TRACE ELEMENTS
IN
OIL SHALE

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for Period June 1, 1976 - May 31, 1977

Environmental Trace Substances Research Program
University of Colorado
Colorado State University
Colorado School of Mines

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FOREWORD

The following report describes the work on ERDA Contract E-76-S-02-4017.*000 for the period June 1, 1976 to February 28, 1977.

During the period from June 1, 1976 to February 28, 1977 Dr. Chappell has devoted approximately 13% of his time to the present effort, while Dr. Runnells has devoted 25% of his time. During the remaining period Dr. Chappell will devote approximately 13% and Dr. Runnells approximately 20% of their time, respectively, to the project. The work to date is in compliance with the contract.

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ABSTRACT

During the initial year of funding a substantial number of samples of water, stream sediment, soils, plants oil shale, spent shale, shale oil and other materials were collected by the investigators for analyses. A considerable amount of effort was also involved in the development and validation of methods for preparing and analyzing these samples for trace element content. Among the results are:

1. Cu, Li, and Zn exhibit well-defined trends in soils over the Piceance Basin, with values increasing from north to south.
2. As, Mo, B, and Se are all elevated in the soils of the Piceance Basin.
3. Mo and B are more soluble in TOSCO spent shale than in unprocessed shale and are also elevated in plants growing on spent shale.
4. F is less soluble in spent (TOSCO) shale than in unprocessed oil shale, but nevertheless, the levels in leachates are quite significant (25 mg/l). Moreover, the F is not readily leached out.
5. Results to date show that As and Se are not very soluble in spent shale (TOSCO) and are not taken up to a significant extent by plants.

PROGRESS REPORT

TRACE ELEMENTS IN OIL SHALE

Chapter I Introduction

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The purpose of this research program is to understand the potential impact of an oil shale industry on environmental levels of trace contaminants in the region. The program involves a comprehensive study of the sources, release mechanisms, transport, fate and effects of toxic trace chemicals, principally the trace elements, in an oil shale industry. The study group is a multi-institutional, interdisciplinary team from the University of Colorado, Colorado State University, and the Colorado School of Mines.

The program is a part of the Environmental Trace Substances Research Program at the University of Colorado. The Co-Principal Investigators are Dr. Willard R. Chappell, Department of Astrogeophysics, and Science Applications, Inc., and Dr. Donald Runnells, Department of Geological Sciences, University of Colorado. The other senior investigators are:

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The present report describes the progress of the first year of funding as of February 15, 1976.

The initial focus of the program is on those toxic trace elements which we believe are likely to be mobile in the environment of the oil shale region. Because of the alkaline nature of the processes we believed that those elements would be As, Mo, Se, F, and B. Much of the effort during the first year has gone into developing methodology. A large number of samples of various types were collected; analyses are complete on some and underway on others.

Dr. Klusman has been directing the study consisting of a regional trace element reconnaissance in order to determine the background on a regional basis. This work also includes a more intensive study of the oil shale lease sites. Last summer Dr. Klusman and his students conducted an extensive sampling survey of the Piceance Basin. Hundreds of samples of soil, stream sediment, and plants were collected for an analysis of variance study to determine the scale and type of variability of various trace elements in these samples. The results obtained to date are described in Chapter Two. Briefly these results are:

For Soils the data to date indicates that:

1. For most elements the greatest variation occurs on a length scale of 0.1 to 3 km. This agrees with the USGS studies elsewhere which show high local variation in soils.
2. Although there is significant visible difference in soil development and characteristic vegetation between ridge tops and bottom valley, the results do not show significant differences in trace element abundance.
3. It was determined that stable geochemical maps can be determined for Fe, Be, Cu, Li, and Zn. All of these show higher concentrations in the southern part of the Piceance Basin and Cu, Li and Zn exhibit well-defined trends from north to south.

4. As, B, Mo, and Se are all elevated in the soils of the Piceance Basin. While F levels are high in the parent material they are not particularly high in the surface soils.

For stream sediments the data show:

1. A significant difference exists for trace elements between streams.
2. That substantial variations occur at small distances.
3. For some parameters such as Mo, Hg, and organic matter, it may be possible to choose streams as localities in characterizing the Piceance Basin as a whole.
4. For Tract C-a the mean values for Mo and As were 4.7 and 9.2 ppm, respectively.

On the basis of the regional data a sampling program was designed for Tract C-a and vicinity. The 6 X 8 mile area was sampled on a 1/2 mile grid yielding 221 sampling locations. The samples are being processed for analyses and substantial data will be available in the next few months.

Dr. Wildeman has been conducting a mass balance study of the Fischer Assay as a model retort. In the process of this work he has also developed "standard" samples of oil shale and spent shale in order to calibrate the analyses of these materials. Several samples of this material have been submitted for analyses. This material also provides the feedstock for the mass balance measurements. Tests for homogeneity were made using an x-ray fluorescence method for Rb and Sr. The conclusion was that the different splits of the standard are homogeneous to within $\pm 5\%$.

The Fischer assay studies were run on 120 splits of 100 g each of the "standard" oil shale. These runs were made on the equipment at the TOSCO Research Center in Golden in order to determine the weight percents of oil, water, and spent shale. In all, 46 percentage determinations were made and the samples prepared for trace element analyses.

Only preliminary results are available for the trace element analyses on the shale standards and Fischer Assay samples. However, analyses by several independent analytical methods are anticipated. The results obtained for As and Mo show close agreement between XRF and wet chemical techniques. The preliminary results on the mass balance study show that

only small amounts of the trace elements are likely to be lost in the Fischer Assay. This fact demands special care in the analyses and hence the use of several analytical techniques.

The work by Dr. Wildeman is described in detail in Chapter Three.

Dr. Runnells has been studying the potential for toxic trace elements to be leached from spent shale and to contaminate surface or groundwater. This study involves both laboratory and field studies. A number of laboratory studies were made to determine the solubilities of various trace elements in spent shale. These studies involved the preparation of slurries of oil shale or spent shale and water that were shaken for varying lengths of time in order to determine the time required to reach equilibrium. To date, the only spent shale used has been the standards prepared by Dr. Wildeman from TOSCO II spent shale.

A number of interesting results have been obtained and are described in Chapter Four. These include:

1. For Mo there is a significant increase in solubility for spent shale (3.2 mg/l) compared to fresh shale (0.8 mg/l). These values are close to or above the effluent guidelines established for the mining and mineral dressing industry by the EPA. The equilibrium concentration is reached very quickly, after only one day of shaking.
2. For B there is a preliminary indication that B solubility is also higher in spent shale compared to fresh shale. Unlike Mo the equilibrium is reached very slowly and was not obtained even after the longest period of shaking; 127 days tried so far. The amount released into solution was about 5 mg/l at the end of 127 days. Some plants are sensitive to B and can tolerate no more than 1 mg/l.
3. For F the data showed lower solubility in spent than in fresh shale. The final concentration for spent shale is 25 mg/l, however, and this is well above the present 2 mg/l drinking standard. Fresh shale releases its F much more rapidly than spent shale with equilibrium being reached for fresh shale within one day and for spent shale within about 30 days.
4. For As and Se the data show that the solubilities in spent and fresh shale are about the same. However, these solubilities are very low, with a mean of about 0.04 mg/l for

As and 0.02 mg/l for Se in the leachate. Since the concentrations of Se and As in the original samples are 3 and 74 ppm, respectively, As is far less soluble than Se. For both As and Se it appears so far that neither will present a hazard insofar as the leaching of TOSCO II spent shale is concerned.

Dr. Runnells is currently engaged in studies of the leachate produced by laboratory columns of spent TOSCO II and Fischer Assay shale. Among the results obtained to date is data showing that the concentration of F remains high (10-20 mg/l). This is in sharp contrast to a rapid drop in specific conductance and the molybdenum concentration after a few pore volumes of water pass through the column. This means there is a large reservoir of F in the shale capable of replenishing F to the percolating water, unlike dissolved salts which are rapidly leached out. Thus, the methods proposed for removing the high salt content will not be adequate for controlling F.

Filtration experiments indicate that As, Se and Mo appear as truly dissolved species in the leachates. Data is not yet available for F and B.

Dr. Lindsay has been studying the uptake of toxic trace elements by plants. He and his students sampled revegetation plots, established by Dr. W.A. Berg of Colorado State University, at Anvil Points and Parachute Creek. Two types of spent shales are involved, TOSCO and USBM. The sites consist of plots having varying amounts of soil cover and different leaching techniques, and were seeded with mixtures of native grasses and shrubs.

Samples of western wheatgrass and fourwing saltbrush were taken for trace element analyses. Results obtained to date show elevated levels of Mo and B in the plants in some of the plots containing spent shale. These results are consistent with the increased solubilities reported by Dr. Runnells. At present the data on Se and As indicate average or low concentrations for these elements. This result is also consistent with the work by Dr. Runnells. At present the F analyses are incomplete. These results could be especially interesting with regard to the results by Dr. Runnells on the effects of leaching.

The analytical laboratory is under the direction of Drs. Walton and Meglen. While there was some difficulty introduced by the decision of Dr. Glenn Bentley, who was previously in charge of the analytical lab, to accept a position at the Los Alamos Scientific Laboratories, we were fortunate in being able to hire Dr. Robert Meglen, who had previously been in charge of the analytical lab from 1971 to 1975. Although this change caused some delays, considerable progress has been made since Dr. Meglen's arrival.

At this point we are confident of our methods for analyzing As, Mo, F, Se, and B in simple aqueous solutions. Geological samples have presented the most complex problems because the treatments used to completely dissolve the silicates often cause a loss of the more volatile elements. Four major types of samples are being examined:

1. Geological
2. Biological
3. Waters
4. Oil

Combined with the five elements this presents 20 basic element/sample types to consider. At present we have validated methods for 11 of these groups. The methods for three more of these groupings are near validation and work is in progress on the remaining six. Most of the difficulties are involved with selenium.

We feel confident that by June 1 we will be performing routine analyses of all but a few of the types of samples and elements of concern. We expect, however, that a need will continue for methodology development and refinement.

PROGRESS REPORT

TRACE ELEMENTS IN OIL SHALE

Trace Element Reconnaissance in the Oil Shale Region

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INTRODUCTION

The anticipation of an oil shale industry in Colorado, Utah, and Wyoming has generated considerable interest and concern in the potential environmental impact which may result from extraction of shale oil from the shale. As a result of this concern, baseline studies of various types are being carried out by several groups including the tract leasees and university groups. These baseline determinations must precede studies dealing with the changes in distribution of elements and compounds resulting from energy resource development.

The present study was initiated in the summer of 1975 with support from the Colorado Energy Research Institute. At that time, an initial reconnaissance sampling of surface soils and stream sediments was carried out according to a plan contained in a proposal to ERDA. Due to delays in ERDA funding, most of the soil samples collected during this first phase were analyzed by the U.S. Geological Survey Regional Geochemistry Section, which had interest in this problem but inadequate funding for its own program. ERDA suggested a refocusing of this phase of the program from a strictly regional study to include a more detailed examination of the areas with prime potential for development. This was done in the second phase of the sampling which was initiated in July, 1976. Plant material was also collected as part of this phase and additional analytical work was carried out on the stream sediments collected during the first phase.

OBJECTIVES

The objectives of the study are twofold: 1) determine if there exist any trace element anomalies in the surficial materials of the Piceance Creek Basin and, 2) determine the natural variability in trace element composition of these materials.

Based on geologic and geochemical conditions of formation of the oil shale, some predictive capability as to which elements are likely to be of environmental concern can be made. Those elements which are toxic to plants and animals and mobile as anions under alkaline conditions are a potential hazard. The trace elements arsenic, boron, fluorine, molybdenum, and selenium are of prime concern, although additional elements have been analyzed in some of the samples.

RESULTS AND DISCUSSION

Rock Samples

Analytical results (Table I) from selected rock outcrop samples taken at the beginning of the study indicated that some of these elements are elevated above crustal abundances in the Parachute Creek member which contains the oil shale and the Uinta Formation which will be potential overburden material. Thus it appeared that this was a reasonable choice of constituents for prime consideration.

