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INTERCOMPARISON STUDY OF ELEMENTAL ABUNDANCES IN RAW AND SPENT OIL SHALES

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INTRODUCTION

Techniques for accurate and sensitive elemental analysis of oil shale materials are important for determinining the fate and effects of various constituents during oil shale conversion. Many routine analytical techniques are not suitable for oil shale materials due to numerous chemical interferences.[1-3] The need for oil shale reference standards was first recognized by Poulson et al.[2]

The purpose of this work was to develop raw and spent oil shale reference samples, to characterize them using an interlaboratory, interinstrumental approach, and to assess the performance of various analytical methods. This study was jointly carried out using the analytical facilities of various Colorado universities (COLO), Battelle Pacific Northwest Laboratory (PNL), the Lawrence Berkeley Laboratory (LBL), and the Lawrence Livermore Laboratory (LLL). Analytical procedures routinely used at those laboratories for similar measurements on other geochemical materials were used. Thus, some laboratories analyzed a single sample rather than several replicates.

Aliquots of the reference standards described in this work may be obtained by writing the authors.

EXPERIMENTAL

Instrumental neutron activation analysis (INAA), X-ray fluorescence spectrometry (XRF), atomic absorption spectroscopy (AA), emission spectroscopy (ES), gamma-ray spectrometry (GS), and colorimetric and fluorimetric methods were used to measure 52 elements in four oil shale reference samples. Preparation of the reference samples and analytical procedures used by the participating laboratories are described. Measurements by the Colorado universities were made under the auspices of the Colorado Environmental Trace Substances Research Program which consists of a number of research groups at various Colorado universities. There is no central laboratory--reported measurements were made at the Colorado School of Mines, the University of Colorado, or Colorado State University. The U. S. Geological Survey neutron activation and delayed neutron analyses were performed on a service basis for the Colorado universities group for this study.

Reference Samples

Four reference samples were prepared for this study. Samples OS-1 and FASS were prepared at the Colorado School of Mines using procedures previously described.[3,4] Sample OS-1 is a raw oil shale from the Dow Mine, Colorado. Twenty-seven kilograms of material were prepared by crushing and grinding to -65 mesh and blending and splitting into 75-g samples. FASS is Fischer Assay spent shale produced by 46 repetitive runs of Fischer Assay retorts charged with OS-1 (Ref. 3).

Samples RAW-1B and SOS-11B were prepared at the Lawrence Berkeley Laboratory using procedures described here. RAW-1B is a raw oil shale from the Anvil Points Mine, Colorado; SOS-11B is a spent shale produced during a high-temperature combustion run of the Lawrence Livermore Laboratory's 125-kg simulated in-situ retort.[5]

RAW-1B was prepared from master batch material received from Lawrence Livermore Laboratory (LLL). The master batch material was prepared by LLL by separating 136,000 kg of Anvil Points oil shale into greater-than and less-than-102-mm fractions with a grizzly; passing the less-than-102-mm material through a roll crusher; and screening the material to the size range of 13 mm to 25 mm. A 25-kg sample of the 13-mm to 25-mm material was split from the master batch and mixed and split into 500-g lots, using the technique described by Wildeman.[4] Random number tables were used to select two lots. Selected lots were ground to less than 3 mm in an alumina-faced jaw crusher, and to less than 0.15 mm, with most passing 0.074 mm in an alumina-jaw pulverizer; they were then split into 15-g samples for use in this work. The 15-g samples were stored in acid-washed glass vials and maintained at 4° C.

SOS-11B was prepared by grinding the charge from the 125-kg retort in a Sturtevant rotary grinder with a built-in splitter. A 25-kg sample was split from the rotary-ground material and prepared for analysis as described for RAW-1B.

A minimum of three separate splits of each of the four standards was tested for homogeneity by measuring elemental abundances by neutron activation analysis and X-ray fluorescence spectrometry.[4] All samples were found to be homogeneous within the analytical precision of the method.

Neutron Activation Analysis

Battelle Pacific Northwest Laboratory -

Two procedures were used by PNL. The first procedure was used to analyze all four samples, and the second was used only for RAW-1B. In both procedures, 0.1 to 0.5 g of sample were weighed into 0.4-dram polyethyelene vials; the vials were then heat sealed. The 0.4-dram vial was placed in a 2-dram polyethylene vial which was also heat sealed. After irradiation, the samples were transferred to fresh vials. Standards used for elemental analysis were Fischer atomic absorption standards for As, Ni, Zn, and Se; National Bureau of Standard's orchard leaves (SRM 1571); U. S. Geological Survey standard rocks BCR-1, W-1, AGV-1, and PCC-1; and IAEA standard Soil-5. Samples were irradiated at the Oregon State University reactor at a power of 1 MW.

Triplicates were analyzed in the first procedure and the reported errors are the larger of 1 standard deviation for the replicates, 1 standard deviation from the counting statistics, or 2% of the reported value. The analysis procedure used one irradiation period and two decay/counting intervals, as shown in Table 1. Following the irradiation, the samples were transferred into clean polyethylene vials and counted on an 80-cc Ge(Li) detector with a resolution of 1.96 keV at 12% relative efficiency after the 7-day cooling period. Counting following the 6-week cooling period was done on an anticoincidence-shielded Ge(Li) detector to reduce Compton background for low- and medium-energy gamma rays, and, in some cases, to remove peak interferences from correlated gammas.

A single aliquot of RAW-1B was analyzed by the second procedure; the reported errors are the larger of 1 standard deviation for the counting statistics or 2% of the reported value. The analysis procedure used one irradiation period and three decay/counting intervals. The samples were counted on a 130-cc Ge(Li) detector with a resolution of 1.8 keV at 25% relative efficiency following the 7-day and 30-day cooling periods. Counting following the 70-day cooling period was done on an anticoincidence-shielded Ge(Li) detector.

Lawrence Berkeley Laboratory -

Two replicates were analyzed. The reported error is an estimate of 1 standard deviation in the accuracy calculated from the counting statistics of both the samples and the standards and the uncertainties in the elemental abundances in the standards. The samples were analyzed using procedures similar to those described elsewhere.[6] Approximately 100 mg of sample were mixed with 50 mg of cellulose and compacted into a 1 cm x 1.2 mm pill using a hand-operated hydraulic press. The samples were wrapped in thin polyethylene and placed in radial array with four

Table 1. NEUTRON IRRADIATION AND COUNTING SCHEDULES USED BY LBL, PNL, LLL, AND THE USGS

	Irradiation time	Neutron flux, n/cm^2-sec	Cooling time	Counting time, min	Elements detected
LBL	18 min	2×10^{11}	8 min	1	Al, Ca, V, Cl, Mg, Ti
			1.25 hr	6	Mn, Na, K, Eu, Ba, Sr, Cu, In, Ga
	8 hr	2×10^{13}	6 days	20	U, Sm, Lu, Ti, La, As, Br, Cd, Mo, W, Ba, Au
			30 days	60,90	Fe, Sc, Ta, Eu, Zn, Co, Cs, Sb, Ce, Ir, Se, Ag, Hf, Th
PNL	2 hr	6×10^{12}	7 days	300	Na, La, Sm, As, Sb, Co, Fe, Rb, Sc, Ba, Hf
			6 weeks	300	Cr, Th, Eu, Sr, Ni, Rb, Zn, Se
PNL	8 hr	6×10^{12}	7 days	100	Sm, Lu, Yb, Ba, La, Na, Br, As, K
			30 days	100	Fe, Cr, Th, Sb, Ce, Co, Hf, Hg, Rb, Sc, Ta, Yb
			70 days	1000	Eu, Sc, Zn, Ni, Sr, Se, Tb
LLL	2 min	2.1×10^{13}	10 min	10,20,40	Al, V, Cu, Ti, Ca, Na, Mg, Cl, Mn, Br, I, Ba, In, Dy, As, Ga, Sm, V, Mo
	72 min	2.6×10^{13}	3 days	133	Na, As, W, Ga, K, Cd, Mo, V, Sm, Au, Hg, La, Sb, Mo, Zn
			15 days	333	Fe, Cr, Co, Zn, Hg, Se, Ag, Sb, Ce, Cs, Eu, Sc, Th, Ni, Ta, Hf, Ba, Rb
USGS	20 min	2.5×10^{10}	10 min	20	Na, K, Ca, Mn, Sr, Ba, La, Dy
	8 hr	2.5×10^{12}	7 days	20	Ca, Cr, Ba, La, Ce, Nd, Sm, Eu, Yb, Ta, U
			14 days	33	Sc, Cr, Fe, Co, Zn, Rb, Sb, Ba, Ce, Nd, Eu, Tm, Lu, Hf, Ta, Th, U
			60 days	167	Sc, Cr, Fe, Co, Zn, Sa, Rb, Sr, Nb, Sb, Cs, Ce, Eu, Gd, Tm, Yb, Hf, Ta, Th

samples and five standards (standard pottery,[6] KCl, $CaCO_3$, and Al foil) in a heavy-duty polyethylene irradiation capsule. The sealed capsule was suspended by a wire in the central thimble of the Berkeley Triga Reactor and rotated during irradiation. The technique used to analyze the resulting pills consists of two irradiation periods and five decay/counting intervals, as summarized in Table 1. Three of these were made with a 7-cc intrinsic Ge detector with a resolution of 1.6 keV at 1 MeV and two were made with a 1-cc Ge(Li) detector with a resolution of 0.54 keV at 103 keV. For the second irradiation, the samples were rewrapped in high-purity Al foil and placed in radial array in an Al irradiation capsule.

