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DOCUMENT TO: Ray Garde DOCUMENT DATE: 07-03-84

ORIGINATOR NAME: Jim Cox ORGANIZATION: HSE-1

SYMBOL: HSE-1-84 PAGE COUNT: 1

SUBJECT/TITLE: Line 167: Concrete Anchors Left in Place

RECORD TYPE (Circle relevant type for primary record; type of attachments should be selected on *Keywords List*):

Analytical Data	FAX	Map	Plan	Study
Chain-of-Custody	Figure	Memo	Procedure	Telephone Record
Computer Output	Form	Minutes	Purchase Request	Transcription
Contract	Interview	Notebook	Receipt Acknowledgment	Video
Controlled Distribution	Letter	Personal Notes	Report	Work Plan
Drawing	Logbook	Photo	Review	Other

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7139

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

memorandum

TO Ray Garde, Radiation Protection Associate Group Leader

DATE July 3, 1984

FROM Jim Cox, Technical Supervisor

MAIL STOP/TELEPHONE E520/7-5420

SYMBOL HSE-1-84

SUBJECT LINE 167: CONCRETE ANCHORS LEFT IN PLACE ON NORTH SIDE OF LOS ALAMOS CANYON

Five concrete anchors (average size 2' x 3' x 6') were used to secure IWL 167, a 3" cast iron pipe, to the north wall of Los Alamos Canyon. For exact locations refer to Engineering Drawing No. C43943, sheet 32. The upper most anchor was removed, but the other four anchors were left in place on June 20, 1984.

The sections of pipe left encased in each of the anchors were approximately 3' long. The sections were decontaminated, the ends were sealed with concrete and the anchors were backfilled to upgrade one foot above the pipe openings.

During the removal of Line 167, soil samples were taken between the anchors, all samples were below established guide lines. Embedded alpha activity inside the pipe was less than 25 pc/g. Beta-Gamma activity were at background levels.

JC:ac

Xc: ALARA File, TA-50, MS E520
R. Romero, HSE-8, MS K490

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CONTROLLED

METALS IN SOIL (FIELD SCREENING)—EDXRF

Analtyes: Metals (K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd, Sb, Ba, Hg, Pb, U, Th)	**Method No.:** EI732
Matrix: Soil or geological samples	**Accuracy and Precision:** For > 1000 ppm, accuracy = 100–105%, precision (1σ) = 2–13% . For 20–1000 ppm, accuracy = 82–128%, precision (1σ) = 8–35%.
Procedure: Energy-dispersive x-ray fluorescence spectrometry	**Minimum Detectable Concentration:** ~10 ppm
Effective Date: 09/01/93	**Author:** Steve Goldstein Alice Slemmons Heather Canavan

SAFETY NOTE: Before beginning this procedure, read SOP-17 of the Environmental Chemistry Safety Manual. Read Sec. 4.3 of the Environmental Chemistry Safety Manual for information on personal protective clothing and equipment. Read Sec. 12 of this procedure and Source Material 13.5 for proper waste disposal practices.

1. Principle of Method

1.1. Soil samples are dried, powdered, and sieved.

1.2. Samples are analyzed for trace metals by energy-dispersive x-ray fluorescence spectrometry (EDXRF).

2. Sensitivity

2.1. Sensitivity is determined by the counter background, excitation, and detection efficiency.

2.2. Detection limits (DLs), screening action levels (SALs), and soil background are shown in Table I. Detection limits for fixed-based, transportable, and field portable instruments are all calculated at the level of 3 times the standard deviation of the background for 200-s livetime. The detection limits decrease with increasing atomic number, as expected, and are typically 5–15 ppm for the fixed-base and transportable instruments. Detection limits are somewhat higher for the portable instrument, with a typical range of 10–100 ppm. Screening action levels for each

element are derived from dose assessment calculations or are set equal to the upper tolerance level of the background, defined as the 99th percentile of the background soil distribution at Los Alamos (Longmire et al., 1995). From these data, it is evident that the detection limits for the fixed-base and transportable instruments are lower than screening action levels for all elements with the exception of arsenic.