Table I

X-Ray Fluorescence Analysis of Selected
Piceance Basin Rock Samples (ppm)

Crustal Abundance		Parachute Cr. Mbr. (n=8)			Uinta Fm.(n=5)		
		Min.	Mean	Max.	Min.	Mean	Max.
Mo	1.5	3	17	40	2	3	6
As	1.6	5	33	110	5	10	21
Se	0.05	2	2	2	2	2	3
Zn	70	29	47	95	19	39	52

Soils

The sampling design for the study of the soils in the Piceance Creek Basin is a partially unbalanced nested analysis of variance design. The sampling localities are shown diagrammatically in Figure 1. The initial sampling design, as used in the field, was balanced. Within each of 36 townships, two sections were chosen at random. Within each section, two samples of surface soil were collected 100 meters apart. All four samples within a given township were collected either from ridge tops or valley bottoms. Four townships were grouped into "supertownships". Ridge tops and valley bottom sampling alternated according to a checkerboard design. By eliminating one sample from one section in each township, a slightly unbalanced design resulted in a reduction of analytical load of 25 percent. These samples were analyzed by the U.S. Geological Survey prior to initialization of the ERDA supported research.

Level 1 (the top level) was designed to examine geochemical differences between soils on ridge tops and those in valley bottoms; level 2 was designed to examine geochemical differences at geographic scales greater than 19 km

Figure 1 --Index map (top) showing location of study area, lease tracts Ca and Cb (stippled), and distribution of the Green River Formation and soil sampling localities. Map (bottom) showing soil sampling design and number of samples at each locality. Piceance Creek Basin, Colorado.

(between supertownships); level 3 examines differences at scales from 3 to 19 km (between townships); level 4 examines differences at scales from 0.1 to 3 km (between sections); level 5 examines differences at a scale of 100 m (between samples); level 6 measures analytical precision and includes errors due to sample inhomogeneity, sample preparation, and analysis.

Logarithmic variance components for 37 elements in surface soils from Piceance Creek Basin (Table II) shows that most of the geographic variation for most elements occurs between sections (0.1 to 3 km). This conclusion supports analysis of variance results for soils from other areas which indicate that most of the variability in soil composition occurs at local scales (U.S. Geological Survey, 1975, p. 20-28, 36-49).

Of the 37 elements listed in Table II, 27 have significant variance components at the section level (Al, Ca, Fe, Mg, K, Si, Na, Ti, As, B, Ba, Be, Co, Cr, Cu, Ga, Hg, Li, Mo, Pb, Rb, Sc, Sr, V, Y, Yb, and Zn).

Only 10 elements (Al, K, Si, Na, Ti, F, Li, Ni, Zn and total C) have significant variance components at the sample level (100-meter distance), and only five elements (Ca, Na, Hg, Sr, and total C) have significant variance components at the township level (3-19 km). More than one-third of the elements listed in Table II (14 of 37) have significant variability between supertownships (<19 km). These 14 elements include Ca, Fe, Mg, Si, Ti, B, Be, Cr, Cu, Ga, Li, Y, Yb, and Zn. Although soil development and characteristic vegetation on ridge tops visibly differ from than in bottom valleys, we were surprised to find that there were no significant elemental differences between soil samples collected on ridge tops and those collected in valley bottoms. This means that the ridge top and valley bottom samples can be viewed as part of the same population. It was expected that there would be differences between ridge tops and valley bottoms due to differences in soil development and vegetative cover.

By a quantitative examination of the distribution of the variance it can be determined that the sampling was adequate to describe the variability for five elements (Fe, Be, Cu, Li, and Zn) in a map form. If most of the variance is at the upper geographic scales, a relatively limited number of samples will produce a stable (reproducible) geochemical map. If the variance is concentrated at local scales as is the case for As, only small scale sampling will allow a map representation of the As concentrations in soils. In this case, sampling and analytical costs restrict the description of the basin-wide data to a mean, range and deviation.

All five elements for which stable geochemical maps can be made show higher concentrations in the southern part of the basin and three (Cu, Li, and Zn) exhibit well-defined trends in that direction. Concentrations of soil Zn increase from 68 ppm in the northeastern part of the basin to almost 100 ppm in the southwestern part. Figure 2 illustrates the Zn distribution. A more detailed discussion of the results of the first phase soil studies is published (Ringrose, et.al., 1976).

The five elements (As, B, F, Mo, and Se) previously discussed as a potential environmental hazard are elevated in concentration in the soils

Table II

Analysis of variance of surface soil chemistry, Piceance Creek Basin, Colorado
 [* indicates component is significantly different from zero at the 0.05 probability level]

Element	Total Logarithmic Variance	Variance components as percentage of total variance					Analytical Error
		Between Ridge Tops and Valley Bottoms	Between Super-townships (>19 km)	Between Townships (3-19 km)	Between Sections (0.1-3 km)	Between Samples (0-100 m)	
Al	0.0044	0	18	0	55*	14*	10
Ca	.1596	0	28*	15*	48*	9	0
Fe	.0080	0	27*	0	38*	2	33
Mg	.0291	0	28*	3	57*	1	11
K	.0075	2	7	0	80*	6*	5
Si	.0038	0	22*	0	46*	22*	10
Na	.0473	0	4	41*	46*	6*	3
Ti	.0064	1	28*	0	54*	9*	8
Total-C	.0535	1	14	26*	19	31*	10
As	.0914	0	0	0	81*	6	13
B	.0173	0	18*	0	57*	5	21
Ba	.0313	0	0	0	35*	6	58
Be	.0264	0	24*	0	37*	0	39
Co	.0624	0	12	0	33*	0	55
Cr	.0452	0	17*	0	37*	0	46
Cu	.0821	0	28*	0	18*	1	52
F	.0331	3	7	0	15	34*	41
Ga	.0677	0	10*	0	59*	0	32
Ge	.1378	0	0	11	0	27	62
Hg	.1631	2	10	36*	31*	4	17
Li	.0363	5	23*	0	58*	10*	5
Mn	.0476	0	0	8	4	0	88
Mo	.0976	0	11	0	48*	7	33
Nb	.1055	0	1	0	17	0	82
Ni	.0694	0	10	0	24	36*	30
Pb	.1029	0	6	0	39*	0	55
Rb	.0127	0	6	0	77*	6	11
Sb	.1867	1	2	0	0	10	86
Sc	.0491	0	5	0	37*	0	59
Se	.0947	1	0	15	0	25	59
Sn	.3488	0	2	0	0	33	65
Sr	.0350	1	19	18*	31*	5	27
V	.0396	0	7	0	52*	0	41
Y	.0330	0	9*	0	42*	0	49
Yb	.0986	0	8*	0	38*	0	54
Zn	.0083	1	31*	12	32*	19*	5
Zr	.0359	2	1	0	28	2	66

Figure 2. Regional distribution of zinc (ppm) in surface soils in the Piceance Creek Basin, Colorado. Values are supertownship means.

Table III

Summary of Geochemical Data on Surface Soils in
Piceance Creek Basin, Colorado (ppm)

Element	Observed range	Geometric mean	Geometric deviation
Al, %	3.4-7.8	5.5	1.17
Ca, %	.46-9.8	1.9*	2.48
Fe, %	1.1-2.9	1.8*	1.22
Mg, %	.51-2.7	1.0*	1.49
K, %	.77-3.2	2.3	1.22
Si, %	15-34	26*	1.15
Na, %	.18-3.5	1.4	1.65
Ti, %	.15-38	.28*	1.21
C(total), %	.87-12	3.0	1.69
As	<2.0-21	6.4	2.01
B	25-102	61*	1.35
Ba	600-13,000	1,400	1.50
Be	.88-4.4	2.4	1.46
Co	1.2-16	7.9	1.77
Cr	12-110	60*	1.63
Cu	<8.7-122	29*	1.94
F	<400-1,600	490	1.52
Ga	<2.2-39	18*	1.82
Ge	<.14-2.5	.87	2.37
Hg	.01-22	.041	2.56
Li	16-140	34*	1.55
Mn	82-1,200	490	1.65
Mo	<1.04-14	5.3	2.05
Nb	<2.2-21	6.9	2.11
Ni	<3.4-42	21	1.83
Pb	<3.3-56	26	2.09
Rb	40-190	105	1.29
Sb	<.14-4.5	.90	2.70
Sc	<2.1-13	6.7	1.66
Se	<.11-1.2	.28	2.02
Sn	<.11-11	.80	3.90
Sr	61-660	280	1.55
V	7.5-120	56	1.58
Y	4.9-36	15*	1.52
Yb	<.28-6.2	2.1*	2.06
Zn	45-140	80*	1.23
Zr	54-700	270	1.55

of the Piceance Creek Basin. A possible exception is fluorine. Fluorine is elevated in the parent material but is not particularly elevated in surface soils. Table III summarizes the geometric mean, geometric deviation, and observed range in concentration of 37 elements in the surface soils of the Piceance Creek Basin.

Stream Sediments

The objectives of this portion of the study are twofold: 1) to determine if there exist any significant trace element anomalies in the stream sediments of the Piceance Creek Basin, and to determine the geochemical variation of five major streams (Roan, Black Sulfur, Parachute, Piceance, and Yellow Creeks) for the purposes of establishing practical baselines. A knowledge of any existing anomalous stream sediment geochemistry will be important for making recommendations for any future oil shale plant sites.

The streams in the Roan Plateau area dissect the Uinta sandstone. The heads of the streams flowing easterly or westerly cut into the upper portion of the Parachute Creek Member. This moderate dissection contrasts with the extreme dissection of streams cutting lithologies in the Roan Creek and Parachute Creek areas.

The sampling design for determining anomalous creeks in the basin is the typical type used in reconnaissance surveys for geochemical exploration. Two 200 g samples 10 meters apart were taken at the junctions of almost all the named streams in the basin (Figure 3). Only one of the two samples was analyzed.

The sampling design used to describe the background variation of the five major streams is considerably more complicated than the design for detecting anomalous creeks and is to describe as much of the geographic variability as possible. Once the variability is known, further sampling designs can be made to determine practical baselines for a more localized area.

For the purpose of this study, a baseline is defined to be a reference that not only describes the mean and limits of concentration inherent in nature, but also accounts for the geographical scale of variability. The most effective way of expressing a baseline is with a geochemical map. But if the variability is local, it would require too many samples to develop a stable or reproducible geochemical map; thus an expected range and deviation would be the appropriate manner of expressing the baseline.

To obtain an estimate of natural variability in the five major streams, a hierarchical or nested sampling design was used which is conceptually similar to that used in the soil sampling but modified to fit a one-dimensional stream channel. Figure 4 illustrates the various sampling levels

Figure 3. Major creeks and stream sediment sampling locations in Priceance Creek Basin, Colorado.

Figure 4. Nested analysis of variance sampling levels for streams.

(2 Km, 200 m, 20 m, and samples) which partition the total variance. Two 2-m segments were chosen 10 m apart. Within each of these 2-m segments, two 200 meter segments were chosen at random, one within each 1 m segment. Then within each 200 meter segment, two 20 meter segments were chosen at random, one within each 100 meter segment. And finally, within each 20 meter segment, 2 samples were chosen, one within each 10 meter segment.

The analysis of variance of the nested design for the major streams in the Piceance Basin is summarized in Table IV. From the table two variance components stand out: the variance from 0 - 10 m for the individual streams, and the variance between streams for all stream data. The significance from 0 - 10 m for Mo cannot be tested because the 0 - 10 m scale of variance and the analytical variance are combined in the lowest level, but the high percentage of the variance at this lowest level is a good indication that 0 - 10 m would be significant if a test could be made. In general, the consistency of the significance at the 0 - 10 m scale may be a reflection of the power (degrees of freedom) of the sample design being concentrated at the lower levels. Except for Zn, there are significant differences between streams for all the constituents. A similar study (McNeal, et al, 1976) done in the same area and in Utah also brought out the significant difference between streams for many other elements. Semi-quantitative optical spectrography data for B in sediments from Roan and Black Sulfur Creeks indicate an elevated concentration (geometric mean of 44 ppm) with most of the variance concentrated at intermediate distances. Summary data published by McNeal, et al, (1976) gives geometric means of 6.5 and 7.8 ppm, respectively for As and F in stream sediments. The As is elevated in concentration with respect to the earth's crust but not with respect to an average shale. The F is substantially depleted, possibly due to solubility under the alkaline conditions of the basin.

The approach toward defining baselines for the above constituents can be done in two ways. First, if interest was being directed toward streams draining possible plant sites, one would want to define a baseline for that particular stream since it has been determined that there can be significant differences between streams. For the constituents being discussed in this paper it would be recommended from the analysis of variance results that an expected range be used as a baseline for all the streams under consideration. In these instances, to develop stable geochemical maps which will describe a reasonable percentage of the variance of the streams, sample localities will have to be chosen a few meters apart.