Lawrence Livermore Laboratory -

A single sample was analyzed using an absolute INAA procedure described elsewhere.[7] Approximately 200 mg of sample were mixed with 200 mg of Avicel, pressed into a 1.59-cm-diameter disc, and stacked in an Al irradiation capsule between polyethylene spacers. Flux monitors consisting of U and Sc were placed at opposite ends of the tube. Following irradiation of the samples, the disc was removed from the outer vial and placed in a second container for counting. The analytical technique uses two irradiation periods and five decay/counting intervals, as summarized in Table 1. The samples were irradiated in the Livermore pool-type reactor which is moderated and cooled by light water and consists of plate-type fuel elements and boron-containing control rods. The samples were counted on 50- to 70-cc Ge(Li) detectors.

Colorado Universities -

Samples OS-1 and FASS were analyzed by the U.S. Geological Survey in Denver under contract to the Colorado School of Mines. The procedure used was similar to that described elsewhere.[8] Three replicates were analyzed. The reported errors are the larger of 1 standard deviation for the replicates or 2% of the reported value. Approximately 0.8 g of a powdered sample were weighed into 2-dram polyethylene vials and irradiated in the General Atomic TRIGA Mark I reactor. Standards used for the analysis were U.S. Geological Survey G-2 and two specially prepared combined quartz standards containing the elements of interest. The analysis procedure used two irradiation periods and four decay/counting intervals. Following the irradiation, the samples were transferred into clean polyethylene vials and counted on a 30-cc Ge(Li) detector with a resolution of 2.0 keV at 12% relative efficiency. A 10-min cooling period was used for the first irradiation. In addition to the high efficiency Ge(Li) detector, a low-energy intrinsic Ge detector with a 1-cc active volume and 0.48 keV resolution at 122 keV was used for the 7-, 14- and 60-day cooling periods.

X-ray Fluorescence Spectrometry

Battelle Pacific Northwest Laboratory -

Three replicates were analyzed. The reported errors are 1 standard deviation for the three analyses. The samples were analyzed using procedures similar to these described elsewhere.[9] Samples were prepared by pressing 0.250 g of powder and an equal weight of cellulose into a 3.2-cm-diameter disc. The samples were analyzed on a Kevex Model 810 energy-dispersive X-ray machine. System resolution was 200 eV at 6.4 keV (Fe Kα X-ray). Excitation was provided by a Zr or Ag secondary source. The X-ray tube was operated at 50 kV with a current of 35 mA. The resulting radiation was measured with a 80-mm^3 detector and a 1000-channel pulse height analyzer. Counting time was 100 min. The elements analyzed were Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Hg, Se, Pb, As, Br, Rb, U, Sr, Y, Zr, Nb, and Mo. Individual calibrations were calculated for each sample matrix from backscatter intensities and a multi-element, thin-sample calibration curve.[9]

Lawrence Berkeley Laboratory -

Two energy-dispersive X-ray fluorescence systems were used. The "low-energy" system was used to analyze for Al, Si, Ti, Fe, Na, K, Ca, and Mg. Two replicates were analyzed. The reported errors are the larger of 10% of the reported values, or 1 standard deviation for the counting statistics. The samples were prepared using a $LiBO_2$ fusion technique.[10] Approximately 200 mg of powdered sample were fused with 1.80 g of $LiBO_2$ in a Pt crucible over a Fischer burner. The temperature of the mixture was slowly raised to 900°C, the mixture was poured into an Al ring, which was resting on a vitreous carbon disc at 250°C, and pressed into a ring with a hydraulic press. Weight loss on fusion was measured and used to compute elemental abundances. The samples were analyzed using a prototype energy-dispersive system designed and built at LBL.[10] The samples were placed in a vacuum chamber maintained at 10^{-4} torr or better and irradiated with a multiple anode soft X-ray generator consisting of six anodes and an electron gun. Emitted radiation was measured using a lithium-drifted silicon detector and a multichannel analyzer.

The "high-energy" system was used to measure the elements Ti and heavier which have X-ray energies >4.5 keV. Two replicates were analyzed. The reported errors are the larger of 1 standard deviation for the two analyses, 2 standard deviations from the counting statistics, or 4% of the reported value. The samples were analyzed using procedures similar to those described elsewhere.[11] Approximately 2 g of powder were pressed into a Lucite cylinder and analyzed on a prototype system designed and built at LBL. The total system resolution FWHM was 190 eV at 6.4 keV (Fe Kα X-ray) at 5,000 counts/sec using 18 μsec pulse peaking time. Excitation was provided by a Mo X-ray tube with external Mo filters. The X-ray tube was operated at 45 kV and with regulated currents that varied from 100 to 245 μA. The resulting X-rays were simultaneously measured by a guard-ring detector with pulsed-light feedback electronics and 512-channel pulse height analyzer. Counting time was 20 min.

University of Colorado -

Six to eight replicates were analyzed. The reported errors are 1 standard deviation for the replicates. Samples were prepared and analyzed (by a procedure described elsewhere)[12,13] by glueing 250 μg of powdered sample into the center of a Forvar foil. The samples were analyzed on a prototype system built at the University of Colorado cyclotron facility. Excitation was provided by a 2-kW tungsten anode X-ray tube operated at 55 kV and with regulated currents varying from 2 to 20 mA. The total system resolution FWHM was 163 eV at 6.4 keV (Fe Kα X-ray). The resulting X-rays were measured on an 80-mm^2, lithium-drifted, silicon X-ray detector, arranged in a compact geometry, and a 512 channel pulse height analyzer. The counting time was not fixed but was normally about 2 hr. The configuration of the system was adjusted so that the background was lowest for the Mo Kα X-ray. This made the background under K, Ca, Ti, Cr, and Mn somewhat high and the uncertainties in the analysis of these elements is correspondingly larger. The data reduction method used peak areas, compared to thin-film, pure-element standards.[12,13]

Atomic Absorption Spectroscopy

Battelle Pacific Northwest Laboratory -

Atomic absorption spectroscopy was used to measure Al, Ca, Fe, Hg, K, Mg, Na, Si, Sr, and Ti. Conventional flame atomic absorption was used for all elements except Hg which was determined by flameless atomic absorption. Measurements were made with a Perkin Elmer 403. Powdered samples were fused with lithium metaborate using a 6:1 $LiBO_2$ sample ratio. The fused sample was dissolved in concentrated HNO_3 and diluted to 200 ml. Commercially prepared aqueous standards were used. USGS standard rock BCR-1 was used as a control.

Mercury was determined using a flameless technique. A 50 to 150-g sample was combusted, the vapors swept into a separation train, and the mercury trapped on gold beads and analyzed by flameless AA. In the separation train, mercury-free air was introduced into a 950°C quartz tube containing the sample overlying a layer of 3-4 cm of gold-coated quartz beads. The high temperature and oxidizing conditions volatilized the mercury from the sample matrix and the gold beads converted it to the elemental form. Elemental mercury was separated from interfering organic vapors by passing the sample gases through an alumina column which selectively retains the organic vapors but passes Hg^o. The Hg^o was collected by amalgamation in a column of gold-coated glass beads maintained at room temperature. This column was detached from the separation train and attached to a flameless AA system. Amalgamated Hg^o was released by heating the column to 500°C in a N_2 gas stream. The Hg^o vapor was swept into a long-path-length gas absorption cell where it was measured by atomic absorption at 254 nm.

Lawrence Berkeley Laboratory -

Zeeman atomic absorption spectroscopy was used to measure Cd, Hg, Cu, Pb, and Zn. The reported error is the larger of 10% of the reported value or 1 standard deviation for three replicates. The instrumental technique has been described elsewhere.[14-18] Electrodeless discharge lamps were used for all elements. Mercury was atomized in a T-shaped combustion tube maintained at 900°C and Cd, Pb, and Zn, were atomized in a Massman-type furnace equipped with a dual chamber graphite rod.[16] Powdered samples for Pb, Zn, and Cd analysis were diluted with graphite powder (Ultra Carbon U.C.P.-2-325) and mixed with a Wig-L-Bug. For the Hg analyses, the sample was directly weighed into a tared Pt boat and inserted into the furnance. For the other elements, the sample was weighed in a tared plastic tip for use with an adjustable micropipette and transferred to a Massman-type furnance by tapping the sides of the tip. The empty tip was weighed to determine transfer efficiency.

Colorado Universities -

Atomic absorption spectroscopy was used to measure Al, As, Ca, Mg, Si, and Na. Sample preparation consisted of standard HF, HNO_3, and $HClO_4$ digestions for Na, Mg, Al, Si, and Ca (Ref. 19) and a sodium peroxide fusion for As (Ref. 3). The solids were spiked prior to digestion and standard additions used to check the analyses. Four replicates were analyzed for Al, Ca, Na, and Mg using standard flame conditions, and three replicates were analyzed for As using the hydride generation method.[3]

Emission Spectroscopy

Battelle Pacific Northwest Laboratory used a dc plasma technique to measure B. Three replicates were analyzed. The reported errors are 1 standard deviation for the three replicates. Samples were prepared by fusing 3 g of sodium carbonate with a 0.5-g sample, dissolving the residue in 8 M HNO_3, and diluting to 100 ml. The samples were analyzed on a Spectrametrics Spectraspan III employing a dc argon plasma excitation system and an Echelle grating spectrometer.