TABLE I. DETECTION LIMITS[a], SCREENING ACTION LEVELS, AND NATURAL SOIL BACKGROUND ABUNDANCES[b] FOR LOS ALAMOS SOILS (ppm)

Element	Laboratory EDXRF DL	Transportable EDXRF DL	Portable EDXRF DL	Screening Action Level	Los Alamos Background
K	120	100	180		
Ca	120	100	80		
Ti	195	30	63		
Cr	11	12	345	400	34
Mn	16	16	318	11000	1030
Fe	110	10	150		
Ni	28	13	96	1600	27
Cu	13	8	57	3000	16
Zn	12	5	57	24000	101
As	33	4	36	12	12
Se	5	4	23	400	2
Cd	2	3	89	80	3
Sb	3	4	33	32	3
Ba	11	10	10	5600	1140
Hg	10	5	49	24	1
Pb	12	7	18	400	39
Th	8	8	9	46	25
U	8	8	11	177	6

[a] Detection limits are defined at 3 times the standard deviation of the background for each x-ray line.

[b] Soil background abundances (Longmire et al., 1995) are those at the upper tolerance limit, which is defined as the 99th percentile of the natural concentration distribution at Los Alamos. Average soil abundances are generally a factor of 5–10 lower than the upper tolerance limit.

3. Accuracy and Precision

3.1. Results for 10 certified soil/rock materials analyzed as open quality control (QC) check standards are summarized in Table II. These standards include the Canadian Certified Reference Material (CCRM) soils SO-1, SO-2, SO-4, the CCRM

reference stream and lake sediment standards STSD-1, STSD-2, STSD-3, STSD-4, and LKSD-3, the CCRM syenite rock standard SY-3, and the National Institute for Standards and Technology (NIST) estuarine sediment reference material 1646. Typically, average accuracy is in the range of 90–110%. Deviations from this are primarily related to the lower concentration range for certain elements (i.e., Cr, Ni, Cu, Zn, As, Sb, U, Th) in these check standards. Of elements present at high concentration (>1000 ppm), only Ti appears to show a significant bias, but this reflects the fact that one of the check standards (SY-3) has a 0% accuracy due to misidentification of the Ti K-alpha line as a lanthanide L line. For certain elements, including Hg, Se, and Cd, no check standards were available with high enough concentrations to permit quantification of these elements and an estimate of accuracy.

TABLE II. QUALITY CONTROL CHECK STANDARD RESULTS

Element	Concentration Range	Accuracy Range	Average Accuracy	Bias[a]
K	1.00–3.49%	92–141%	105%	no
Ca	0.83–5.90%	91–129%	104%	no
Ti	900–8600 ppm	0–95%	83%	?
Cr	12–116 ppm	97–525%	164%	?
Mn	370–3950 ppm	81–133%	102%	no
Fe	2.37–6.00%	91–114%	100%	no
Ni	30–94 ppm	61–260%	128%	no
Cu	16–65 ppm	20–124%	85%	no
Zn	94–246 ppm	84–128%	97%	no
As	7–42 ppm	25–114%	82%	no
Se				?
Cd				?
Sb	3-7 ppm	58–189%	112%	no
Ba	400-2000 ppm	97–117%	104%	no
Hg				?
Pb	16–130 ppm	78–146%	105%	no
Th	9-990 ppm	63–117%	88%	no
U	8-650 ppm	103–137%	126%	no

[a] Elements marked with "?" may show a small bias based on the accuracy results or have no suitable standards for which to evaluate accuracy.

3.2. Results for a portable instrument and fixed-base instrument are compared in the table below for a set of 25 soil samples from Los Alamos. These results are obtained on the same sample cup for both instruments, hence differences reflect biases due to instrumental analysis only. Consistent results are obtained for the two

instruments, with agreement to within 20% for most elements. However, some elements show large positive biases (factor of 5–40) for the portable instrument, including As, Th, and U. This may be due to the somewhat poorer energy resolution and greater spectral overlap for these elements with the portable instrument, which has a HgI detector. Nominal energy resolution for fixed-base and portable instruments are 200 and 300 eV for the Cu K-alpha, respectively.