Secondly, if one were interested in characterizing the Piceance Creek Basin as a whole, it might be feasible, for Mo, Hg and organic matter, to choose streams as localities. From the analysis of variance results for these constituents, one could conclude that a few samples a short distance apart within these localities would provide enough information

Table IV

Geochemical Summaries for Stream Sediments of Major Creeks in the Piceance Basin

[Date given in parts per million; an asterisk (*) indicates variance component is significantly different from zero at the .05 probability level]

ELEMENT	STREAM	ANALYSIS OF LOGARITHMIC VARIANCE							Summary Statistics			
		TOTAL LOG ₁₀ VARIANCE	PERCENT OF TOTAL VARIANCE						Geometric Mean	Geometric Deviation	Geometric Error	Expected 95% Rang
			Between Streams	1 - 10 Km	100 m - 1 Km	100 m - 10 m	0 - 10 m	Anal. Error**				
MO	All	.0052	73*	.2	0	3	17	6	4.2	1.64	1.09	1.6-11.1
	Roan	.0159	-	0	13	0	87	-	3.5	1.28	-	2.1-5.7
	Black Sul.	.0365	-	15	1	0	76	8	2.9	1.41	1.09	1.5-5.6
	Piceance	.0143	-	0	0	21	79	-	4.2	1.33	-	24 -7.4
	Parachute	.0044	-	5	4	0	91	-	95	1.14	-	7.3-12.3
	Yellow	.0215	-	38	0	4	58	-	3.3	1.34	-	1.8-5.9
ZN	All	.0066	36	18	2	3*	33*	7	61.0	1.20	1.03	28.6-129
	Roan	.0134	-	27	10	0	47	17	63.8	1.28	1.08	39.9-102
	Black Sul.	.0030	-	46	3	10	37*	4	53.3	1.12	1.01	42.5-66.
	Piceance	.0011	-	0	0	9	91*	0	67.8	1.08	1.00	58.1-79.
	Parachute	.0012	-	14	0	37	40	9	68.9	1.06	1.02	61.3-77.
	Yellow	.0036	-	30	0	9	48	14	52.5	1.13	1.04	41.7-66.
HG	All	.0614	66*	6*	0	0	20*	8	.29	1.67	1.12	.11-78
	Roan	.0162	-	8	6	0	80*	9	.58	1.27	1.07	.37-.92
	Black Sul.	.0375	-	38	0	13	43*	6	.36	1.44	1.08	.18-.73
	Piceance	.0214	-	11	0	23	54*	12	.23	1.35	1.09	.13-41
	Parachute	.0333	-	0	6	0	61*	33	.28	1.39	1.19	.16-.49
	Yellow	.0085	-	1	0	26	0	73	.15	1.19	1.14	.12-.19
ORGANIC	All	.1831	69*	12*	3	0	16*	0	.19	2.47	1	.15-5.55
	Roan	.0835	-	20	6	4	71*	0	1.26	1.87	1	.36-4.41
	Black Sul.	.1416	-	50	8	0	39*	0	.79	2.01	1	.20-3.19
	Piceance	.0198	-	60	10	0	30	-	1.02	1.30	-	.60-1.72
	Parachute	.0011	-	17	43	12.4	22	5	254	1.07	1	2.22-2.9
	Yellow	.0326	-	1	22	0	76	1	.24	1.46	1	.11-.51

** The analytical component is included in the 0 - 10 m component.

to make a stable geochemical map that would express a large percent of the total variation. The analysis of variance predicts Hg and organic matter could be treated in a similar manner.

It should be clarified that the objective of the stream junction sample design is not to describe as much of the geochemical variability as possible, but to determine whether there are any streams with unusually high concentrations of any of the constituents under consideration (As, Cd, Mo, Hg, and Zn).

When locality is used in the discussion of stream junction sampling, it will represent the stream channel about the junction. It was thought that random sampling within a locality (stream) will not express an anomalous locality as effectively as will sampling on the down stream end of the locality. Of course, this assumption is dependent on the nature of the dispersion train from the anomalous source. If, for example, an anomalous source were located at the head of a typical sampled stream, a halo of 10 miles or longer may be required for detection at the mouth of the stream. Thus, only strong targets or relatively large size targets will be detected by this sample design.

Table V is a comparison between the expected range of the constituents (one sample taken from each locality and analyzed once) and their average abundance in the earth's crust and in shale.

Note the expected range in Table V and Table VI as compared with the expected ranges from the nested model design (Table IV). The ranges from the nested model are smaller. The analytical error is removed from the nested ranges, but analytical errors are too small to account for the difference. The most probable explanation is that stream junction samples are being affected by geographic variance at a larger scale than the upper limit (10 Km) expressed by the nested model. As will be recalled, the nested model does predict a large percentage of variance at the between-stream level. The level could also be interpreted as expressing a variance of larger scale than 10 Km as well as the between stream level.

Since the Piceance Creek drainage is much larger than the 10 Km scale and since it was more extensively sampled than the other creeks, it appears to show the higher scale variance for Zn and Mo. Both distributions of Zn and Mo for the stream junction samples (data transformed to $\log_{10}$) are bimodal or trimodal. The upstream end of Piceance Creek has high Zn and low Mo concentrations where the creek cuts through the Green River Formation. The bi- or trimodal character for these elements is probably a reflection of the geology.

From stream junction data, it is found that for all the measured constituents - Zn, Mo, Hg, and organic carbon - there is a significantly greater concentration in the population of individuals making up the perimeter of the basin (all samples in the Green River Formation and Wasatch Formation) as compared to the population of the interior (all

Table V

Stream Junction Data of Piceance Creek Basin Compared
With Average Crustal and Shale Abundances

Element	GM (ppm)	GD	Expected Range @ 95% Level (ppm)	5 Highest Ranked Values (ppm)	Ave. Crustal Abundance (ppm)	Ave Shale Abundance (ppm)
Cd ^U	2.4	1.56	1.0-5.9	4.7, 4.8, 4.8, 5.0, 5.9	.2	3
As	9.2	2.38	1.6-52	21, 28, 30, 36, 50	1.8	6.6
Zn	60	1.34	33-108	70, 82, 83, 84, 116	70	80
Hg	.33	1.50	.14-74	.62, .64, .65, .73, .91	.04	.40
Mo	4.7	2.14	1.0-21.6	11.1, 11.2, 12.8, 13.0, 17.7	1.5	2
Organic Carbon %	.54	2.50	.09-3.38			

^U Treated as Censored Data, Parameters Calculated Accordingly

samples in the Uinta Formation). There is also a significantly greater concentration of Mo, Zn, Hg and organic carbon in samples taken south of the Roan Plateau as compared to samples taken north of the plateau. This is similar to the data for Zn, Cu, Li, and Be in surface soils (Ringrose, et al, 1976).

From this comparison, it appears that the stream junction expected (Tables V and VI) is a more realistic estimate than the nested expected range because it reflects a larger scale variance component and/or the between stream variance component more completely. If the result of the two sampling plans had shown the majority of the variance at the low scale level, the nested and stream junction samples could have been combined in estimating the expected range.

Tract C-a and Vicinity

At the suggestion of ERDA, subsequent studies are focusing on sites of potential development. The sampling program initiated under ERDA support collected surficial materials from Colorado lease tract C-a and vicinity in the summer of 1976. Media collected included surface soils, stream sediments, and three species of plants: big sage (*Artemisia tridentata* - subspecies *tridentata* and subspecies *wyomingensis*), Indian rice grass (*Oryzopsis hymenoides*), and western wheat grass (*Agropyron smithii*). The plant species selected are based upon suggestions from range specialists at Colorado State University, Area Oil Shale Supervisors' Office, Meeker offices of the BLM and SCS. The plants selected are based primarily upon availability in the area sampled, use by cattle and native herbivores and potential for use in vegetation of spent shale dumps.

The work on the basin-wide study of soil variance indicates a substantial number of elements including As, B, Mo of the five selected as high priority have a significant component of the variance at the 0.1 - 3 Km scale (Table II). This suggests that a sampling interval in this range is appropriate for smaller scale studies such as those being carried out on tract C-a and vicinity. The area selected for more detailed soil and plant sampling is a 48 square mile area containing tract C-a (Figure 5). This area contains the entirety of tract C-a, the proposed processing plant site, the proposed dump site on 84 Mesa, the vegetation study site of Phil Sims' group at Colorado State University, and considerable area both downwind and downstream from the tract.

The 6 X 8 mile area was sampled on a 1/2 mile (0.8 Km) grid (13 X 17 samples) totaling 221 sample locations. This seemed to be a maximum practical number for economic reason and a short enough interval to include the bulk of the natural variance. At each sample location surface soil and each of the three plants species were collected if available. Each plant species was not available at all locations. Of the 221 locations, big sage was available at 220, rice grass at 213, and wheat grass at 110. A sample location is considered an area of 100-200 m² and material from

Table VI

Stream Junction Data Grouped by Individual Streams

Mo	Gm (ppm)	GD	Expected Range @ 95% Level
Piceance	2.8	2.72	.3-20.6
Roan	5.6	1.56	2.3-13.2
Parachute	5.5	1.55	2.3-13.2
Yellow	6.7	1.42	3.3-13.5
Zn			
Piceance	53.8	1.22	36.1-80.1
Roan	66.4	1.34	37.0-119
Parachute	64.8	1.16	48.2-87.2
Yellow	53.7	1.20	37.3-77.3
Hg			
Piceance	.33	1.50	.15-.73
Roan	.34	1.16	.25-.45
Parachute	.38	1.22	.25-.57
Yellow	.24	1.35	.12-.46
Organic Carbon %			
Piceance	.32	2.20	.06-1.77
Roan	1.23	2.35	.22-6.80
Parachute	1.09	1.75	.36-3.32
Yellow	.41	1.82	.12-1.38

this area was composited into a sample. In this way most of the variance at scales of 0-10 m can be eliminated which is normally not of interest. Plant material is from several to many individuals over this 100-200 m² area in order to minimize the very local variance.

A small scale analysis of variance experiment is also being carried out in the 48 square mile area in order to confirm the conclusions of the basin-wide study on soils and to obtain variance data on plant material. Four sections were selected at random in the 48 square mile area (Figure 5). Each of these were quartered with two being selected at random. The two selected quarters were quartered with two being selected at random. In each of the selected quarter-quarters, two sample locations 50 m apart were selected at random. At each of these locations surface soils and the three plant species were sampled. For the four sections there are 2⁵ (32) sample locations. These samples will give variance data for scales of 0-50 m, 50 m - 1/4 mile (400 m), 1/4 mile - 1/2 mile (800 m), and 1/2 mile - 3 miles (4800 m). The sections sampled are shown in Figure 5 and a schematic of the locations is shown in Figure 6.

A second component of the sampling was to collect stream sediments downstream from tract C-a. The data from Table IV, for the entire basin suggests that the 1/2 mile (0.8 Km) interval is appropriate for sediments if material from a location is composited. A large component of the variance for stream sediments is in the 0-10 m scale. As a result, the stream sediment sample is a composite of material from the stream bed, composited over a distance of at least 10 m. Using this procedure, approximately 250 stream sediment samples were collected at 1/2 mile (0.8 Km) intervals from Yellow Creek, Trail Canyon, Big Duck Creek, Little Duck Creek, Corral Gulch, Box Elder Gulch, Stake Springs Draw, and unnamed gulches in the tract C-a area.

All of the analysis of variance samples have been prepared and submitted for analysis as well as the 220 big sage samples from the grid study. The 221 soil grid samples and the 213 rice grass samples have been prepared but not submitted for analysis. The samples from the analysis of variance experiment are the highest priority for analysis and the results will be used to determine priority on analysis of the remaining samples.

SUMMARY AND CONCLUSIONS

A regional study of soil and stream sediments in the Piceance Creek Basin, Colorado is underway at the Colorado School of Mines. The data indicate that As, B, F, Mo and Se tend to be elevated in this region and may pose potential pollution hazards during development of an oil shale industry. Surface soils have geometric means of 6.4 ppm As, 61 ppm B, 490 ppm F, 5.3 ppm Mo, and 0.28 ppm Se. Most elements exhibit considerable variability at local scales as determined by analysis of variance, making map representation of regional data difficult. Zinc, Cu, Li, Fe, and Be have a significant regional trend with high concentrations in the southern part of the basin.

Figure 5. Grid sampling for soils and plants in vicinity

Figure 6. Schematic of analysis of variance sampling for each randomly section in vicinity of Colorado tract C-a.

Figure 7. Yellow Creek drainage basin.