Molecular Absorption

The Colorado universities used molecular absorption of AlF in an air-acetylene flame to determine F in a fused sample.[4] The analytical method was developed by Tsunada, Fujiwara, and Fuwa,[20] and was modified for oil shales by Meglen and Krikos.[21]

Gamma-Ray Spectrometry

The Lawrence Berkeley Laboratory used gamma-ray spectrometry to measure U, Th, and K (Ref. 22). Approximately 50 g of powdered sample were packaged in a 3.8-cm-diameter plastic container and counted for 1,490 to 3,829 min in a lead-shielded compartment with an 20-cm-diameter by 10-cm-thick NaI(Tl) crystal. The spectra were taken by a 1600-channel pulse-height analyzer covering the interval 0.1 to 4.0 MeV, and reduced

by a computer program that fits, channel-by-channel, standard and sample spectra over selected energy intervals.

Fluorimetric and Colorimetric Methods

The Colorado universities used these techniques to measure Si, Se, Mo, and B. Silicon was determined colorimetrically by the standard molybdenum blue procedure.[23] Selenium was determined by a fluorimetric method which uses 2, 3-diaminonaphthalene.[24] Molybdenum was determined colorimetrically using potassium thiocyanate[25] and B was determined using an Azomethine-H method.[26] The fusions and digestions used with these procedures have been previously described.[3]

Delayed Neutron

The U.S. Geological Survey determined U under contract to Colorado School of Mines by this technique. Approximately 10 g of powdered sample were analyzed by procedures given by Stuckless et al.[27]

RESULTS

Analytical results for the four samples are summarized in Tables 2 through 5. The data are grouped by analytical technique so that the performance of each method may be readily assessed. The data in Tables 2 to 5 were reduced using statistical techniques; the results are plotted in Figures 1 through 4. A minimum handling error of 2% was assigned to all values with unrealistically small errors. This is frequently a problem in neutron activation work when the analyst reports counting errors.

The error-weighted average ($\bar{X}$) was computed and the value

$$Z_i = \left(\frac{X_i - \bar{X}}{\sigma_i} \right)$$

was determined for each point, where X_i is the ith measurement of an element and σ_i is the associated standard deviation. Chauvenet's criterion[28] was applied to the largest Z_i for each element set for $N \geqslant 2$ where N is the total number of measurements for a given element. A value was rejected if

$$|Z_i| \geqslant P$$

where P was a 1/3 N probability function based on the normal curve of error. If a value was rejected, N was reduced by 1 and a new error-weighted average was computed. This procedure was applied only once per element for each sample. Finally, the percent deviation from the mean was computed for each value in an element set as

$$\%DEV = 100 \left(\frac{X_i - \bar{X}}{\bar{X}} \right)$$

Table 2. ELEMENTAL COMPOSITION OF ANVIL POINTS RAW OIL SHALE PREPARED BY LBL, RAW 1B (ppm)

	Neutron Activation Analysis				X-ray Fluorescence Spectrometry				Other			Average		
	(A-1)	(A-2)	(B)	(C)	High energy (A)	High energy (B)	High energy (D)	Low energy (B)	(A)	(B)	(D)	Conc	No. of Values	
Al (%)	-	-	3.83±0.12	4.04±0.19	-	-	-	4.0±0.2	3.88±0.34[a]	-	-	3.93±0.12	(4)	Al
As	54±1	62±1	45±4	39±1	38±3	37±1	40±9	-	-	-	33±3[a]	42±1	(7)	As
B	-	-	-	-	-	-	-	-	108±11[g]	-	-	108±11	(1)	B
Ba	540±50	-	498±26	479±19	-	-	520±36	-	-	-	-	495±19	(4)	Ba
Br	0.52±0.16	-	-	-	-	< 1.5	0.55±0.01	-	-	-	-	0.55±0.01	(2)	Br
Ca (%)	8.25±0.6	-	10.3±0.5	9.41±0.19	10.5±0.8	-	11±1	9.2±0.5	10.0±0.5[a]	-	-	9.6±0.2	(6)	Ca
Cd	-	-	-	-	-	-	-	-	-	0.72±0.07[b]	-	0.72±0.07	(1)	Cd
Ce	46±2	-	44±2	41.2±0.8	-	-	-	-	-	-	-	42±1	(2)	Ce
Cl	-	-	< 830	-	-	-	-	-	-	-	-	<830	(1)	Cl
Co	9.3±0.3	8.8±0.2	9.18±0.29	8.56±0.17	-	< 31	-	-	-	-	-	8.8±0.2	(4)	Co
Cr	45±1	49±1	37±2	33.1±0.8	-	-	-	-	-	-	-	46±1	(3)	Cr
Cs	-	-	4.46±0.33	4.40±0.10	-	-	-	-	-	-	-	4.41±0.10	(2)	Cs
Cu	-	-	-	< 98	43±4	40±3	34±3	-	-	40±4[b]	-	39±3	(3)	Cu
Dy	-	-	2.48±0.13	2.13±0.14	-	-	-	-	-	-	-	2.32±0.13	(2)	Dy
Eu	-	0.59±0.03	0.63±0.02	0.59±0.01	-	-	-	-	-	-	-	0.60±0.01	(3)	Eu
F	-	-	-	-	-	-	-	-	-	-	990±20[a]	990±20	(1)	F
Fe (%)	2.41±0.05	2.29±0.05	2.21±0.06	2.16±0.04	2.2±0.2	2.18±0.09	2.10±0.04	2.1±0.1	2.24±0.31[a]	-	-	2.18±0.04	(8)	Fe
Ga	-	-	-	-	10.1±1.2	9.8±1.8	6.5±0.7	-	-	-	-	10±1	(3)	Ga
Ge	-	-	-	-	-	< 2.4	-	-	-	-	-	<2.4	(1)	Ge
Hf	1.7±0.1	-	1.72±0.14	1.68±0.04	-	-	-	-	-	-	-	1.68±0.04	(3)	Hf
Hg	0.06±0.01	-	-	-	-	< 4	-	-	0.086±0.005[a]	0.077±0.008[b]	-	0.083±0.004	(2)	Hg
In	-	-	< 0.18	-	-	-	-	-	-	-	-	<0.18	(1)	In
Ir	-	-	< 0.01	-	-	-	-	-	-	-	-	<0.01	(1)	Ir
K (%)	1.83±0.19	-	1.79±0.14	1.77±0.06	1.67±0.12	-	-	1.7±0.1	1.61±0.11[a]	-	-	1.73±0.04	(6)	K
La	21.2±0.5	20.2±0.4	20.8±0.7	23.4±0.3	-	-	-	-	-	-	-	20.6±0.4	(3)	La
Lu	0.26±0.03	-	0.19±0.01	0.214±0.008	-	-	-	-	-	-	-	0.21±0.01	(2)	Lu
Mg (%)	-	-	3.5±1.6	3.6±0.09	-	-	-	3.5±0.2	3.52±0.10[a]	-	-	3.6±0.1	(4)	Mg
Mn	-	-	343±12	334±7	350±30	341±21	300±8	-	395±70[a]	-	-	337±6	(5)	Mn
Mo	-	-	20±2	19±1	21±2	-	20±2	-	-	-	19±2[c]	20±1	(5)	Mo
Na (%)	1.54±0.03	1.58±0.03	1.56±0.04	1.53±0.03	-	-	-	1.7±0.1	-	-	-	1.56±0.03	(5)	Na
Nb	-	-	-	-	-	-	5.7±0.1	-	-	-	-	5.7±0.1	(1)	Nb
Nd	-	-	19±4	14±3	-	-	-	-	-	-	-	16±3	(2)	Nd
Ni	25±2	26±1	21±4	< 36	23±3	20±4	29±1	-	-	-	-	24±2	(5)	Ni
Pb	-	-	-	-	24.5±0.5	24±2	23±1	-	-	23±3[b]	-	24±0.5	(4)	Pb
Rb	76±5	74±1	85±8	74±3	79±6	74±2	82±1	-	-	-	-	75±2	(6)	Rb
Sb	2.0±0.1	1.99±0.10	2.1±0.1	1.90±0.07	-	-	-	-	-	-	-	1.98±0.07	(4)	Sb
Sc	6.8±0.1	7.0±0.1	6.47±0.20	5.93±0.05	-	-	-	-	-	-	-	6.8±0.1	(3)	Sc
Se	2.6±0.3	2.6±0.3	-	2.38±0.30	2.2±0.5	2.1±0.7	-	-	-	-	-	2.5±0.3	(5)	Se
Si (%)	-	-	-	-	15.0±1.0	-	-	15.0±0.8	14.9±1.2[a]	-	-	15.0±0.8	(3)	Si
Sm	3.6±0.1	3.5±0.1	3.08±0.12	3.19±0.07	-	-	-	-	-	-	-	3.25±0.07	(3)	Sm
Sr	840±50	740±40	-	683±29	-	698±19	798±4	-	720±60[a]	-	-	712±19	(5)	Sr
Ta	0.55±0.02	-	0.46±0.02	0.47±0.04	-	-	-	-	-	-	-	0.46±0.02	(2)	Ta
Tb	0.37±0.04	-	0.40±0.07	0.36±0.02	-	-	-	-	-	-	-	0.36±0.02	(3)	Tb
Th	7.0±0.1	7.0±0.2	6.70±0.26	6.18±0.07		6.8±1.7	-	-	-	-	-	6.95±0.10	(4)	Th
Ti (%)	-	-	0.16±0.05	0.17±0.03	0.17±0.03	0.18±0.02	-	0.16±0.01	0.17±0.03[a]	-	-	0.16±0.01	(6)	Ti
U	-	-	4.10±0.16	3.63±0.20	-	-	-	-	-	-	-	3.92±0.16	(2)	U
V	-	-	107±24	92±5	-	-	-	-	-	-	-	93±5	(2)	V
W	-	-	-	-	-	-	-	-	-	-	-	-	-	W
Y	-	-	-	-	12±2	13±1	12±1	-	-	-	-	12±1	(3)	Y
Yb	1.6±0.1	-	1.38±0.05	1.31±0.03	-	-	-	-	-	-	-	1.33±0.03	(2)	Yb
Zn	70±6	65±5	-	75±3	69±7	67±3	63±2	-	-	-	-	65±2	(5)	Zn
Zr	-	-	-	-	56±8	-	49±3	-	-	-	-	50±3	(3)	Zr