TABLE III. COMPARISON OF PORTABLE AND FIXED-BASE EDXRF

Element	Number of Samples	Average Portable/Fixed-Base	Bias[a]
K	25	125%	no
Ca	25	120%	no
Ti	25	86%	no
Cr	1	66%	?
Mn	13	102%	no
Fe	25	98%	no
Ni	0		?
Cu	2	71%	?
Zn	24	144%	no
As	7	1660%	yes
Se	1	4090%	?
Cd	0		?
Sb	0		?
Ba	25	77%	no
Hg	0		?
Pb	6	79%	no
Th	22	460%	yes
U	20	3380%	yes

[a] Elements marked with "yes" show a large bias between portable and laboratory EDXRF based on a large population of samples, while those with "?" may show a small bias or are based on too small a sample population to evaluate the two methods.

3.3. Results for EDXRF and standard nitric acid digestion/inductively coupled plasma (ICP) methods prescribed by the United States Environmental Protection Agency (EPA) are shown in Table IV. Average XRF/ICP results are 78 for K; 2–6 for Mn, Fe, Pb, Cr, Cu, Ca, and Ba; and 0.8–1.1 for As, Ti, and Zn. These differences most likely reflect the fact that the XRF technique is measuring total amounts of the analyte, whereas standard EPA methods are measuring only the nitric acid-digestable part of the soil and not the matrix. These results are somewhat consistent with prior studies comparing wet chemical analysis after

hydrofluoric acid digestions with nitric acid digestions. The hydrofluoric acid digestion provides total dissolution of the sample, whereas the nitric acid digestion does not dissolve the silicate matrix constituents. Results of this comparison show that totally dissolved samples can have up to factors of 2–10 greater concentrations for certain elements than nitric acid digested samples (Kane et al., 1993; NIST, 1993; Longmire et al., 1995). From these data, it is evident that XRF and EPA methods are not directly comparable for relatively pristine soils, For these samples, the EDXRF technique will provide a much more conservative estimate of elemental contamination than standard EPA procedures. However, in contaminated soils where most of the analyte is nitric-acid-leachable, EDXRF and standard EPA methods should give more similar results.

TABLE IV. COMPARISON OF EDXRF AND NITRIC ACID DISSOLUTION/ICP DATA

Element	Number of Samples	Average XRF/ICP	Standard Deviation	Comments[a]
K	20	77.5	49.9	>
Ba	20	6.2	3.4	>
Ca	20	3.9	1.7	>
Cu	7	3.3	1.4	>
Cr	6	3.1	1.9	>
Pb	17	2.6	1.5	>
Fe	20	2.3	0.9	>
Mn	20	2.1	1.0	>
Zn	20	1.1	0.4	=
As	1	1.0	0.4	?
Ti	1	0.8		?
Se				?
Cd				?
Sb				?
Hg				?
Th				?
U				?

[a] Elements marked with "=" show no difference between methods, whereas elements with ">" indicate a significant difference. Elements with "?" have too few data to make a valid comparison.

4. Interferences

4.1. Spectral overlaps are automatically corrected by the data analysis program.

5. Collection and Storage of Samples

5.1. Soil samples are collected in polybottles. A 10-g sample is required for analysis. Samples are stored under chain-of-custody rules, using "do not tamper" seals, in a locked laboratory. If samples are to be extracted for organic analyses, they should be processed within 40 days of receipt.

6. Apparatus

6.1. XRF Spectrometer: Spectrace 5000 or 6000 EDXRF spectrometer, equipped with x-ray tube excitation, electrically cooled SiLi detector, and IBM-compatible 386/486 computer for system operation, spectral processing, analysis, and storage.