Regional trace element data for stream sediments indicate Mo and As are elevated in concentration (geometric mean of 4.7 ppm and 9.2 ppm respectively) with respect to both the earth's crust and shales. Cadmium and Hg are elevated with respect to the earth's crust but not with respect to an average shale having a geometric mean of 2.4 and 0.33 ppm, respectively. Analysis of variance results on Piceance, Roan, Black Sulfur, Parachute and Yellow Creeks indicate considerable variability in sediment composition at distance of 1-10 Km, between streams, and at very local scales of 0-10 m. The data suggest that each stream has its own character and a stream can be described by sampling at channel distance of approximately 1 Km. However, a given sample must be a composite of material from the stream channel over a distance of at least 10 m.

The data from the regional soil and stream sediment study was used to design a sampling plan for soils, plants, and stream sediments in the vicinity of Colorado lease tract C-a. The analytical portion of this component of the geochemical survey is underway.

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PROGRESS REPORT

TRACE ELEMENTS IN OIL SHALE

Mass Balance Studies on Oil Shale Retorting

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FISCHER ASSAY RETORTING STUDIES

The bulk of Fischer assays of the standard oil shale were completed in August, 1976. At the end of this section is a preprint which shows the results of those assays and summarizes progress on the project through September 3.. This phase of the work will be described at the Symposium on Tar Sands and Oil Shale at the ACS Meeting, March 20-25, 1977. The oil yields on the assays averaged 39.8 ± 0.98 gal/ton. Assay by TOSCO of a different split of the same shale by the total mass balance method gave a yield of 39.0 gal/ton. Since the water yield was only 1.38%, assays on 10,000 g gave only slightly more than 100 ml of retort water. This small amount of water has necessitated that we proceed with care on the analyses of this phase so that the most information can be obtained on the small amount of sample.

ANALYSIS OF FISCHER ASSAY FRACTIONS

The standard oil shale (OS-1), the TOSCO process spent shales (SS-1 and SS-2) and the Fischer Assay spent shale (FS-1) serve as the primary materials used by the leaching and plant availability portions of the project. Also, these four oil shale fractions will serve as standards for the central analytical laboratory. As such, analyses are required on these standards for more than just the five elements that are of environmental interest and all analyses must be as precise and accurate as possible. These objectives of precise and accurate values for many are found to be a chore. The analytical portion of this summary presents some of the problems encountered; I can add to the list. What is needed is analyses by more than one independent method for each element. In order to have independent checks on the analyses, we have visited several other laboratories. Precise and accurate analyses on oil shale are not routinely performed so some persuasion is necessary to interest the analyst in the project. One positive factor in this approach is the situation that these are currently the only oil shale standards that are available; one negative factor is that oil shale research is at an ebb so that analysis of these standards is not glamorous. Progress on analyses is summarized below:

Thin Film X-ray Fluorescence

This technique has been tried on OS-1 and SS-1; analyses are also being performed on SS-2, the oil and the water. The primary constraint is that less than 1 mg is used for the target. This is not a representative sample; consequently, evaporated targets of digestions have to be used. The method gives results for K, Ca, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Nb, Mo, Sn, Ba, Hg, and Pb. The Co and Se are below detection limits, and K, Ca, Br, Hg, and Pb are bordering on the detection limit.

Standard X-ray Fluorescence (XRF)

This method should give a reasonable major element analysis except for Na and Mg. The technique is useful only for solid samples. Marathon Oil Company has facilities for analysis of petroleum products by this method and attempts will be made to try analyses at their research center. The XRF analyses will be performed in February.

Instrumental Neutron Activation Analyses (NAA)

The analysis of As and Se in coals by NAA is almost becoming the standard method because no digestion is needed for the determination. Whether As and Se can be analyzed in oil shales is uncertain because the abundance of Na may be high enough to mask other gamma-ray peaks. Currently, the same INAA procedures that are used on coals are being tried on all the oil shale fractions by the NAA group at the U.S. Geological Survey in Denver under the direction of Dr. Hugh Millard. Preliminary results will be available in March. In addition to As and Se analyses, values will be determined for Na, K, Fe, Mn, Co, Ba, U, Th and some of the rare earth elements.

Atomic Absorption Spectroscopy Analysis (AAS)

This method is the routine method that will be used for As, Se, and Mo. Of course, solids have to be digested for AAS and as is summarized in the analytical section, the first concern is to develop a digestion procedure that will retain volatile elements. In addition, preliminary digestions and analyses for Na, K, Mg, and Ca were performed on the oil shales and spent shales.

Summary of Analytical Work

It is obvious that much of March will be spent comparing analytical results. Analysis of the oil and water will present special problems since many of the XRF methods are designed for solid samples. No mineral separations have been performed since analysis of the separates is useless until proper procedures are developed for the bulk samples. This detail

to preparation and analysis of standards will hopefully yield results which can be trusted in all phases of the project.

PROFESSIONAL ACTIVITIES

The Annual Meeting of the American Association for the Advancement of Science will be held from February 20-25, 1977 in Denver. In connection with the meeting, I have organized a symposium on Western Resources and the Environment. In the symposium, Kenneth Stollenwerk will report on the leaching studies that are being performed under Dr. Runnells' direction. Also, a Laramie group under the Direction of Dr. F.R. McDonald will be reporting on monitoring gaseous effluents using a mobile laboratory at the same symposium.

From March 20-25, 1977, I will be at the ACS Meeting in New Orleans to attend the symposium on the analytical chemistry of oil shale and tar sands. I will present a paper on Fischer Assay of the standard oil shale. This talk will include preliminary results on our analyses of major and trace elements. A copy of the preprint for the talk is contained at the end of this report.

PRELIMINARY RESULTS

The following table lists some of the analytical results. They are preliminary in nature and we want to check them by independent methods. However, some conclusions can be made concerning the results:

1. For the Fischer Assay mass balance the one element that is deficient is Zn. Deficiencies in As and Pb do not occur because the oil acts as a sink for these elements. Likewise, the water acts as a sink for Se.
2. Based on Conclusion 1, Cd may be significant because of its chemical similarity to Zn.
3. For the Fischer Assay mass balance, the elemental composition of the water is negligible. In this case, the composition of the water is only of environmental interest.
4. For those trace elements analyzed, the Fischer assay sour water is within the U.S. Public Health drinking water standards.
5. Note that for As and Mo two sets of analyses by different analytical methods are provided. The correlation between the two results is reasonably good. At the trace level, correlation

at about 10% in the relative standard deviation is about as well as can be expected.

6. Comparison of the Rb and Sr results in the following table with those that were determined independently which are reported in the retorting paper are very good, to within $\pm 5\%$ in all cases.

The necessity for accurate results is highlighted in the table. Most of the elements are retained in the spent shale. Only minute amounts escape in the Fischer Assay. The more accurate the analyses, the more accurately the differences can be pinpointed.

Element	Value	Method*	OS-1	SS-2	Spent	Fischer Assay		Fischer Mass Balance			Sum
						Oil	Water	Spent	Oil	Water	
Na	%	AA	1.55	1.91	1.84	4.3×10^{-3}	1.7×10^{-3}	1.48	6×10^{-4}	2×10^{-5}	1.48
Mg	%	AA	2.74	3.27	2.94	--	--	2.36	--	--	--
K	%	AA	1.17	1.56	1.52	--	--	1.22	--	--	--
Ca	%	AA	7.34	8.08	9.30	--	--	7.48	--	--	--
Fe	ppm	XRF	13,600	18,200	16,300	6	1.75	13,100	0.9	0.02	13,100
Ni	ppm	XRF	24	30	28	1.1	4.4	22	0.2	0.06	22
Cu	ppm	XRF	39	50	52	0	0.25	42	0	0.003	42
Zn	ppm	XRF	62	86	67	<1	0.67	54	0	0.009	54
As	ppm	XRF	61	82	79	24	4	64	4	0.05	68
	ppm	AA	75	86	87	29	--	70	4	--	74
Se	ppm	XRF	3.1	3.9	3.5	0.2	4.4	2.8	0.02	0.06	2.9
Rb	ppm	XRF	63	86	83	0.10	<0.02	67	0.01	--	67
Sr	ppm	XRF	584	674	726	0.35	0.06	584	0.05	0.001	584
Mo	ppm	Color.	26	30	28	--	--	22	--	--	22
	ppm	XRF	28	38	35	<0.1	0.134	28	--	--	28
Pb	ppm	XRF	27	34	33	7.8	<0.1	26	1.1	--	27

* AA = Atomic absorption XRF = X-ray fluorescence Color. = Colorimetric

SYMPOSIUM ON ANALYTICAL CHEMISTRY
OF TAR SANDS AND OIL SHALE (COMPARISON WITH
COAL AND PETROLEUM) PRESENTED BEFORE
THE DIVISION OF PETROLEUM CHEMISTRY
AMERICAN CHEMICAL SOCIETY
NEW ORLEANS MEETING, MARCH 20-25, 1977

PREPARATION AND FISCHER ASSAY OF A STANDARD OIL SHALE

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PREPARATION OF THE STANDARD SAMPLE

The feed stock was mined from a fresh face in the Upper Bench of the Dow Mine of the Colony Development Co. at the head of Parachute Creek in the Picaence Creek Basin, Colorado in 1974; crushed to $-\frac{1}{2}$ mesh and delivered in a 100 ton lot to the TOSCO research facility in Golden, Colorado (1, 2, 3). A 50 kg sample, OS-1, was taken from a residual pile of approximately 3 tons of feed stock which assayed at 37-38 gal/ton.

The raw shale required extensive crushing and grinding to prepare it for blending and splitting. The objective was to grind to minus 65 mesh since the analysts at TOSCO have shown that this will provide a more representative sample of the bulk feed stock when 100 gm is used for Fischer assay (4). First, the half inch feed stock was crushed in a hardened steel jaw mill to minus 4 mesh particles and then in a hardened steel roller mill to minus 10 mesh particles. Grinding was then attempted using a ceramic ball mill but the shale particles are surprisingly hard and resinous and the ceramic balls just bounced off the particles. Grinding to minus 65 mesh would have taken at least one day for each charge, so this method of grinding was abandoned. Instead, a "shatterbox" was used. This was quite effective, but the action of the grinding rings generated some heat. Charges were ground for no more than 30 sec. so the loss of volatiles would be kept to a minimum. The ground shale was sized by passing through a 70 mesh stainless steel mechanical sieve. The full 50 kg of shale feed stock was processed in this fashion. The crushing and grinding operations also blended the bulk sample to some extent.

Blending and splitting were performed simultaneously by taking each split and recombining and mixing and then splitting again. This was done 5 times on the first two splits and 4 times on the subsequent two splits. The 16 fractions resulting from the splitting were then blended by hand on a polyethylene sheet, and two 75 gm samples were taken and 7-100 gm Fischer assay charges were also taken from each 1/16 fraction. What remained of each sixteenth fraction was placed

in a polyethylene bottle and retained for future experiments. All bottles were rinsed with 1-1 HNO₃ and deionized water and dried before use and the bottled samples are stored in sealed polyethylene containers in a refrigerator. Figure 1 is a diagram of the splitting scheme for OS-1.

COMMENTS CONCERNING CONTAMINATION

The steel crushers, grinders and sieves used to process OS-1 can all be a source of contamination to various degrees. A U.S. Geological Survey group, in a study of contamination by steel crushers and grinders, found that Fe can be increased by as much as 1.5%, Ni - 60ppm, Mo - 20ppm, V - 10ppm, Cu - 30ppm, and Mn - 1000ppm (5). The main source of contamination appeared to be disc-type metal grinders. Another study on the grinding and sieving of small samples showed that contamination will most likely be inhomogeneous and cause a widely aberrant result in a trace element analysis (6). Stainless steel sieves can contribute about 3ppm Ni, 3 ppm Mn, and 20ppm Fe to a sample. Flannagan, in the preparation of the U.S.G.S. standard rocks (7), could detect no contamination from the use of jaw crushers and rollers in those samples. The following is an assessment of the level of contamination introduced during the preparation of OS-1.

First, all implements had been previously used for crushing and grinding oil-shale, and were also cleaned with some of the sample which was discarded so there is little possibility of cross contamination from previous samples. Processing by the jaw crusher and roller crusher may have added bits of steel in an inhomogeneous fashion but this could be eliminated by passage of a magnet over the powder. The shatterbox actually grinds the sample against itself and when the steel rings are touching, the sound changed and the grinder was stopped and a new charge added. Thus, contamination will be much less severe than that by using steel plates. Contamination could come from the stainless steel sieve. Comparing the levels of contamination mentioned above with typical elemental abundances in oil shale, it is likely that grinding added up to 10% of Ni and Mn to OS-1, up to 5% of Fe, Cu, and Mo, and up to 1% V to the sample (8).