A = Battelle Pacific Northwest Laboratory, B = Lawrence Berkeley Laboratory, C = Lawrence Livermore Laboratory, D = University of Colorado
E = U. S. Geological Survey, a = atomic absorption spectroscopy, b = Zeeman atomic absorption spectroscopy, c = colorimetric,
d = fluorimetric, e = delayed neutron, f = gamma-ray spectrometry, g = emission spectroscopy

Table 3. ELEMENTAL COMPOSITION OF DOW MINE RAW OIL SHALE, OS-1 (ppm)

	Neutron Activation Analysis			X-Ray Fluorescence Spectrometry				Other			Average		
	(A)	(B)	(E)	High energy (A)	High energy (B)	High energy (D)	Low energy (B)	(A)	(B)	(D)	Conc	No. of Values	
Al	-	3.41±0.12	-	-	-	-	3.4±0.2	3.4±0.3[a]	-	3.5±0.1[d]	3.43±0.10	(4)	Al
As	77±2	77±6	-	65±5	65±3	64±6	-	-	-	75±6[d]	75±2	(5)	As
B	-	-	-	-	-	-	-	77±8[g]	-	110±25[c]	80±8	(2)	B
Ba	-	1225±47	1410±60	-	-	-	-	-	-	-	1295±47	(2)	Ba
Br	-	-	-	-	<1.5	-	-	-	-	-	<1.5	(1)	Br
Ca (%)	-	10.1±0.5	-	10.3±0.7	-	7.9±1.3	9.0±0.4	9.9±0.5[a]	-	7.3±0.7[a]	9.6±0.4	(5)	Ca
Cd	-	-	-	-	-	-	-	-	1.05±0.11[b]	-	1.05±0.11	(1)	Cd
Ce	-	36±2	34±2	-	-	-	-	-	-	-	35±2	(2)	Ce
Cl	-	<700	-	-	-	-	-	-	-	-	<700	(1)	Cl
Co	9.2±0.2	10.8±0.3	18±5	-	<30	-	-	-	-	-	9.7±0.2	(2)	Co
Cr	28±1	35±2	46±7	-	-	-	-	-	-	-	29±1	(2)	Cr
Cs	-	4.49±0.34	4.4±0.2	-	-	-	-	-	-	-	4.4±0.2	(2)	Cs
Cu	-	-	-	49±5	52±4	44±2	-	-	-	-	46±2	(3)	Cu
Dy	-	1.87±0.11	2.4±0.2	-	-	-	-	-	-	-	2.0±0.1	(2)	Dy
Eu	0.49±0.04	0.54±0.02	0.54±0.01	-	-	-	-	-	-	-	0.54±0.01	(3)	Eu
F	-	-	-	-	-	-	-	-	-	1020±100[a]	1020±100	(1)	F
Fe (%)	1.87±0.04	1.89±0.06	1.87±0.04	1.95±0.31	1.88±0.07	1.5±0.2	1.8±0.1	1.94±0.31[a]	-	-	1.87±0.04	(8)	Fe
Ga	-	-	-	8.7±1.1	8.1±0.2	3.7±0.4	-	-	-	-	8.1±0.2	(2)	Ga
Ge	-	-	-	-	2.8±1.6	-	-	-	-	-	2.8±1.6	(1)	Ge
Hf	-	1.44±0.12	1.45±0.03	-	-	-	-	-	-	-	1.45±0.03	(2)	Hf
Hg	-	-	-	-	-	-	-	0.14±0.007[a]	0.16±0.02[b]	-	0.14±0.01	(2)	Hg
In	-	<0.20	-	-	-	-	-	-	-	-	<0.20	(1)	In
Ir	-	<0.01	-	-	-	-	-	-	-	-	<0.01	(1)	Ir
K (%)	-	1.36±0.13	1.33±0.06	1.25±0.01	-	-	1.2±0.1	1.17±0.11[a]	1.20±0.02[f]	-	1.23±0.02	(6)	K
La	18.4±0.4	18.8±0.8	19±1	-	-	-	-	-	-	-	18.5±0.4	(3)	La
Lu	-	0.16±0.02	0.20±0.02	-	-	-	-	-	-	-	0.18±0.02	(2)	Lu
Mg (%)	-	2.3±1.1	-	-	-	-	2.6±0.1	2.60±0.1[a]	-	2.7±0.2[a]	2.6±0.1	(4)	Mg
Mn	-	275±9	272±14	262±22	258±26	196±16	-	290±70[a]	-	-	272±9	(5)	Mn
Mo	-	32±4	-	27±2	-	29±2	-	-	-	26±2[c]	28±2	(4)	Mo
Na (%)	1.31±0.03	1.40±0.04	1.47±0.06	-	-	-	1.4±0.1	1.46±0.2[a]	-	1.54±0.04[a]	1.36±0.03	(5)	Na
Nb	-	-	-	-	-	4.5±0.2	-	-	-	-	4.5±0.2	(1)	Nb
Nd	-	16±4	15±1	-	-	-	-	-	-	-	15±1	(2)	Nd
Ni	32±3	30±4	-	33±4	26±5	25±1	-	-	-	-	31±3	(4)	Ni
Pb	-	-	-	32±3	30±3	28±1	-	-	29±2[b]	-	29±1	(4)	Pb
Rb	72±4	80±8	68±2	72±5	65±5	68±3	-	-	-	-	68±2	(6)	Rb
Sb	2.6±0.1	3.2±0.2	3.2±0.1	-	-	-	-	-	-	-	3.2±0.1	(2)	Sb
Sc	4.5±0.1	5.16±0.16	5.0±0.1	-	-	-	-	-	-	-	5.0±0.1	(2)	Sc
Se	4.2±0.3	-	-	4.6±0.6	4.1±1.0	-	-	-	-	3.5±0.2[d]	4.3±0.3	(3)	Se
Si (%)	-	-	-	13.5±1.0	-	-	13.0±0.6	13.5±1.0[a]	-	13.0±0.3[a]	13.1±0.3	(4)	Si
Sm	3.0±0.4	2.49±0.11	2.7±0.1	-	-	-	-	-	-	-	2.6±0.1	(3)	Sm
Sr	653±40	-	650±40	-	595±23	620±12	-	660±60[a]	-	-	620±12	(5)	Sr
Ta	-	0.39±0.02	-	-	-	-	-	-	-	-	0.39±0.02	(1)	Ta
Tb	-	0.28±0.05	0.33±0.03	-	-	-	-	-	-	-	0.32±0.03	(2)	Tb
Th	4.6±1.0	5.17±0.20	4.8±0.1	-	6.0±2.0	-	-	-	5.35±0.21[f]	-	4.9±0.1	(5)	Th
Ti (%)	-	0.13±0.05	-	0.18±0.01	0.14±0.02	-	0.11±0.01	0.14±0.03[a]	-	-	0.12±0.01	(4)	Ti
U	-	4.54±0.18	6.1±0.5	-	-	-	-	-	4.24±0.09[f]	5.4±0.3[e]	4.4±0.1	(4)	U
V	-	127±30	-	-	-	-	-	-	-	-	127±30	(1)	V
W	-	2.8±0.4	-	-	-	-	-	-	-	-	2.8±0.4	(1)	W
Y	-	-	-	8.2±1.0	7.8±1.6	8.3±0.4	-	-	-	-	8.3±0.4	(3)	Y
Yb	-	1.04±0.04	1.0±0.1	-	-	-	-	-	-	-	1.03±0.04	(2)	Yb
Zn	91±5	-	-	72±6	74±4	70±5	-	-	91±9[b]	-	74±4	(4)	Zn
Zr	-	-	63±2	54±7	-	49±1	-	-	-	-	49±1	(2)	Zr

A = Battelle Pacific Northwest Laboratory, B = Lawrence Berkeley Laboratory, C = Lawrence Livermore Laboratory, D = University of Colorado, E = U. S. Geological Survey, a = atomic absorption spectroscopy, b = Zeeman atomic absorption spectroscopy, c = colorimetric, d = fluorimetric, e = delayed neutron, f = gamma-ray spectrometry, g = emission spectroscopy

Table 4. ELEMENTAL COMPOSITION OF SPENT OIL SHALE FROM RUN S-11 OF LLL'S 125-kg RETORT PREPARED BY LBL, SOS-11B (ppm)

