkg)]

Source	Element	MDL (ppm)
Fe-55	K	117
	Ca	53
	Ti	45
	Cr	78
Cd-109	Mn	174
	Fe	105
	Co	97
	Ni	60
	Cu	41
	Zn	34
	As	27
	Se	17
	Sr	4
	Zr	3
	Mo	4
	Hg	30
	Pb	15
	Rb	5
Am-241	Cd	90
	Sn	56
	Sb	33
	Ba	10

MDL(ppm)

U 10 ppm
Th 6 ppm
Ag 55 (ppm)

Precision data was calculated for three soil samples. The following table lists the mean, standard deviation and relative standard deviation data for 10 replicate analyses.

Element	Sample 1	Sample 2	Sample 3
Pb	286 ± 7.4; 2.4%	5826 ± 35; 0.6%	3393 ± 34; 1.0%
Cu	494 ± 23; 4.6%	576 ± 22; 3.8%	2220 ± 69; 3.1%
As	434 ± 19; 3.8%	ND	21370 ± 140; 0.7%
Cr	141 ± 38; 27%	364 ± 37; 10%	ND

ND = not detected

CONCLUSION

The Spectrace 9000 is a field portable, high performance EDXRF analyzer for contaminated soil site investigation or remediation. The lightweight handheld probe and electronics subsystem archive up to 300 seperate soil sample measurements and allow downloading of results and spectra to a personal computer for processing or storage. The ability of the analyzer to screen soils for metals is exceptional due to the resolving power of the mercuric iodide detector. Quoted detection limits and the relationship between concentration and precision indicated in this study might suggest the ability or inability of an in-situ measurement by the Spectrace 9000 to provide acceptable sensitivity for a specific element. However, above the detection limits of the mercuric iodide system, excellent correlation between the portable EDXRF and independent analysis is realized and illustrated in correlation plots of results by the two techniques. Precision and accuracy provided by portable EDXRF indicates that the Spectrace 9000 is ideal for on-site in-situ screening of contaminated soil.