HOMOGENEITY TESTS

A simple test of the homogeneity of the standard samples has been made using an x-ray fluorescence analysis method for Rb and Sr devised by Doering (9). This method uses rock powder ground to minus 200 mesh packed in a planchet. The analysis has been calibrated using standards in which the Rb and Sr contents have been analyzed by isotope dilution and yields the Rb/Sr to +3% at the 95% confidence level and the abundances of Rb and Sr to +6% at the 67% confidence level.

Eight samples of about 10 g were randomly chosen from eight different 75 g splits of the standard and were ground in Spex Mixer/Mill using a tungsten carbide chamber to -200

mesh and all analyzed on the same day to eliminate instrument drift and bias in packing the charges in the planchets. The results are summarized in Table I. The mean, range, standard deviation, and relative standard deviation are used according to the prescribed definitions. The mass absorption coefficients were determined by making a count of the Compton scattered photons at a 2θ angle of 21° .

The range and trend in the values for the mass absorption coefficient directly correlate with the Rb and Sr abundances. Coarser material won't pack as densely into the planchet thus yielding a lower mass absorption coefficient and also a lower value for the abundance of Rb or Sr. Thus, the deviations in the results appear to be caused by grinding and packing and not by true differences in the abundances of the two trace elements in the different splits. The conclusion is corroborated by the fact that the results for a series of spent shales, which are much finer in grain size, exhibit better precision. The conclusion is that the different splits of the standard are homogeneous to within $\pm 5\%$.

FISCHER ASSAY STUDIES

The Fischer assay studies were primarily made to obtain representative and reproducible fractions of oil, water, and spent shale for use in mass balance studies. To this goal, 120 splits of 100 g each of OS-1 were retorted using the equipment at the TOSCO Research Center in Golden. The procedure used was the TOSCO Modified Fischer Assay developed by Goodfellow and Atwood, where the product gas is not collected (4). Two or three runs on each of 10 different retorts were made each day and were bunched so that weight percents of oil, water and spent shale were determined on 200 or 300 gms of feed stock. In all, 46 percentage determinations were made and specific gravity measurements were made on the oils from 9 of the bunches, so the oil yields in gal/ton could be calculated. Besides adding more data to the analytical lore concerning Fischer assays, the results are interesting because they indicate how well novices at petroleum analysis can expect to do on Fischer assays.

EXPERIMENTAL PROCEDURES

Since the ultimate object of the study is to determine trace element abundances on the various retort products, all the retorts were cleaned and inspected for leaks and flaws and all the glassware was new and decontaminated with nitric acid and deionized water prior to the study. The TOSCO retorting procedure was followed, and the analyses of the solid and liquid products were made in the usual manner (4). The determinations of the volume of water in the receiver were made with somewhat less precision than normal since the primary objective was to recover as much water as possible without contaminating it.

During retorting, the internal temperatures were monitored on two of the 10 retorts. Table II gives the average temperature profile based on monitoring 19 runs. Retorting proceeded for 72.5 minutes, and included a 20 minute soak period during which the average internal temperature was 490°C (914°F).

RESULTS AND DISCUSSION

Table III lists the results of the oil yield determinations made on the 9 batches where the specific gravity of the oil was determined. Table IV lists the percentages of products from the 46 weight determinations. The amount of gas plus loss is determined by difference. The percent of liquid product is determined by the weight of liquid in the receiver and the weight of oil is determined by subtracting the volume of water from the weight of liquid. The standard deviation and the relative standard deviation are calculated by the perscribed definitions (10). TOSCO sets the oil yield of Upper Bench shale at 37-38 gal/ton based on Fischer assays and pilot plant studies made over a number of years. Typically, they set the standard deviation at ± 0.3 gal/ton on their Modified Fischer Assay.

There are two obvious differences in the work reported here and in the studies TOSCO has done on Fischer assays:

1. These results are definitely higher; they just barely overlap the TOSCO results at the 95% confidence level.
2. The standard deviation on the oil yield is 5 times larger in this work than that of TOSCO.

Concerning the first difference, there are no obvious answers, however, the recent work of Heistand offers some clues (11). If the difference occurred in selecting the 25 kg sample, then I selecting larger chunks and TOSCO included more fines since the fines appear to contain less oil (11). If the difference occurred in preparation of the batch, then my standard is less pulvervised than a typical TOSCO sample since again it appears that the oil yield decreases with decreasing particle size of the charge (11). If the high yield is a result of retorting differences, then, the slow rise time and moderate soak temperature that I used in comparison to the typical TOSCO temperature profile may have caused the difference. It is certain that the retort temperature profile will cause Fischer assay variations, but it is uncertain whether the differences between these two profiles would cause the discrepancy seen here (4, 11). One thing is certain, I am not claiming that I instantly made the Dow Mine richer by 2 gal/ton of oil.

Concerning the difference in standard deviations of Fischer assays, the cause is immediately obvious. Determination of the oil yield requires knowledge of the weight and density of the oil. As seen in Table III, the deviation in the specific gravity is low but the oil weight varies just as much as the assay. The oil weight is derived from the liquid product weight and this value also has a relative standard deviation of 2.5%. Now, this liquid product weight is measured to 4 places immediately upon taking the receiver from the ice bath, so the variation is due to retorting differences and not weighing procedures. Furthermore,

the temperature of the receivers and the condensers were stringently maintained at 0°C, so the deviations in the yield of liquid product were caused by variations in the temperature program from retort to retort and in the same retort from day to day. In Table IV it is seen that the variance of the percent of liquid product in the 46 runs is just as high as in the 9 assays, so performing more assays would not necessarily have increased the precision on the oil yield.

It is in this area of retorting where I think that the novice will have problems with Fischer assays. I didn't realize how much slight changes in the heating rate and in the position of the retort in the heater would change the weight of liquid product. Two retorts came to the soak temperature at a rate that was noticeably slower than the others and they did have liquid product yields that were 15.85% and 15.98%. In the other retorts, there is no trend in the high and low values. Neither is there any trend in day-to-day results which one might expect if considerable oil was absorbed on the sides of the clean retorts in the earlier runs. In lieu of experience, I would suggest that Fischer assay temperature programs be controlled continuously which now is done in many instances (4, 11). Also, I feel that an assay in which the gas is collected, such as the TMBA method of TOSCO, provides more information and eliminates the uncertainty of what might be lost (4).

ACKNOWLEDGEMENTS

This study owes half of its existence to Mark Atwood and Larry Goodfellow of TOSCO, who not only provided the shale and retorting facilities, but also advice and opinions; the other half is owed to ERDA who provided the financial support under Grant No. E(11-1)-4017.

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TABLE 1. RESULTS OF HOMOGENEITY TESTS FOR R_B AND Sr ON THE STANDARD OIL-SHALE, OS-1 AND A SPENT SHALE SS-2

	OS-1	SS-2
NUMBER OF SAMPLES	8	8
RANGE FOR Sr (PPM)	553-615	747-793
AVERAGE FOR Sr (PPM)	584	771
STANDARD DEV. FOR Sr (PPM)	24	17
RELATIVE STD. DEV. FOR Sr (%)	4.1	2.2
RANGE FOR R_B (PPM)	55.8-63.9	78.6-82.2
AVERAGE FOR R_B (PPM)	60.1	80.7
STANDARD DEV. FOR R_B (PPM)	2.7	1.5
RELATIVE STD. DEV. FOR R_B (%)	4.5	1.9
RANGE FOR R_B/Sr	0.101-0.105	0.101-0.107
AVERAGE FOR R_B/Sr	0.103	0.105
STANDARD DEV. FOR R_B/Sr	0.001	0.002
RELATIVE STD. DEV. FOR R_B/Sr	1.1	2.1
RANGE FOR MA^*	7.71-8.43	9.61-10.45
AVERAGE FOR MA	8.06	10.3
STANDARD DEV. FOR MA	0.27	0.3
RELATIVE STD. DEV. FOR MA	3.3	2.8

* MA IS MASS ABSORPTION COEFFICIENT IN cm^2/gm

TABLE II. AVERAGE FISCHER ASSAY TEMPERATURE PROFILE IN °C

TIME (MIN.)	TEMP. AVG.	STD. DEV.	TOSCO PROFILE(4)
0	--	--	25
2.5	57	15	--
5	--	--	45
7.5	78	11	--
10	--	--	100
12.5	105	13	--
15	126	10	155
20	166	13	215
25	218	13	280
30	270	14	350
35	332	16	405
40	389	16	460
45	443	16	490
50	472	10	500
52.5	481	8	500
55	486	8	500
60	492	7	500
65	493	7	500
70	494	7	500
72.5	497	7	500

TABLE III. FISCHER ASSAY RESULTS ON OS-1

	AVG.	STD. DEV.	REL. STD. DEV. IN %
OIL YIELD (GAL/TON)	39.81	0.98	2.5
% SOLID RESIDUE	80.38	0.33	0.4
% LIQUID PRODUCT	16.48	0.41	2.5
% WATER	1.38	0.06	4.1
% OIL	15.10	0.41	2.7
% GAS + LOSS	3.13	0.49	15.6
OIL SPECIFIC GRAVITY	0.9093	0.0034	0.4

TABLE IV: WEIGHT FRACTION RESULTS ON
46 RETORT RUNS

	AVG.	STD. DEV.	REL. STD. DEV. IN %
% SOLID RESIDUE	80.45	0.40	0.4
% LIQUID PRODUCT	16.29	0.42	2.6
% WATER	1.35	0.11	8.0
% OIL	14.93	0.39	2.6
% GAS + LOSS	3.26	0.44	13.4

BLENDING & SPLITTING OF OS-1

25 kg

5 MIXES

5 MIXES

4 MIXES

4

MIXES

BLEND

BATCH 1
SPLIT 5
700 9

BATCH 2
SPLITS
8 & 10
75 g EACH

7 - 100 g
FISCHER
ASSAY
SAMPLES

BATCH 1
SPLIT 12
700 g

BATCH 2
SPLITS
23 & 24
75 g EACH

7 - 100 g
FISCHER
ASSAY
SAMPLES

Figure 7. Splitting and blending scheme for OS-1.

PROGRESS REPORT

TRACE ELEMENTS IN OIL SHALE

Release, Transport, and Fate of Some Potential Pollutants

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INTRODUCTION

Our proposal to ERDA last year outlined our intention to study the release and mobility of certain potentially toxic trace and minor elements from oil shale. We emphasized those elements that form anionic (negatively charged) species in water, including boron, fluoride, molybdenum, selenium, and arsenic. These elements are of special interest because of their known toxic effects on plants and animals, and because they may exhibit increased solubility and mobility at the elevated values of pH that result from interaction between oil shale and water. This projected chemical behaviour is in sharp contrast to that of some other trace species, such as lead, copper, zinc, and mercury, which form insoluble hydroxides at elevated pH and become less soluble and mobile. Ward and others (1971) found that the pH of slurries of water and fresh spent oil shale ranged from 7.8 to 9.9, and various published analyses of the oil shale show the presence of significant quantities of the five elements of interest.

Our concern really lies with the question of whether or not crushed fresh oil shale or spent oil shale (shale that has been through a retort or *in situ* combustion) will release significant quantities of toxic contaminants to water that passes through piles of the material. The percolating water might consist of rainfall or snowmelt, or in the case of *in situ* extraction of oil from the shale, the water might be ground water that percolates through abandoned underground chambers. If such waters pick up significant quantities of toxic contaminants, they could carry these contaminants into valuable ground water and surface water resources of the region. In a semi-arid region, such as the Piceance Creek Basin of northwestern Colorado, any threat to existing water resources must not be ignored.

WORK PROPOSED LAST YEAR

In our original proposal, we outlined three phases of our study, as follow: 1) analysis of a variety of materials from the Piceance Basin, including soils, weathered shale, ground water, fresh shale, and spent shale, 2) laboratory experiments on the solubility and mobility of the elements of interest from the various samples of shale, and 3) as a later

phase of the work, investigation of the chemical interaction between leachates from the shales and the native soils of the region, with the objective of determining whether or not the soils will offer an effective barrier to downward migration of the contaminants that are dissolved in the leachate.

We feel that our work is progressing satisfactorily on topics (1) and (2) above, and we have included topic (3) in our proposal for continued funding for 1977-1978. A summary of our results through February 1st, 1977 comprises the remainder of this report.