	Neutron Activation Analysis			X-Ray Fluorescence Spectrometry				Other			Average		
	(A)	(B)	(C)	High energy (A)	High energy (B)	High energy (D)	Low energy (B)	(A)	(B)	(D)	Conc	No. of Values	
Al	-	5.81±0.18	5.86±0.12	5.68±0.3	-	-	5.6±0.3	-	-	-	5.81±0.12	(4)	Al
As	59±1	65±6	54±2	58±5	56±3	60±2	-	-	-	51±4[a]	58±1	(7)	As
B	-	-	-	-	-	-	-	140±15[g]	-	-	140±15	(1)	B
Ba	-	725±50	680±23	-	-	740±31	-	-	-	-	704±23	(3)	Ba
Br	-	-	-	-	<1.8	<1.6	-	-	-	-	<1.6	(1)	Br
Ca (%)	-	14.0±0.7	12.3±0.2	14.5±0.5	-	16±2	12.3±0.6	13.9±0.5[a]	-	-	12.7±0.2	(5)	Ca
Cd	-	-	-	-	-	-	-	-	0.77±0.08[b]	-	0.77±0.08	(1)	Cd
Ce	-	63±4	58.1±1.2	-	-	-	-	-	-	-	58.5±1.1	(2)	Ce
Cl	-	<1180	-	-	-	-	-	-	-	-	<1180	(1)	Cl
Co	11.8±0.2	12.6±0.4	11.9±0.2	11.8±0.2	<38	-	-	-	-	-	11.9±0.2	(4)	Co
Cr	50±2	60±3	50.4±1.0	-	-	-	-	-	-	-	50±1	(2)	Cr
Cs	-	6.96±0.52	6.89±0.14	-	-	-	-	-	-	-	6.89±0.14	(2)	Cs
Cu	-	-	<98	63±5	55±5	48±2	-	-	50±5[b]	-	49±2	(3)	Cu
Dy	-	3.65±0.52	3.22±0.22	-	-	-	-	-	-	-	3.46±0.20	(2)	Dy
Eu	0.86±0.03	0.93±0.04	0.86±0.02	-	-	-	-	-	-	-	0.87±0.02	(3)	Eu
F	-	-	-	-	-	-	-	-	-	980±60[a]	980±60	(1)	F
Fe (%)	3.28±0.02	3.09±0.09	3.03±0.06	3.19±0.22	3.22±0.12	3.2±0.2	2.9±0.2	3.15±0.31[a]	-	-	3.08±0.06	(7)	Fe
Ga	-	-	-	14.6±1.6	13±2	10.4±0.4	-	-	-	-	14.0±1.2	(2)	Ga
Ge	-	-	-	-	<2.1	-	-	-	-	-	<2.1	(1)	Ge
Hf	-	2.84±0.23	2.58±0.05	-	-	-	-	-	-	-	2.59±0.05	(2)	Hf
Hg	-	-	-	-	<4.5	-	-	<0.005[a]	<0.01[b]	-	<0.01	(1)	Hg
In	-	<0.31	-	-	-	-	-	-	-	-	<0.31	(1)	In
Ir	-	<0.01	-	-	-	-	-	-	-	-	<0.01	(1)	Ir
K (%)	-	2.66±0.24	2.55±0.10	2.35±0.17	-	-	2.5±0.1	2.39±0.19[a]	-	-	2.50±0.10	(5)	K
La	30.0±0.4	31.8±1.1	29.8±1.5	-	-	-	-	-	-	-	30.5±0.6	(3)	La
Lu	-	0.32±0.03	0.33±0.01	-	-	-	-	-	-	-	0.33±0.01	(2)	Lu
Mg (%)	-	4.9±1.2	5.2±0.1	4.97±0.10	-	-	4.7±0.2	-	-	-	5.04±0.10	(4)	Mg
Mn	-	482±16	478±10	507±40	481±37	459±48	-	495±40[a]	-	-	480±10	(6)	Mn
Mo	-	27±4	25±2	28±2	-	27±1	-	-	-	33±3[c]	27±1	(4)	Mo
Na (%)	2.41±0.05	2.45±0.07	2.41±0.05	-	-	-	2.4±0.1	-	-	-	2.42±0.05	(4)	Na
Nb	-	-	-	-	-	8.9±0.6	-	-	-	-	8.9±0.6	(1)	Nb
Nd	-	27±5	26±3	-	-	-	-	-	-	-	26±3	(2)	Nd
Ni	36±5	32±7	<41	40±5	31±7	40±3	-	-	-	-	38±3	(5)	Ni
Pb	-	-	-	38±4	37±3	40±2	-	-	30±8[b]	-	39±2	(4)	Pb
Rb	110±11	110±11	102±3	103±7	105±4	123±1	-	-	-	-	104±3	(7)	Rb
Sb	2.9±0.1	3.1±0.2	2.95±0.08	-	-	-	-	-	-	-	2.9±0.1	(3)	Sb
Sc	10.1±0.03	9.28±0.29	8.26±0.16	-	-	-	-	-	-	-	8.51±0.16	(2)	Sc
Se	1.7±0.3	-	1.5±0.4	1.4±0.4	1.4±1.2	-	-	-	-	-	1.6±0.3	(4)	Se
Si (%)	-	-	-	21.5±1.8	-	-	21.7±1.1	22.1±1.2[a]	-	-	21.8±1.1	(3)	Si
Sm	5.2±0.1	4.48±0.20	4.51±0.11	-	-	-	-	-	-	-	4.50±0.11	(2)	Sm
Sr	1040±50	-	965±59	995±60	944±37	1071±21	-	960±60[a]	-	-	1043±21	(5)	Sr
Ta	-	0.69±0.03	0.69±0.04	-	-	-	-	-	-	-	0.69±0.03	(2)	Ta
Tb	-	0.60±0.14	0.51±0.02	-	-	-	-	-	-	-	0.51±0.02	(2)	Tb
Th	9.9±0.2	9.85±0.39	8.93±0.08	-	-	-	-	-	-	-	9.89±0.20	(2)	Th
Ti (%)	-	0.23±0.10	0.22±0.05	0.22±0.02	0.24±0.02	-	0.21±0.02	0.20±0.03[a]	-	-	0.22±0.02	(6)	Ti
U	-	6.33±0.26	6.25±0.30	-	-	-	-	-	-	-	6.30±0.26	(2)	U
V	-	146±34	127±6	-	-	-	-	-	-	-	128±6	(2)	V
W	-	1.8±0.4	<2.5	-	-	-	-	-	-	-	1.8±0.4	(1)	W
Y	-	-	-	20±3	21±2	18±1	-	-	-	-	19±1	(3)	Y
Yb	-	2.06±0.07	1.98±0.04	-	-	-	-	-	-	-	2.00±0.04	(2)	Yb
Zn	130±5	-	124±3	130±10	116±4	105±4	-	-	109±11[b]	-	123±3	(5)	Zn
Zr	-	-	-	86±12	-	107±47	-	-	-	-	86±12	(3)	Zr

A = Battelle Pacific Northwest Laboratory, B = Lawrence Berkeley Laboratory, C = Lawrence Livermore Laboratory, D = University of Colorado, E = U. S. Geological Survey, a = atomic absorption spectroscopy, b = Zeeman atomic absorption spectroscopy, c = colorimetric, d = fluorimetric, e = delayed neutron, f = gamma-ray spectrometry, g = emission spectroscopy

Table 5. ELEMENTAL COMPOSITION OF FISCHER ASSAY SPENT SHALE (FASS)