6.2. Convection/microwave oven: Sears Kenmore micro\convection oven #89561 or standard convection oven.

6.3. Mixer/mill: Spex 8000 mixer mill.

6.4. Grinding vials: Spex #8005 zirconia ceramic vial set.

6.5. Sieves: 100- and 10-mesh, nylon screen with plastic frame, 70-mm-diam, Spex #3536.

6.6. XRF sample cups: disposable, polyethylene, 31-mm-diam, Chemplex #1430.

6.7. X-ray film: Prolene, 0.00016-in. gauge, Chemplex #416.

6.8. Petri dish: Pyrex, 94-mm-diam.

6.9. Weighing paper.

7. Reagents

7.1. No reagents are required.

8. Calibration and Standards

8.1. Calibration of the EDXRF spectrometer.

8.1.1. Energy calibration of the spectrometer is performed daily using the copper K-alpha line. Stability and resolution are checked on a monthly basis, with the following specifications for copper:

Full-width half maximum (FWHM): <220 ev ± 5 ev maximum
Peak centroid: 8041 ± 3 ev maximum
Total counts: 2 million or more ± 0.5% maximum
Peak counts: 1 million or more ± 0.5% maximum
Elapsed time: 8 h

8.2. Pure-element standards.

8.2.1. Reference spectra are acquired for each analyte as well as major or minor components that have interfering x-ray lines. Pure-element metals or compounds are used to acquire these spectra.

8.3. Soil standards.

8.3.1. Peak intensities are converted to concentrations using a fundamental parameters analysis method, with seven soil standards used to determine pure-element count rates. Standards and samples are analyzed under identical conditions. Typical agreement of pure-element count rates is ±12% (1σ) with best standardization (<10%) for U, Mn, Ca, K, Fe, Cr, Cd, and Ba and less robust (~20%) calibration for Ti, Ni, and As.

8.3.2. We used seven soil/rock standards to represent a broad range in composition and location: NIST 2704 (Buffalo River Sediment), NIST 1648 (Urban Air Particulate Matter), NIST 2709 (San Joaquin Soil), NIST 2710 and 2711 (Contaminated Montana Soils), CCRM SY-2 (Syenite Rock Standard), and CCRM BL-4 (Uranium Ore). These are all essentially silicate-based materials with standards 1648, 2710, and 2711 having elevated transition metal concentrations and SY-2 and BL-4 having high actinide and lanthanide concentrations.

8.3.3. For QC purposes, at least one standard per 10 samples should be analyzed as an unknown.

8.3.4. Standardization is performed approximately every 2 months or more frequently if required because of instrument repair or relocation.

8.4. Open and blind QC standards.

8.4.1. One each of open and blind QC soil or geological standards should be analyzed per 10 samples at the beginning and end of each run.

9. Procedure

9.1. Sample preparation—soils.

9.1.1. Shake the sample container and transfer approximately 20 g of sample into a petri dish.

9.1.2. Microwave on 50% power for 5 min or heat in convection oven at 100°C for 1 h or overnight until dry.

9.1.3. For rapid analyses, samples are sieved through a 100-mesh screen without the 10-mesh prescreen or mixing/milling. Go to Step 9.1.7.

9.1.4. Pass the sample through a <10-mesh screen to remove large objects and pass <10-mesh sample through a 100-mesh screen. Discard the >10-mesh fraction.

9.1.5. Transfer the >100-mesh fraction to a zirconia vial. Mill/mix the sample for 5 min.

9.1.6. Pass the milled sample through a 100-mesh screen.

9.1.7. Transfer the <100-mesh sample to an XRF sample cup. Fill the sample cup to the top with sample.

9.1.8. Cover the sample cup with prolene film and label the cup with the request and sample number.

9.1.9. Between samples, clean the equipment with a dry Kimwipe. At the end of preparation, clean with water or blow dry-clean. This procedure has a cross-contamination factor of 1 part in 1000–10000, which is adequate for field characterization.

9.2. Sample analyses.

9.2.1. Samples are analyzed under the following conditions:

Low Z (K-Fe lines):
- 0.127-mm Al filter
- tube voltage = 13–15 kV
- live time = 200 s.

Mid Z (Ni-Se K lines, Hg-U L lines):
- 0.127-mm Al + 0.127-mm Rh filter
- tube voltage = 30–35 kV
- live time = 200 s.

High Z (Cd-Ba K lines):
- 0.127-mm Al + 0.63-mm Cu filter
- tube voltage = 50 kV
- live time = 200 s.

9.2.2. Open and blind QCs, standards, and duplicate samples are analyzed at a frequency of 10%.

10. Operation of the X-Ray Fluorescence Spectrometer

10.1. Refer to the operating manual for the XRF spectrometer.

11. Calculations

11.1. Total peak and background counts are determined for each analyte. Net counts are converted to concentration by use of a fundamental parameters (FP) program, using five standards to determine pure-element count rates for each analyte. The FP program corrects for any matrix enhancement or absorption effects.