RESULTS

Analytical Chemistry

As outlined by other investigators in their sections of this progress report, all of us have faced great difficulty in obtaining meaningful analytical data for the elements of interest in the various natural materials. Even routine analytical methods begin to fail when applied to such unusual materials as the kerogen-rich, dolomitic oil shale. We had expected some considerable difficulty in selecting and calibrating our analytical methods, based on the contradictory analytical results published earlier by others (Stanfield and others, 1951; Smith and Stanfield, 1964; Desborough and others, 1974). However, in all candor, we must admit that we had underestimated the analytical problems that we would face; these difficulties were compounded by the arrival, and subsequent resignation of a new chief analytical chemist. As a result, those of us who were not directly involved in the frustrating analytical problems found ourselves lacking the data that we had hoped to have early in our work. Toward the end of 1976, however, the experienced and dedicated chemist who had previously headed our analytical laboratory returned to the C.U. campus, and things have smoothed out rapidly since that time. We are now receiving useful and reliable analytical data on our materials, and rapid progress is being made on the more intractable analytical problems. We feel confident that we are "over the hump" in terms of many of the analytical questions and delays.

Because of the analytical problems, we chose in our own research effort to go ahead with the leaching experiments of phase (2) of our program without waiting for chemical analyses of our materials. To have waited would have greatly delayed our program. We therefore initiated the experiments on the solubility and leaching of the trace substances from various source materials, while at the same time submitting the materials for chemical analyses that we knew would be tardy. This procedure seems to have worked out satisfactorily. We are now receiving quite a lot of data on both the original study materials and the leachates derived from them.

Dr. Tom Wildeman of our project supplied a suite of "standard" spent and fresh oil shales for our experiments. These are the shales that he

obtained from TOSCO (The Oil Shale Corporation), and which are described in his section of this report. We have used several of these standards in shaker-type and column-type studies of the leaching of the trace contaminants by water. When Dr. Wildeman obtains the complete analyses for these materials, we will be able to report them in our work. At this time we have only scattered results for a few of the key elements. Additionally, we have some multi-element analyses of the shales and leachates from our x-ray fluorescence facility. Considerable effort was exerted during the fall of 1976 to obtain reliable analyses of the bulk chemistry of the oil shales so that the proper absorption corrections could be applied to the raw data from the x-ray fluorescence laboratory. We have been successful in this effort, as shown by excellent agreement between results by wet chemistry and by x-ray fluorescence for such elements as As and Mo.

Similarly, when we get into our future work with soils, we will rely on chemical data gathered by Dr. Klusman. Using the analyses that he has gathered, we will select sites and types of soils for our work on absorption and retention of the contaminants from the leachates. At this time we have not begun this phase (item [3] above) of the study.

One of the strengths of an interdisciplinary effort, such as this project, is that we can interact with other investigators in a manner that supports the efforts of each. It would have been far less efficient for each investigator to be forced to fully develop all of the chemical techniques and background data required before getting into his own special area of work.

We have continued to gather published information on the chemistry of ground waters in the Piceance Creek Basin, but we have not ourselves initiated any study of the ground water. This aspect of the overall study will receive more emphasis in the next year, as outlined in our proposal for continued funding through 1977-1978.

Trace Contaminants Released in Shale Slurries

The first of our efforts was directed toward measuring the solubility of the five anionic elements in slurries of oil shale and water. We used this approach initially because it is far easier and faster to collect leachate from slurries than from laboratory columns of oil shale. In addition, by shaking the slurries for varying lengths of time, we can determine how much time is required for chemical equilibrium to obtain between the shale and the water. This information on time of equilibration can then be carried into the more tedious experiments with columns, and the rate of flow through the columns can be controlled to insure a reasonably close approach to solution equilibrium.

The shales that we used in the slurry experiments were supplied by Dr. Thomas Wildeman of this project. They represent spent shale from the TOSCO II process (supplied by The Oil Shale Corporation) and crushed fresh

shale from the Mahogany Zone at the Colony Development site near Grand Valley, Colorado. Elsewhere in this report Dr. Wildeman describes the source and preparation of these standard samples. We used his fresh shale (OS-1) and two spent shales (SS-1 and SS-2). Spent shale SS-2 represents the residue from retorting of fresh shale OS-1. Spent shale SS-1 represents the residue from retorting of fresh shale OS-1. Spent shale SS-1 came from feed stock mined from a lower stratigraphic interval in the Mahogany Zone at the Colony site.

Wildeman reports that SS-1 and SS-2, as collected at the TOSCO plant, were very fine grained, with 90% passing a 200 mesh sieve (0.074 mm). The other 10% of the material was very coarse, greater than 10 mesh (2.0 mm). He ground the coarser fragments by hand until 95% would pass a 100 mesh screen (0.15 mm). The original coarse-grained fresh shale was ground so that all of it would pass a 65 mesh screen (0.23 mm). The crushed samples were then blended by Wildeman, and 14 splits were sent to us.

Preliminary shaker studies: Prior to funding by ERDA, we had a small grant from the Colorado Energy Research Institute (CERI) for exploratory work on the solubility of trace contaminants. In this section we summarize the relevant results from that work. Our purpose in including a brief summary of this older material is to have all of our results on the leaching studies assembled in one document at this early stage of the research.

In the earliest slurry experiments, we used both spent shales (SS-1 and SS-2) and the fresh shale (OS-1) from the Mahogany Zone. Three 10 gm and three 25 gm quantities of each sample were weighed into six 250 ml glass flasks, and 50 ml of deionized water was added to each. A seventh flask with deionized water only was carried through as a blank control on contamination. The flasks were sealed and placed on a reciprocating shaker table for seven days. After the period of seven days, the flasks were removed, and the supernatant solution was centrifuged and filtered through a 0.01 micron membrane filter. We analyzed the solutions in our laboratory for fluoride ion and boron. For fluoride we used a specific-ion electrode (Orion Model 9409) with Orion TISAB buffering solution for control of pH and complexing of interferents. We determined dissolved boron by a modified colorimetric (curcumin complex) method, following Goldman and others (1975). Molybdenum was determined colorimetrically, using the thiocyanate complex (Barakso, 1967), in the central analytical laboratory. At this time we did not have the capability on the project to analyze the leachates for As or Se. The pH of the various slurries ranged from 8.1 to 8.4 for both raw and retorted materials. The results are presented in Table I.

Table I

Mo, B, F from First Leachate Batch, September 4, 1975.

All slurries contained 50 ml deionized water and were shaken for seven days.

	<u>Mo mg/l</u>	<u>B mg/l</u>	<u>F mg/l</u>
Blank	0	.008	.019
SS-1 10 g	1.7	2.3*	6.4*
SS-1 25 g	3.2	4.2*	9.0*
SS-2 10 g	2.2	3.0*	11*
SS-2 25 g	4.9	6.0*	12*
OS-1 10 g	.43	1.3*	13*
OS-1 25 g	.67	2.8*	18*

* adjusted for blank

The data in Table I show that both spent shales released significantly larger amounts of Mo into the water than did fresh shale. This was true at both ratios of water to solid. Similar results are seen for B, but the differences are probably not statistically significant. The results for F are also questionable; although SS-1 clearly released less F than the fresh shale, it came from a different feedstock. Spent shale, SS-2, which came from the same original feedstock as OS-1, released a quantity of F that is probably not significantly different from the fresh shale. This early work gave us the first indication of the relatively high solubility of Mo, and the hint that F might be less soluble from spent shale than from fresh shale.

Chemical analyses of some of the 14 splits of shale prepared by Wildeman are shown in Table II. The elements listed and followed by x-ray were analyzed in solid form at the x-ray fluorescence facility at C.U. The other elements were all determined by a commercial laboratory (Skyline Laboratory) in Denver; the technique employed is shown in parentheses. Unfortunately, we do not have estimates of the precision of the analyses.

The results in Table II suggest no apparent enrichment of As, Se, Mo, or B in the spent shale (SS-1) relative to a fresh shale (OS-1); however, these two samples are not directly comparable because they came from different stratigraphic intervals in the Mahogany Zone.

The results in Table II are quite useful in giving an idea of the concentrations of the several elements and of the heterogeneity among splits of the same batch. Wildeman estimates that up to 50% of the total Mo observed in OS-1 could have come from the steel used in grinding the samples.

Recent Shaker Studies: The early work described above gave direction to the shaker experiments that we conducted after funding by ERDA. Because the results in Table I suggest that the ratio of solid to water in the slurries is not a major control on the solubility of the trace elements, we have used a ratio of 25 ml deionized water to 10 grams powdered shale in all current work. In addition, we have found that for long periods of contact (up to 127 days) significant quantities of F are lost from test solutions in Pyrex flasks, apparently by absorption into the glass walls of the flask. After about seven days of contact, the slurries also begin to pick up significant quantities of boron from the Pyrex. These data are summarized in Table III.

The data in Table III indicate that the slurry leachates contain the same concentrations of Mo, As, and Se, regardless of whether glass or plastic flasks are used. As a result of these studies, all of the slurry data reported later in this summary represent experiments in plastic flasks.

The analytical results shown in Table III were obtained by a variety of methods. Fluoride and B were determined in the leachates in our laboratory, by specific-ion electrode and the curcumin colorimetric method, respectively. Molybdenum was measured colorimetrically in the central analytical

Table II

Results of Analyses of Dr. Wildeman's
Reference Samples of Oil Shale (1975)

Fresh Oil Shale No 1 (OS-1)

Batch No. 1

	<u>Split 1</u>	<u>Split 2</u>	<u>Split 3</u>
As (x-ray)	60	50	47
Se (x-ray)	2	1	2
Se (color.)	5	5	5
F (electrode)	1600	1700	1400
Mo (x-ray)	25	23	27
B (e. spec.)	50	50	30

Batch No. 2

As (x-ray)	51
Se (x-ray)	3
Se (color.)	2
F (electrode)	1600
Mo (x-ray)	27
B (e. spec.)	30

Spent Oil Shale No. 1 (SS-1)

Batch No. 1

	<u>Split 1</u>	<u>Split 2</u>	<u>Split 3</u>	<u>Split 4</u>
As (x-ray)	68	52	49	46
Se (x-ray)	5	< 2.5	2	4
Se (color.)	5	5	8	8
F (electrode)	2500	2400	2200	2400
Mo (x-ray)	29	18	22	25
B (e. spec.)	50	50	30	50

Batch No. 2

As (x-ray)	57
Se (x-ray)	3
Se (color.)	5
F (electrode)	2100
Mo (x-ray)	27
B (e. spec.)	50

Table III

Comparison of the composition of slurry leachates in plastic (polyethylene) versus Pyrex 250 ml erlenmeyer flasks.

All experiments involved 25 ml of deionized water and 10 grams of standard spent shale (Wildeman SS-1, Batch 1, Split 13).

(-) = analysis not obtained; n.d. = not detectable

<u>Days Shaken</u>	<u>Type Flask</u>	<u>mg/l in solution</u>				
		<u>F</u>	<u>B</u>	<u>Mo</u>	<u>As</u>	<u>Se</u>
1	p (polyethylene)	14	3.3	3.2	.04	.02
	g (Pyrex)	15	3.7	3.0	.05	n.d.
2	p	18	4.0	2.9	(-)	(-)
	g	16	3.8	2.9	(-)	(-)
4	p	20	3.8	3.1	.05	n.d.
	g	19	3.8	3.1	.04	n.d.
6	p	24	4.2	3.1	.04	n.d.
	g	16	4.2	3.0	.05	.02
8	p	18	4.2	3.4	(-)	(-)
	g	17	4.6	3.2	(-)	(-)
12	p	26	4.1	3.0	.04	.02
	g	16	4.6	3.0	.05	.02
20	p	20	4.6	3.0	(-)	(-)
	g	18	5.2	2.9	(-)	(-)
3	p	21	4.6	3.2	.02	(-)
	g	14	5.1	3.1	.03	(-)
127	p	23	(-)	(-)	(-)	(-)
	g	19	(-)	(-)	(-)	(-)

Analytical techniques: F by electrode; B and Mo colorimetrically (curcumin); As and Se by x-ray fluorescence analysis of evaporated residue. Approximate average analytical error is $\pm 30\%$ of the value shown. Samples of leachate were successively filtered through Fisher qualitative filter paper, 0.045 micron membrane, and 0.01 micron membrane filters to clarify the samples prior to analysis.

laboratory, using the thiocyanate colorimetric technique. Arsenic, Se, and also Mo were determined by x-ray fluorescence analysis of the evaporated residue from the leachate. This analytical work was done before we were certain of our methods. but an estimate of $\pm 30\%$ is probably a reasonable figure for the accuracy and precision. The x-ray fluorescence procedure has since been improved by using better matrix corrections derived from total wet analysis of the major components of the shale.

A comparison of the wet chemical technique and the results of x-ray fluorescence for Mo in these same samples is shown in Table IV. The consistency of the results is very reassuring.

Table IV

Comparison of the analytical results for Mo dissolved in leachates from shaker experiments.