	Neutron Activation Analysis			X-ray Fluorescence Spectrometry				Other			Average		
	(A)	(B)	(E)	High Energy (A)	High Energy (B)	High Energy (D)	Low Energy (B)	(A)	(B)	(D)	Conc	No. of Values	
Al (%)	-	4.05±0.13	-	-	-	-	4.0±0.2	4.04±0.25[a]	-	4.2±0.1[c]	4.12±0.10	(4)	Al
As	91±2	89±8	-	86±6	79±3	79±3	-	-	-	87±4[a]	82±3	(5)	As
B	-	-	-	-	-	-	-	91±9[g]	-	145±12[c]	110±9	(2)	B
Ba	-	1761±55	1940±50	-	-	-	-	-	-	-	1859±50	(2)	Ba
Br	-	-	-	-	<1.8	-	-	-	-	-	<1.8	(1)	Br
Ca (%)	-	12.2±0.6	-	13.3±1.0	-	9.7±1.2	10.8±0.5	12.7±0.5[a]	-	9.3±0.2[d]	9.8±0.2	(5)	Ca
Cd	-	-	-	-	-	-	-	-	1.28±0.13[b]	-	1.28±0.13	(1)	Cd
Ce	-	44±2	41±1	-	-	-	-	-	-	-	42±1	(2)	Ce
Cl	-	<1355	-	-	-	-	-	-	-	-	<1355	(1)	Cl
Co	11.0±0.2	13.1±0.4	15.8±0.2	-	<34	-	-	-	-	-	11.5±0.2	(2)	Co
Cr	34±1	43±2	52±8	-	-	-	-	-	-	-	36±1	(2)	Cr
Cs	-	5.65±0.42	5.6±0.1	-	-	-	-	-	-	-	5.60±0.11	(2)	Cs
Cu	-	-	-	68±7	66±5	47±1	-	-	-	-	67±5	(2)	Cu
Dy	-	2.28±0.12	2.7±0.1	-	-	-	-	-	-	-	2.5±0.1	(2)	Dy
Eu	0.58±0.02	0.65±0.03	0.68±0.01	-	-	-	-	-	-	-	0.68±0.01	(2)	Eu
F	-	-	-	-	-	-	-	-	-	1420±200[d]	1420±200	(1)	F
Fe (%)	2.23±0.04	2.34±0.07	2.36±0.05	2.5±0.3	2.42±0.09	1.8±0.2	2.2±0.1	2.68±0.31[a]	-	-	2.31±0.04	(7)	Fe
Ga	-	-	-	10.7±1.3	8.4±2.0	4.6±0.1	-	-	-	-	10.0±1.3	(2)	Ga
Ge	-	-	-	-	2.8±1.8	-	-	-	-	-	2.8±1.8	(1)	Ge
Hf	-	1.78±0.14	1.82±0.04	-	-	-	-	-	-	-	1.82±0.04	(2)	Hf
Hg	-	-	-	-	<3.9	-	-	0.041±0.001[a]	0.035±0.003[b]	-	0.040±0.001	(2)	Hg
In	-	<0.21	-	-	-	-	-	-	-	-	<0.21	(1)	In
Ir	-	<0.01	-	-	-	-	-	-	-	-	<0.01	(1)	Ir
K (%)	-	1.51±0.14	1.54±0.03	1.6±0.1	-	-	1.5±0.1	1.41±0.11[a]	-	1.52±0.03[a]	1.53±0.03	(6)	K
La	21.0±0.4	22.0±0.9	23±1	-	-	-	-	-	-	-	21.2±0.4	(2)	La
Lu	-	0.15±0.02	0.16±0.01	-	-	-	-	-	-	-	0.16±0.01	(2)	Lu
Mg (%)	-	3.0±1.3	-	-	-	-	3.1±0.2	3.2±0.1[a]	-	2.94±0.08[a]	3.0±0.1	(4)	Mg
Mn	-	339±11	340±10	370±30	351±32	224±25	-	375±70[a]	-	-	342±10	(5)	Mn
Mo	-	38±5	-	39±3	-	36±2	-	-	-	28±2[c]	37±2	(3)	Mo
Na (%)	1.62±0.03	1.74±0.05	1.76±0.04	-	-	-	1.8±0.1	1.67±0.10[a]	-	1.90±0.07[a]	1.77±0.04	(5)	Na
Nb	-	-	-	-	-	5.6±0.2	-	-	-	-	5.6±0.2	(1)	Nb
Nd	-	19±4	18±1	-	-	-	-	-	-	-	18±1	(2)	Nd
Ni	38±1	33±5	-	41±5	33±6	29±3	-	-	-	-	38±1	(4)	Ni
Pb	-	-	-	43±4	38±3	37±3	-	-	32±8[b]	-	38±3	(4)	Pb
Rb	91±10	97±10	87±2	81±6	82±3	86±1	-	-	-	-	86±2	(6)	Rb
Sb	3.6±0.1	3.8±0.2	4.1±0.2	-	-	-	-	-	-	-	3.6±0.1	(2)	Sb
Sc	5.3±0.1	6.35±0.20	6.2±0.1	-	-	-	-	-	-	-	6.24±0.12	(2)	Sc
Se	5.2±0.3	-	-	4.9±0.7	4.9±1.0	-	-	-	-	4.3±0.2[d]	5.1±0.3	(3)	Se
Si (%)	-	-	-	16.1±1.0	-	-	15.6±0.8	16.3±1.2[a]	-	15.7±0.3[a]	15.7±0.3	(4)	Si
Sm	3.6±0.2	3.01±0.13	3.3±0.1	-	-	-	-	-	-	-	3.4±0.1	(2)	Sm
Sr	790±50	-	860±50	810±60	770±30	771±40	-	-	-	-	790±30	(5)	Sr
Ta	-	0.47±0.02	-	-	-	-	-	-	-	-	0.47±0.02	(1)	Ta
Tb	-	0.35±0.06	0.46±0.02	-	-	-	-	-	-	-	0.45±0.02	(2)	Tb
Th	5.4±1.0	6.35±0.25	5.9±0.1	-	7.2±2.2	-	-	-	-	-	6.0±0.1	(4)	Th
Ti (%)	0.23±0.04	0.15±0.06	-	-	0.16±0.02	-	0.13±0.02	-	-	-	0.14±0.02	(3)	Ti
U	-	5.38±0.22	7±1	-	-	-	-	-	-	6.4±0.2[e]	6.4±0.2	(2)	U
V	-	161±36	-	-	-	-	-	-	-	-	161±36	(1)	V
W	-	3.1±0.4	-	-	-	-	-	-	-	-	3.1±0.4	(1)	W
Y	-	-	-	12.6±1.9	12±2	10.2±0.7	-	-	-	-	10.6±0.6	(3)	Y
Yb	-	1.25±0.05	1.3±0.1	-	-	-	-	-	-	-	1.3±0.1	(2)	Yb
Zn	109±5	-	-	96±9	92±4	72±3	-	-	103±10[b]	-	99±4	(4)	Zn
Zr	-	-	110±20	72±10	-	61±2	-	-	-	-	61±2	(2)	Zr

A = Battelle Pacific Northwest Laboratory, B = Lawrence Berkeley Laboratory, C = U. S. Geological Survey, D = University of Colorado, E = U. S. Geological Survey, a = atomic absorption spectroscopy, b = Zeeman atomic absorption spectroscopy, c = colorimetric, d = fluorimetric, e = delayed neutron, f = gamma-ray spectrometry, g = emission spectroscopy