11.2. Calculations are made using the following formulas.

11.2.1. Detection limit.

$$C_{LLD} = \frac{3 \times C_{Std} \times \sqrt{N_b}}{N_n} ,$$

where C_{LLd} = detection limit,
C_{Std} = concentration of analyte in the standard,
N_b = total background counts, and
N_n = net peak counts.

For a 200-s live time, typical detection limits are approximately 10 ppm.

11.2.2. Precision due to counting statistics.

$$\%RSD = \frac{\sqrt{N_g + N_b}}{N_g - N_b} \times 100\% ,$$

where %RSD = percent relative standard deviation,
N_g = gross counts, and
N_b = background counts.

The precision calculation is due to counting statistics only and is only one source of variance in the measurement. Other contributors to variance include instrumental precision, sample preparation, and sampling. Analysis of replicates is a more reliable but tedious way to determine overall precision.

12. Proper Waste Disposal Practices

12.1. Soil samples are returned to the Sample Management team for disposal.

13. Source Materials

13.1. W. Watson, J.P. Walsh, and B. Glynn, "On-Site X-Ray Fluorescence Spectrometry Mapping of Metal Contaminants in Soils at Superfund Sites," *American Laboratory 21*, 60 (1989).

13.2. D. E. Leyden, "Energy-Dispersive X-Ray Spectrometry," *Spectroscopy* **2**, 28-36 (1987).

13.3. A. R. Harding, "Fundamental Parameter Method EDXRF Analysis of Contaminated Soils," *Spectrace Technical Review*.

13.4. Spectrace 5000 and 6000 Operators, Technical, and Software Manuals.

13.5. "Hazardous and Mixed Waste," Administrative Requirement 10-3, in *Environment, Safety, and Health Manual*, Los Alamos National Laboratory Manual, Chapter 1 (most recent edition).

13.6. "Handling and Disposal of Hazardous Materials," SOP-3, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Appendix III, Los Alamos National Laboratory document (most recent edition).

13.7. "Operation of an Energy-Dispersive X-Ray Fluorescence Spectrometer," SOP-17, in *Environmental Chemistry Group: Environment, Safety, and Health Program*, Appendix III, Los Alamos National Laboratory document (most recent edition).

13.8. P. Longmire, S. Reneau, P. Watt, L. McFadden, J. Gardner, C. Duffy, and R. Ryti, draft manuscript (1995).

13.9. J. S. Kane, S. A. Wilson, J. Lipinski, and L. Butler, *Am. Env. Lab. Application Note* (1993).

13.10. National Institute of Standards and Technology, Addendum to SRM Certificates 2709, 2710, and 2711 (1993).

13.11. J. W. Criss and L. S. Birks, *Anal. Chem.* **40**, 1080 (1968)

13.12. G. R. LaChance and R. J. Traill, *Canadian Spectroscopy* **11**, 43 (1966).

13.13. P. A. Pella, G. Y. Tao, and G. Lachance, *X-ray Spectrom.* **15**, 251 (1986).

13.14. D. B. Bilbrey, G. R. Bogart, D. E. Leyden, and A. R. Harding, *X-Ray Spectrom.* **17**, 63 (1988).

13.15. D. K. G. de Boer, J. J. M. Borstrok, A. J. G. Leenaers, and H. A. van Sprang, *X-Ray Spectrom.* **22**, 33 (1993).

Revisions or additions to the procedure are marked ( ). Where a section heading is marked, the entire section has been revised.

CONTROLLED

ANALYTICAL PROCEDURE REVIEW AND APPROVAL

Method: Metals in Soil (Field Screening)—Energy-Dispersive X-Ray Fluorescence Spectrometry (EDXRF)

Method No.: EI732 **Revision No.:** 1

Team Leader Steve Goldstein **Date:** 1/27/96

Group Leader Lara C Lacati **Date:** 1/28/96

QA Concurrence Margaret A. Gautier **Date:** 1/28/96