Second column is result from analysis of evaporated residue using x-ray fluorescence. Third column is result from wet colorimetric analysis (thiocyanate technique) on leachate solution.

<u>Days Shaken</u>	<u>mg/l Mo in leachate</u>	
	<u>*X-ray Fluorescence</u>	<u>**Wet Chemistry</u>
1	2.9	3.2
4	3.1	3.2
6	3.1	3.1
12	3.0	3.0
33	3.3	3.2

* Statistical error of counting = $\pm 2\%$ of value shown.

** Precision (one standard deviation) = 10% of value shown.

Results of our shaker experiments for Mo, B, and F are summarized in Figures 1, 2, and 3, respectively. Limited shaker facilities prevented us from running both spent shales for comparison to the fresh shale, so we chose spent SS-1 for comparison to fresh OS-1, even though they do not represent the same feedstock. Our early data (Table I) indicated that the extent of leaching of Mo, B, and F from SS-1 and SS-2 were sufficiently similar to justify our choice of either one as a material for comparison to fresh OS-1. In addition, we felt that by using SS-1 instead of SS-2 for comparison to the fresh material, we could cover a wider range of variables with the limited facilities and time available. We may verify this comparison, as time permits, by running a few shaker studies on SS-2.

Figure 1 shows the results of shaking 25 ml of deionized water with 10 grams of shale (spent SS-1 and fresh OS-1) for periods of time up to 127 days. The supernatant solutions were analyzed for Mo in the central laboratory, using the thiocyanate colorimetric technique. The precision of analysis is approximately $\pm 10\%$ of the value shown. The values along the ordinate in Figure 1 are mg Mo leached per kg of shale. To convert to mg/l dissolved Mo in the leachate solution, the values should be multiplied by 0.4. The original concentrations of Mo in the solid shale samples are labeled along each curve in Figure 1. As seen in Figure 1, the original concentration of Mo in the fresh shale was 26 mg/kg, compared to 28 mg/kg in the spent SS-1; these values are the same within analytical error and suggest that no significant difference in content of Mo was produced by retorting. We also have two analyses of SS-2 (the actual spent equivalent of OS-1); they show 29 and 30 mg/kg Mo in the solid, supporting our choice of SS-1 for use in the leaching studies.

Figure 1 shows a dramatic increase in the availability of Mo from retorted (TOSCO II) shale relative to fresh shale. The final concentrations of Mo in the leachate reached a value of about 8 mg leached per kg of shale (corresponding to 3.2 mg/l in solution). In comparison, the fresh shale released about 2.5 mg per kg of shale, or 25% as much. This is an increase of about 300% in solubility of Mo from the retorted material. Whether or not such a change will be environmentally significant remains to be seen, but it is of interest to know that one state, New Mexico, has now set a standard of 1.0 mg/l for dissolved Mo in irrigation water (New Mexico Environmental Improvement Agency, New Mexico Water Quality Commission Regulations, January 11, 1977). If the leachate from our experiments were to meet this irrigation standard, it would have to be diluted by a factor of three.

Another interesting feature shown in Figure 1 is the rapid rate at which the water equilibrated with the shale. After only one day of shaking the concentration of Mo in solution was approximately equal to the final value that was achieved after 127 days of shaking. We consider data on the rates of approach to equilibrium to be the most valuable results of our shaker experiments. In the case of Mo, the rapid rise of the dissolved

Figure 1. Amount of Mo leached from shale, in mg Mo per kg shale, for fresh and spent shales. Initial value in the shale is shown by labels on the curves. The value for OS-1, batch 1, split 2, is the average 3 colorimetric determinations on separate aliquots of the sample and 6 x-ray fluorescence analyses of separate targets of the one sample. The value shown for SS-1, batch 1, split 13 is the average of 2 colorimetric determinations and 6 x-ray fluorescent measurements on separate aliquots of the sample.

Figure 2. Leaching of B from spent and fresh shale by deionized water, in shaker experiments.

Figure 3. Leaching of F from spent and fresh shale by deionized water in shaker experiments.

Mo to a constant value may give us information about the source and origin of Mo in shales. In addition, from the data on rates we are able to judge the velocity at which we should pass water through our columns in order to approach solution equilibrium. We think that the absolute concentrations of the elements in solution in the shaker leachates are of very limited value in trying to judge the impact of the disposal of the waste shales. We intend to place much greater reliance on column studies in trying to model the actual situation that prevails in the field.

Figure 2 shows the results of our shaker studies for boron, using OS-1 and SS-1. Unfortunately, we do not have reliable initial values for the content of B in these two solid samples. Our central analytical facility is close to having a reliable technique for B in solid samples, but it is not yet operational. The data used to construct Figure 2 were obtained on the liquid leachates, using the colorimetric curcumin method. As a consequence of the temporary lack of data on the original content of B in the solid samples we are not able to say that the differences in release of the B shown in Figure 2 are due solely to retorting. It is possible that the two shales contain different initial amounts of the element. However, if the two shales prove to be comparable, Figure 2 shows that retorted shale releases nearly twice as much B to solution as does fresh shale. In addition, Figure 2 shows unequivocally that the rate of approach to equilibrium is much slower for B from both samples than it was for Mo; in fact, B had not yet reached a steady value after our longest period of shaking, 127 days. The analytical error in these determinations is probably large, on the order of $\pm 15\%$ of the amount shown, but the two curves in Figure 2 are significantly different. Based on this slow rate of approach to equilibrium, we will be able to more accurately gauge the role of the velocity of percolation of the water in our considerations of the leaching of spent shale by rain and snow melt.

The amount of B released into solution by spent shale SS-1 (Figure 2) was about 5 mg/l at the end of 127 days. Some crops are sensitive to B and can tolerate no more than 1.0 mg/l. Included among these are plums, pears, apples, cherries, and peaches (Wilcox, 1958). Such crops are important in various parts of Colorado, and a leachate containing 5 mg/l dissolved B would cause damage to these. The leachate would have to be diluted 5 to 1 to be tolerated by these crops.

Finally, in Figure 3 we present results for fluoride from the shaker experiment. In this case the fresh oil shale apparently shows a higher solubility for F than the spent shale. Unfortunately, we do not yet have analyses for F in the solid materials, and SS-1 and OS-1 represent different feedstocks, so the results in Figure 3 may not be directly comparable. However, our preliminary experiments (shown in Table I) verify this reversal for the two shales from the same feedstock, OS-1 and SS-2.

The results for F in Figure 3 are very interesting in that they suggest that the retorted waste from the TOSCO II process will probably release less F to the environment than would a similar pile of natural, crushed shale. Whatever control might have been operating to increase the solubility of Mo and B upon retorting, the opposite effect is seen for F.

The rates of approach to equilibrium for F in Figure 3 are also interesting. The fresh shale releases its F much more rapidly than does retorted material.

The final concentrations for F in solution in Figure 3 are not much different from fresh and spent shale, both approaching about 25 to 35 mg/l. However, these values are both well above the value of about 2 mg/l that is the required limit for drinking water for humans (U.S. Environmental Protection Agency, 1975). Treatment or considerable dilution would be required to make this leachate acceptable for drinking water. This might be an important observation in view of the possibility of contamination of either ground water or the Colorado River in the vicinity of the retorting operations.

Table V

Content of As and Se in various solid shales, using three analytical techniques. n.d. = not determined.

Sample Number	As		Se	
	*X-ray Fluor.	**Cold a.a.	*X-ray Fluor.	***Wet Optical Fluor.
OS-1 Batch 1, Split 2	61 ± 5	80,76,68	3.1 ± 0.3	n.d.
OS-1 Batch 1, Split 19	n.d.	n.d.	n.d.	1.9
OS-1 Batch 1, Split 27	n.d.	n.d.	n.d.	2.8
SS-1 Batch 1, Split 13	74 ± 8	76,72	2.9 ± 0.3	3.3
SS-1 Batch 1, Split 20	n.d.	n.d.	n.d.	3.5
SS-2 Batch 1, Split 12	n.d.	n.d.	n.d.	3.1.
SS-2 Batch 2, Split 1	n.d.	85,86	n.d.	n.d.

* Average of x-ray fluorescence analysis of six replicates. Error shown is range of six values used in average. Absolute error of counting is 2%.

** Cold atomic absorption, using arsenic hydride gas. Estimated analytical error is ± 10%.

*** Optical fluorescence of dissolved Se, following fusion and digestion. Estimated analytical is ± 15% (Crenshaw and Larkin, 1974).

Table V shows a summation of our present analytical results for As and Se in the solid shales. Considering the fact that analysis for these two elements is not routine in any laboratory, we feel that the consistency shown among the various techniques is acceptable. For example, the concentrations of As shown for OS-1, batch 1, split 2 (first item in first column) agree reasonably well within the estimated analytical error. However, the agreement between the two methods for SS-1, batch 1, split 13 is much better (fourth item in first column). This points to a general problem that the analytical laboratory has encountered with fresh shale, namely, the difficulty of obtaining a clean and reliable fusion in the presence of the abundant fresh kerogen. The kerogen causes the fusion mixtures to react violently, with possible loss of volatile substances. Finally, the agreement for Se by two methods for SS-1, batch 1, split 13 is very good indeed.

The shaker experiments produced leachates that were uniformly low in As and Se. In addition, the analytical results showed considerable scatter. We present a summary of these results in Table VI; note that the values are for periods of shaking up to 33 days. We do not have results for 127 days. The most interesting thing about the results in Table VI is the consistently low concentrations of both of these elements found in the leachates. The mean values (in the last column of Table VI) correspond to about 0.02 to 0.05 mg/l in the leachate. These concentrations are close to drinking water standards (U.S. Environmental Protection Agency, 1975). In addition, it is interesting that As is far less soluble than Se, based on the original contents of the two elements in the solid material (shown in the third column of Table VI). These very low concentrations in the leachate lead us to believe that As and Se will not be a problem in natural leachates resulting from rain and snow melt on the waste piles of oil shale. We are therefore reducing the emphasis and amount of time that we might otherwise have spent on further investigation of these two elements. We will wait for additional results from the work of Dr. Lindsay of this project to see if uptake of As and Se by plants from soils of the region suggests that we should continue our work on these elements. If the plants do not take up meaningful quantities of As and Se, we would see no reason to include As and Se in our future work.

In summary, we feel that our shaker-type experiments have yielded useful information on the relative availability and rate of equilibration of the five anionic elements from fresh and spent shale. We have concluded that Mo, B, and F deserve further study, and As and Se leached from shale do not seem to pose much of a problem to the environment. Table VII is a brief summary of the approximate average percentage of leaching of Mo, B, and F that we found during our shaker experiments for fresh OS-1, spent SS-1, and spent SS-2.

Table VI

Results of shaker experiments for As and Se in 33 day time period.

Reported here in unites of mg of the element leached per kg shale.
Multiply 0.4 to obtain dissolved element in mg/l in the leachate.

Sample	Element	*Conc. in solid mg/kg	**Range	***Mean
SS-1	As	74	.05-.13	.10 ± .006
Batch 1				
Split 13	Se	3.1	.05-.06	.05 ± .003
OS-1	As	71	.09-.24	.15 ± .006
Batch 1				
Split 2	Se	3.1	.04-.19	.09 ± .003

* Average of all values shown in Table V for these samples.

** Results on three targets of solid residue after evaporation of solution by x-ray fluorescence.

*** Mean value is based on the three targets for each aliquot shown in preceding column. Error is absolute error of counting in x-ray fluorescence. Estimate total error by x-ray fluorescence is ± 15% of amount shown.

Table VII

Average percentage of Mo, B and F leached from spent shale relative to fresh shale (amount leached from spent shale/amount leached from fresh X 100).

Data from Figures 1,2, and 3 averaged for interval up to 33 days. Data for week-long period from early studies summarized in text. Averages are approximate.

Ratio of Samples	Shaking Time Interval	Percentage Ratio of Element Leached from Spent Shale Relative to Fresh Shale		
		<u>Mo</u>	<u>B</u>	<u>F</u>
SS-1/OS-1	up to 33 days	285%	170%	65%
SS-1/OS-1	one week	450%	150%	50%
SS-2/OS-1	one week	715%	210%	65%

The significance of the data in Table VII is twofold. First, the data show that spent shale releases more Mo and B, and less F, than fresh shale. And second, spent shale SS-2 behaves chemically in similar fashion to SS-1.

Column Studies

We are currently engaged in a study of the leachate produced by water that percolates through laboratory columns of spent TOSCO II and Fischer Assay shale. At this time we have six columns in operation under various conditions and rates of flow. However, data are relatively complete only for two of these. The two that we report here were packed with TOSCO II spent shale SS-1, batch 1, split 1 and spent shale SS-2, batch 1, split 1.