RAW OIL SHALE - RAW 1B

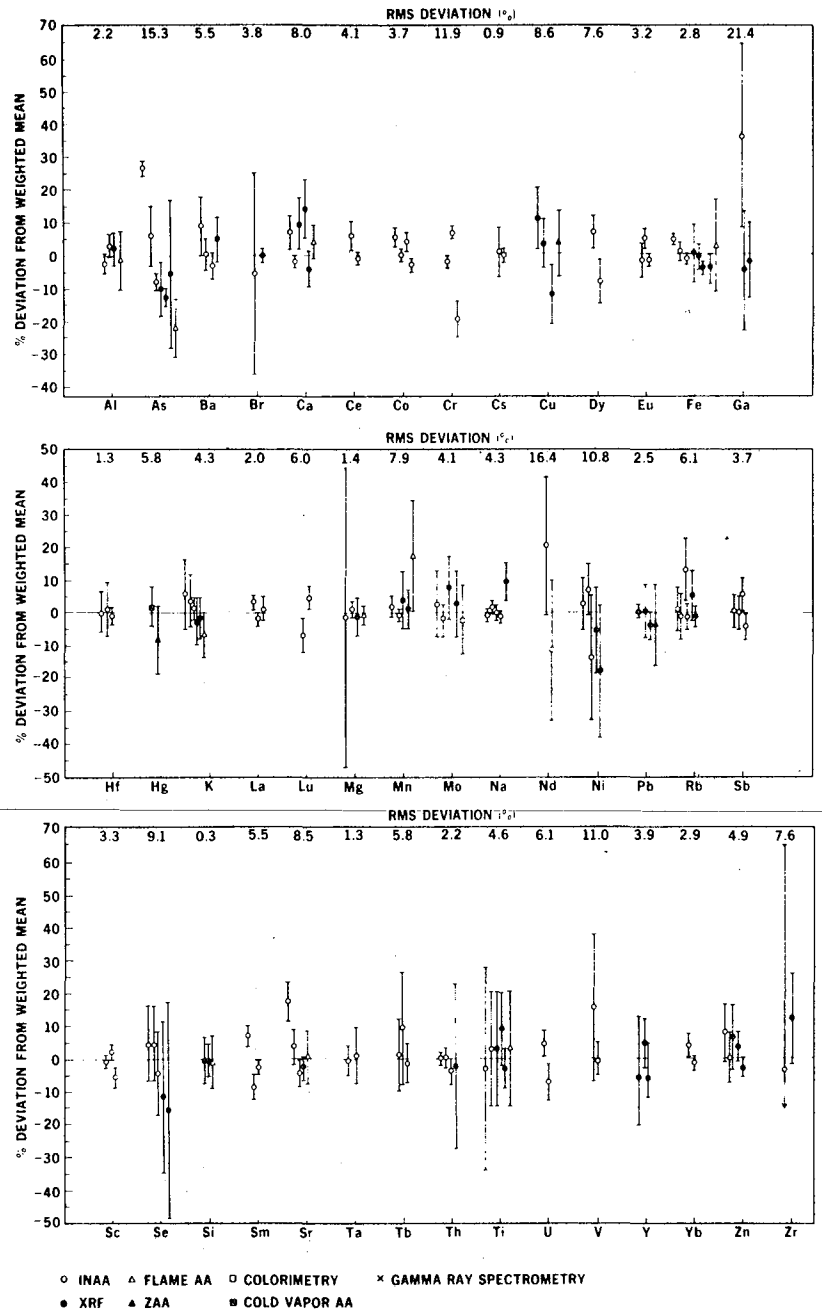

Figure 1. Relative performance of analytical techniques on raw oil shale RAW 1B

RAW OIL SHALE - OS - 1

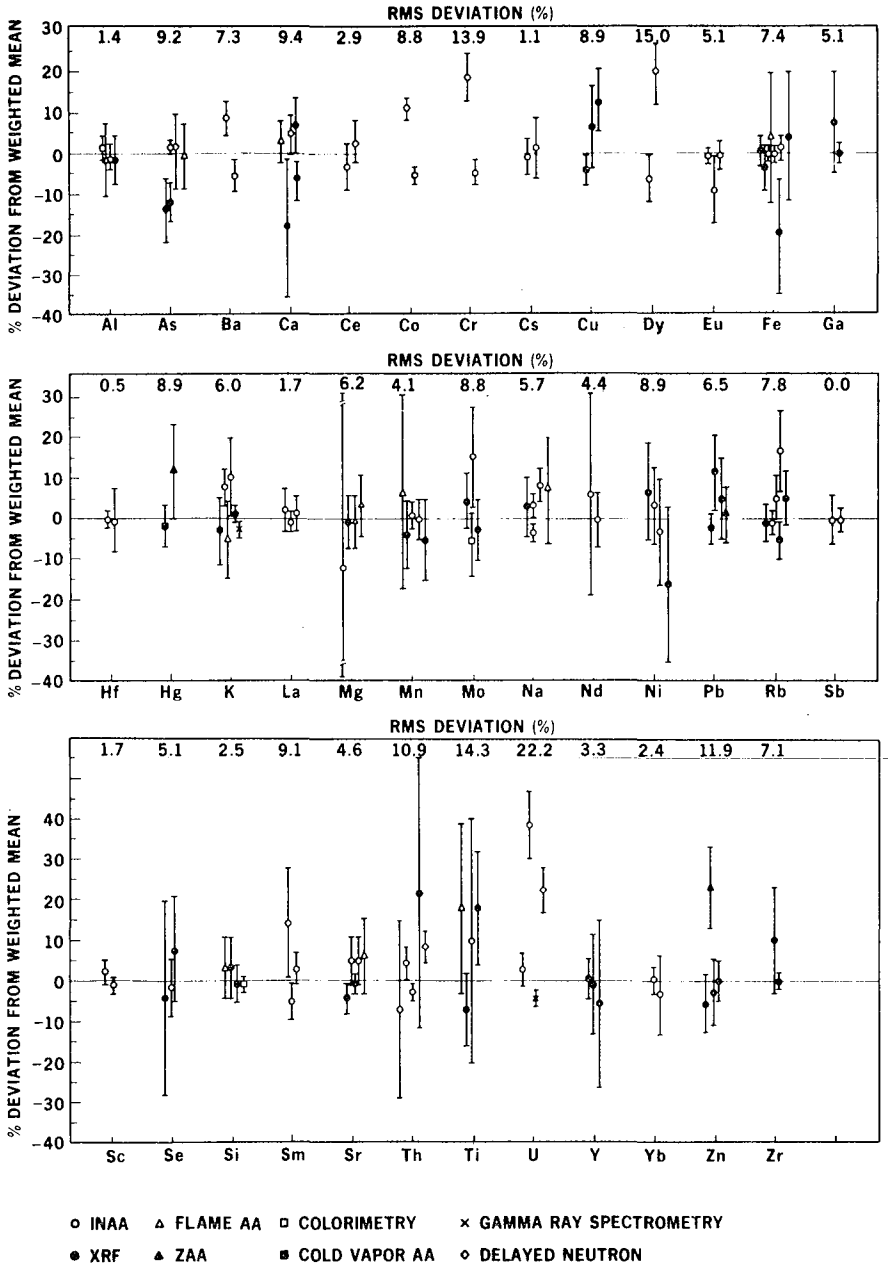

Figure 2. Relative performance of analytical techniques on raw oil shale OS-1

SPENT OIL SHALE - SOS - 11B

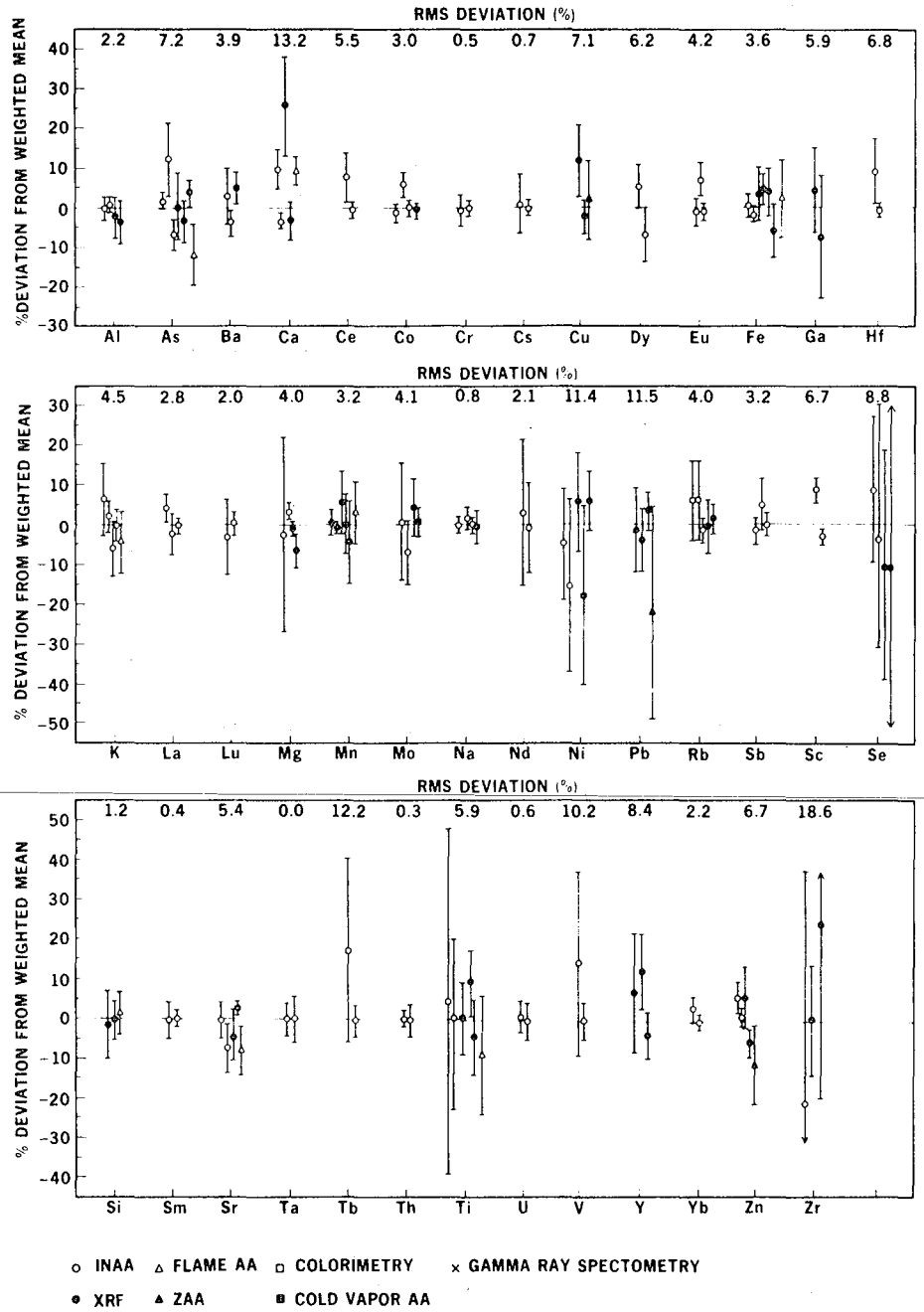

Figure 3. Relative performance of analytical techniques on spent oil shale SOS-11B

FISCHER ASSAY SPENT SHALE - FASS

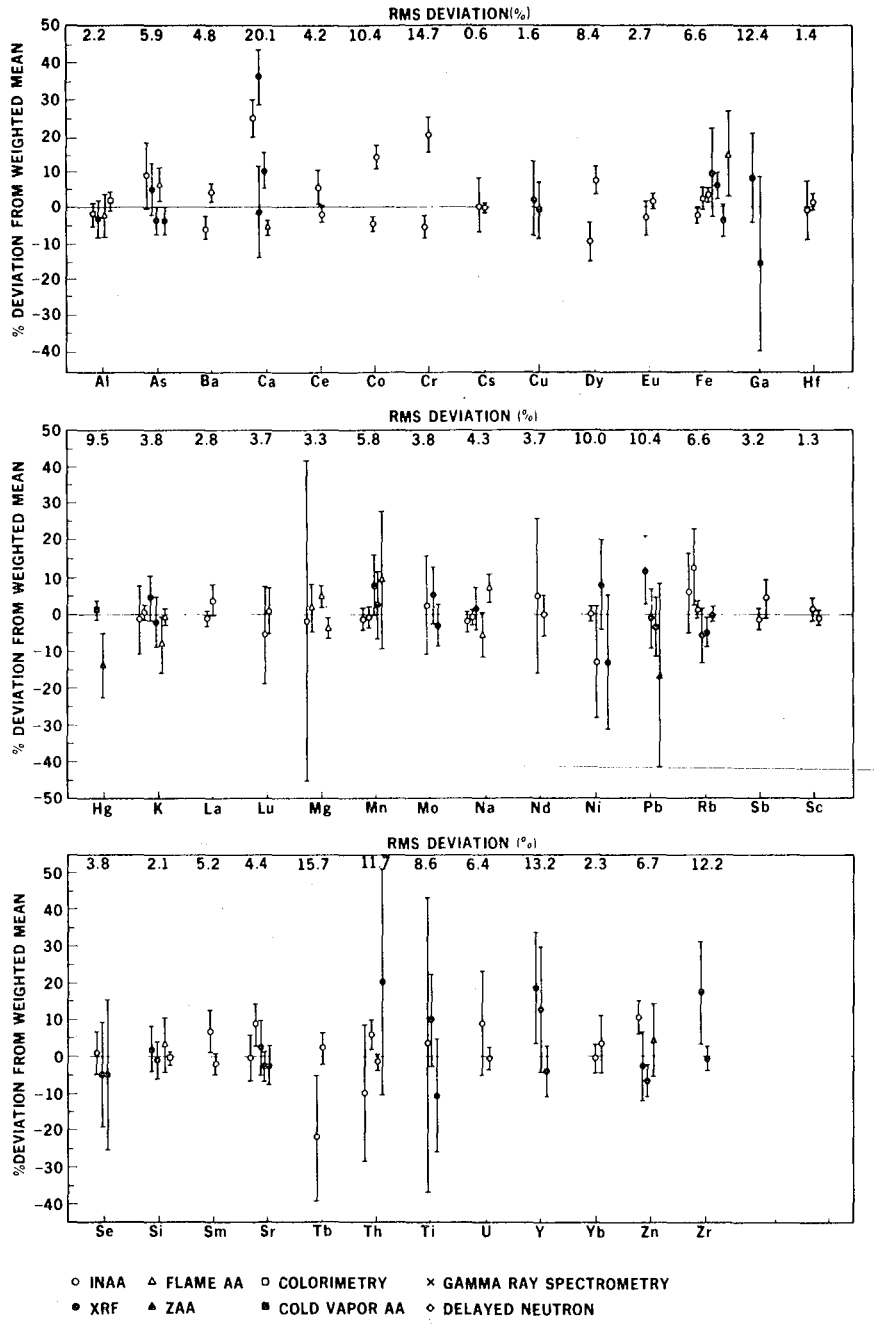

Figure 4. Relative performance of analytical techniques on Fischer assay spent shale FASS

and the percent root-mean-square deviation for the element set determined as

$$\%RMS = 100 \left[\sum_{i=1}^{N} \left(\frac{X_i - \bar{X}}{\bar{X}} \right)^2 N^{-1} \right]^{1/2}$$

The results of applying this procedure to the data developed in this study are shown by the last column in Tables 2 to 5 and by Figures 1 to 4. The last column of each table summarizes the error-weighted average obtained for each sample after applying Chauvenet's criterion[28] and the number of separate determinations included in the average. Application of this criterion resulted in the rejection of 12 values for SOS-11B, 16 values for OS-1, 21 values for FASS, and 19 values for RAW-1B. The errors reported in the last column are the larger of the error-weighted standard deviation of the laboratory values included in the average, or the smallest reported error of the individual laboratory values included in the average.

Figures 1 through 4 summarize the %RMS deviation, %DEV, and the coefficient of variation for each technique in an element set. The %RMS deviation is recorded along the top of each graph and is a measure of the uncertainty in the determination of the reported means for an element set. The %RMS deviation ranged from 0.0 to 22.2 in this study, with 85% of the values falling below 10%. The %DEV is plotted for each technique and is indicated by a geometrical symbol that designates the technique. The corresponding error bars are the percent standard deviation for each technique.

One interesting feature of this type of plot is that since an error-weighted average was used, the points will not necessarily distribute symmetrically about zero. This is particularly the case if a single point with a very small error dominates the average. Thus, a careful error analysis is critical. This is particularly serious for a small number of points. These problems have been partially alleviated by assigning a minimum analytical error of 2% to all points, and by evaluating the %RMS deviation. An analysis of this type assumes a normal distribution of errors. In some cases, such as in the reported results for arsenic, there may be a bimodal distribution caused by a systematic difference between methods. If the cause of the discrepancy was known, or at least suspected, the offending datum was rejected. Otherwise, the values were retained. One such example involved a large fission product interference in the INAA analysis of Zr.

DISCUSSION

The results of this study show that most elements studied here can be reliably and accurately determined in raw and spent oil shales if careful measurements are made. Of the 52 elements surveyed, 20 were determined by more than one technique and a minimum of two measurements was obtained on 40 elements. Typically, only a single measurement, or an upper limit, was obtained for B, Cd, F, Hg, In, Ir, and Nb. Excellent agreement between laboratories and techniques was obtained for most elements

all samples. There was no significant difference in the results obtained for the raw and spent oil shale samples. The %RMS deviation was less than or equal to 10% for all elements on all samples except Ca, Cr, Ga, Pb, Ni, Tb, Zr, Y, Dy, Th, U, Zn, Ti, V, As, and Nd. The elements As, Ca, Fe, Rb, Se, Ti, and Zn were the most frequently measured elements and the major elements Al, Mg, Na, Si, and Fe were precisely measured by at least three laboratories and by using three separate techniques.

This is the first major interlaboratory comparison of energy-dispersive X-ray fluorescence spectrometry with other techniques. Intercomparison studies heretofore focused on neutron activation analysis and atomic absorption spectroscopy.[29,30] This work affords the first opportunity to assess the performance of recently developed X-ray techniques on geochemical samples for a range of elements.

More than one technique was used for the analysis of 38% of the elements (Al, As, Ca, Fe, Ga, K, Mn, Mo, Na, Ni, Pb, Rb, Se, Si, Sr, Th, Ti, U, Zn, Mg). The agreement between techniques for these elements was excellent with a few exceptions as discussed below.

Neutron activation analysis determined the most elements (38) and typically produced the most accurate and precise results. This is the only technique that was used to measure Ba, Ce, Cr, Cs, Eu, La, Sb, Sc, Sm, Yb, Dy, Cu, Nd, and Tb in all samples. Good interlaboratory agreement was obtained on all elements by INAA except Co, Cr, Dy, and Sm. Good agreement was obtained between the absolute INAA method of analysis used by LLL and the calibration method used by PNL, USGS, and LBL.

X-ray fluorescence spectrometry was used to measure 27 elements in this study. It was the only technique used for Cu, Nb, Ga, and Y. These techniques are not as precise as INAA; precisions of 10% were typical. Interlaboratory agreement was excellent and generally better than for INAA, presumably due to the larger analytical errors. Two types of XRF systems and various sample preparation and data reduction procedures were used in this study. High-energy XRF, in which the elements Si and heavier were measured, was used to analyze thin-film and thick samples using pure-element and standard rock calibration standards, respectively. Low-energy XRF, in which elements 11 through 20 were determined, was used to analyze $LiBO_2$ discs using standard rocks. These techniques agreed well with other methods of analysis except the high-energy system that used thin-film samples. That technique yielded low results for Mn and Zn and erratic results for other elements. Approximately 25% of the measurements made by the thin-specimen technique were discarded when Chauvenet's criterion was applied to the data set. This is believed to be due to X-ray absorption and matrix correction procedures.[12,13]

An analytical problem was noted for As in the raw oil shales in this study. The results obtained by INAA were typically about 15% higher than the results obtained by XRF. This same trend was evident in more than 100 samples not reported here. This disagreement was investigated by both PNL and LBL during the course of this study but its source was not identified. There are no obvious interferences in the measurement of

As by either INAA or XRF. Additional work completed by some of the authors, in which material balances were calculated for various retorting processes, suggests that the problems lies with the XRF technique.

Atomic absorption spectroscopy was used to determine Hg, Al, Ca, Fe, K, Mg, Mn, Na, Sr, As, and Ti, and Zeeman atomic absorption spectroscopy was used to determine Cd, Hg, Pb, and Zn. Both of these AA techniques produced accurate and precise results. The interlaboratory and inter-instrumental agreement was good except for Ca by AA in two samples and Na in one sample.

The colorimetric procedures used for Si and Mo agreed well with instrumental techniques but the fluorimetric procedure for Se yielded low results on the two samples reported here. However, good agreement between the Se fluorimetric procedure and instrumental techniques was obtained on other samples not reported here.

Additional work is required to develop reliable analytical techniques for B and F, which are important constituents in oil shales due to their leaching potential. Neither of these elements can be readily measured by the instrumental methods INAA, SRF, and AA, and chemical methods have not been adequately developed for oil shale matrices. In this study, B was measured by dc emission and colorimetrically. The results obtained by these two techniques disagree by more than 2 standard deviations of the reported errors. Similarly, F was measured by only a single technique. Additional work is required to develop and validate reliable techniques for the measurement of both B and F.

SUMMARY

Two samples each of raw oil shale and spent oil shale were prepared as reference samples and analyzed by four laboratories using neutron activation analysis, X-ray fluorescence spectrometry, atomic absorption spectroscopy, and other techniques. Excellent agreement was obtained between techniques and laboratories except for the thin-film XRF technique. The %RMS deviations were less than or equal to 10% for 85% of the values. In general, the INAA analysis procedures yielded the most accurate and precise results. The XRF and colorimetric methods compared well with INAA but they were not as precise. Poor interlaboratory agreement was obtained for Cr, Co, Dy, and Sm by INAA, and an analytical problem was noted for As and Zr. Additional work is required to develop and validate reliable methods for B, F, Cd, and As.

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