The columns are made of Pyrex glass, approximately 2.5 cm inside diameter and 30 cm high. Based on our experience with the shaker experiments, we do not feel that loss of F or gain of B will be significant because of the limited surface contact between solution and the walls of the columns. The columns are packed about half full of finely powdered shale. This is done by pouring in small increments, followed by compaction with a rubber plunger. We have used both dry and wet packing, including an optimal 20-25% moisture for maximum compaction. The degree and nature of compaction certainly have strong effects on the permeability of the shale (Woodward-Clyde Consultants, 1975), but we have not been greatly concerned about this in the early stages of our study of the chemistry of the leachate. In future work we will determine the density of our column packing so that it can be compared to the degree of compaction used by other researchers. Based on the measured head of water, the length of the columns, and the rate of flow, we calculate a darcy permeability of between 1×10^{-5} and 6×10^{-5} cm/sec for most of our columns of shale. In some of our columns we have observed a decrease in permeability with continued flow of water, whereas in others the permeability has increased with time; these phenomena remain to be investigated. We have used deionized water as the leaching fluid in all of our work; this is intended to simulate rain water or snow melt on the piles of spent shale in the field. We feed the water into the top of the column, either by gravity or by means of a constant-flow syringe pump. A constant head of about 2 cm of water is maintained at all time by an overflow outlet above the shale-water interface. The columns are filled initially from the bottom to allow air bubbles to escape. The rate of flow has been maintained at between 15 and 30 ml/day in all experiments so far. We will vary this parameter in the future. The volume of the shale is calculated by weighing the column before and after packing. The porosity is measured by allowing water to flow from a burette into the shale until saturation is attained; the volume of water lost from the burette is then observed, and a correction applied for the volume that goes into the fiberglass plugs at the bottom and top of the column of shale. We feel that our calculated porosities are accurate to within one percent of the true value.

The leachate from each column is collected in a plastic volumetric cylinder. The cylinder and the column are nearly completely closed to the atmosphere to reduce evaporation. After measuring the volume of leachate, a portion is poured into a mini-conductance cell and the specific resistance is measured; this is converted to specific conductance by calculation. A second small portion is used for determination of pH by glass electrode. Another aliquot is diluted and sent to the central analytical laboratory for wet analysis for B and F. Finally, about 20 microliters are measured out with a micropipette and evaporated to dryness on a "formvar" film mounted in an aluminum ring. The film-ring assemblage is sent to the x-ray fluorescence laboratory for analysis. By preparing the x-ray targets in our laboratory at the time of sampling we avoid possible loss of elements due to storage in a container and the many possible problems of contamination. Two x-ray targets are prepared and analyzed for each aliquot of leachate; this gives us some idea of the overall precision of our preparation and the analysis. As shown in the tables that follow, the overall precision by x-ray is about $\pm 25\%$ for As and Se and 2% for Mo. The precision and accuracy of the electrode method for F seems to be about $\pm 10\%$. The curcumin method for B is highly suspect, and only partial; early results are given for B in the tables that follow. Dr. Robert Meglen of our central analytical laboratory now seems close to having developed a new, accurate method for B.

Results of leaching of one of the columns are shown in Table VIII. The most striking results shown in Table VII are the very low concentrations of Se and As in the leachates. The data confirm our earlier results (Table VI) from the shaker studies. The absolute values shown here for the concentrations in the leachate also check very well with those from Table VI (when the latter are multiplied by 0.4 to convert from the solid to the liquid phases), suggesting that equilibrium was approached in both sets of experiments. Again, our conclusion is strengthened that Se and As are probably not of environmental concern in leachates from spent oil shales.

The pH of the leachate, shown in the second column of Table VIII, remains relatively constant at about 8 to 8.6. These values are lower than those of 7.4 to 11.4 found for leachate from spent Paraho shale (Woodward-Clyde, 1975). This can probably be attributed to the lower temperature of retorting of the TOSCO II material, resulting in less calcining of the carbonate minerals.

In the third column of Table VII it is seen that the salinity of the leachate decreased from over 17,000 micromhos/cm in the first 1.1 pore volumes (29.7 ml) to 260 micromhos/cm after 15.7 pore volume (about 425 ml) of leachate had passed. Using an empirical correction factor of 0.62 (Pfeffer, 1974) for converting to total dissolved solids, these values correspond to 10,500 mg/l and 161 mg/l, respectively. This remarkable drop in salinity is good evidence that the easily soluble salts produced by retorting are quickly rinsed out by percolating water. We are now allowing some columns to age after the first set of percolation experiments; when these columns are again activated we will be able to determine if the salinity is regenerated by aging.

Table VIII

Column Leaching Study.

Sample of spent shale SS-1, batch 1, split 1 (TOSCO II). Shale mixed with 23% by weight water and packed into volume of 60.3 cc. Porosity approximately 45%, corresponding to a 27.1 ml pore volume. Free water head of 2.8 cm above shale surface. n.d. = not determined.

Sample No. of Leachate	Leach. pH	Specific Conductance (micromhos/ cm)	Permeability (cm/sec)	No. Pore Vols. Passed	*mg/l in leachate				
					F	B	Mo	Se	As
RW5139	n.d.	17,710	2.1×10^{-5}	1.1	12.0	7.4	11.8	.032	.037
RW5143	7.7	5492	2.0	1.6	9.5	7.7	3.3	.004	.016
RW5145	8.5	3851	1.7	1.4	9.4	n.d.	1.6	.002	.013
RW5154	8.6	3662	**4.9	1.5	10.5	n.d.	1.5	.005	.022
RW5155	8.6	2260	4.3	2.9	10.5	n.d.	.47	not detec- ted	.012
RW5156	8.6	2083	4.2	3.0	13.0	n.d.	.22	.004	.002
RW5157	7.9	412	5.1	3.1	16.1	n.d.	.26	.002	.011
RW5158	8.0	260	5.7	1.1	17.2	n.d.	.23	.002	.012

* Analytical error for F is $\pm 10\%$ of amount shown; done by electrode. Error for B is large; done colorimetrically. Mo, Se, and As done by x-ray fluorescence; Error is $\pm 2\%$ for Mo, and $\pm 25\%$ for Se and As. See text for discussion.

** At this point in the experiment the column seemed to plug up. The head of water was increased to 5.5 cm above the shale to maintain flow.

The permeabilities shown in Table VIII, about 2 to 6×10^{-5} cm/sec, are reasonable in comparison with data on poorly compacted Paraho spent shale (Woodward-Clyde, 1975). We will test the effect of other degrees of compaction as allowed by our apparatus. Of interest is the fact that the column used for Table VII seemed to plug up after about four pore volumes of leachate had passed. It was necessary to double the head of free water (from 2.8 to 5.5 cm) to maintain flow. After doubling the head, the apparent permeability also increased.

A very interesting feature appears in Table VII for the concentration of F in the leachate. The concentration of this element remained high, about 10 to 20 mg/l, throughout the experiment; this is in sharp contrast to the rapid drop in specific conductance. This clearly means that there is a solid reservoir of F in the shale that is capable of replenishing and restoring the F to the percolating water, unlike the total dissolved salts which seem to be simply rinsed out. The most obvious probable source of the F would be a solid mineral phase. The importance of this observation is that the F cannot simply be rinsed out of the spent shale by passage of one or two pore volumes of irrigation water or rainfall. Instead, the F will remain at a high concentration in the percolating waters for extended periods. This has significant implications in trying to devise a plan to handle any leachates that might contaminate resources of ground water or surface water in the region. The problem of F will not be as easy as simply trying to dilute or divert the first slug of leachate that emerges from the waste shale.

The concentrations shown in Table VIII for F are still well above the value of about 1 mg/l considered to be safe for drinking water for humans, but they are below those calculated from the results shown for the shaker study in Figure 2; this may indicate that we have not allowed adequate time for equilibration between the shale and percolating water in the column. We intend to use different rates of percolation in trying to answer this question about the approach to equilibrium.

Finally, in the column study of Table VIII, we see that the concentration of Mo in the leachate decreased rapidly with continued passage of leachate. In contrast to the F, the behavior of Mo is more like that of total dissolved solids. It indicates that the substrate which supplies F is quite different from that of Mo, either in form or ease of dissolution. The values for Mo in the leachate from the column bracket those found in the shaker study (Figure 1) on the same shale, suggesting that equilibrium may have been achieved for this element. We will not discuss the tentative results for B because of the difficulty in analyzing for this element.

In Table IX we present data from a continuing experiment with a column of spent shale SS-2. These data are useful for comparison with those for SS-1 in Table VIII. In the future, we will also prepare some columns with fresh shale OS-1 for comparison with its retorted equivalent, SS-2.

Table IX

Column Leaching Study on Spent Shale SS-2, Batch 1, Split 1 (TOSCO II).

Volume of shale = 67.1 cc. Packed with 23% moisture content. Porosity of approximately 45%, corresponding to 30.2 ml per pore volume. Level of water was 1.3 cm above shale-water interface. All errors on analytical data are the same as those given in Table VIII. n.d. = not determined

Sample No. of Leachate	Leachate pH	Specific Conductance (micromhos/ cm)	Permeability (cm/sec)	No. of Pore Volumes Passed	<u>F</u>	<u>B</u>	<u>Mo</u>	<u>Se</u>	<u>As</u>
RW5141	n.d.	22,885	3.5×10^{-5}	1.5	14.1	10.2	11.7	.016	.038
RW5144	8.1	1452	4.5	2.8	17.0	6.9	2.4	.005	.010
RW5146	8.2	758	4.3	2.8	18.0	n.d.	1.4	.003	.007
RW5149	8.3	495	7.8	9.2	18.1	n.d.	.86	.003	.012
RW5151	7.8	220	1.4	2.8	14.5	n.d.	.12	.002	.007

A question that always arises in considering trace elements in waters is whether or not the elements are in truly dissolved form. That is, is an analysis of the total concentration of a trace element, how much is truly dissolved and how much is present in particulate form? We have attempted to answer this question for the leachates from the column studies by passing the leachates through a 0.001 membrane filter prior to chemical analysis, then comparing the results after filtration with the total concentration in the non-filtered sample. The results of this investigation are shown in Table X. It is clear from these data that no significant difference exists between the non-filtered and filtered leachates. This leads us to conclude that As, Se, and Mo are present in truly dissolved form in the leachates. Of course, this study does not tell us whether they are present as the free ions or as complex ions.

Table X

Effect of Filtration Through 0.01 Micron Membrane Filters on Column Leachate.

Analytical results by x-ray fluorescence. Error shown is the absolute statistical error of counting the emitted radiation. Leachates were the first clear portion collected from new columns. All values in mg/l dissolved in leachate.

Spent Shale SS-1, Batch 1, Split 1					
Non-filtered			Filtered		
As	Se	Mo	As	Se	Mo
.037	.032	11.8	.032	.028	11.0
±	±	±	±	±	±
.005	.005	.18	.004	.003	.17

Computer Modeling

We intend to make use of computer techniques to help us understand the chemistry of the leachates and to predict how these leachates may impact the environment. In this regard, we have acquired two computer models related to such problems. The first, WATEQF (Plummer, Jones, and Truesdell, 1976) calculates the equilibrium chemistry of an aqueous solution, determining the various dissolved complexes and measuring the state of saturation of the water with respect to more than 100 minerals. We have modified the WATEQF program to include Mo species and made it operational on the CDC 6400 computer at the University of Colorado. We intend to use this program to help us determine the controls on the solubility and mobility of the trace ions, including the interesting control on F. The other program is one developed by Harter and Foster (1976) to predict the rate of movement of dissolved phosphorous downward through soils. We have also made this program, originally written in BASIC, operational in FORTRAN IV on the C.U. computer system. We hope to use it to predict the future downward migration of the trace contaminants from oil shale through the soils of the Piceance Creek Basin.

Leachate from Paraho Spent Shale

Our hope for our column work is that we can construct reasonable laboratory models for the processes that will occur in nature when natural precipitation falls on the disposal sites associated with the surface re-torts. However, we recognize the difficulties involved in this, and we therefore arranged with Dr. William Berg of Colorado State University to collect leachate from the very large lysimeters that he and Dr. H.P. Harbert have constructed at the paraho site (Harbert and Berg, 1976). Drs. Berg and Harbert are chiefly interested in salinity of the water in the spent Paraho shale and its effect on revegetation, and they have offered to let us study the content of trace substances in the leachate. These very large lysimeters will offer a reasonable model of the natural situation that will prevail if large amounts of Paraho waste are placed on the surface in this region.

We have so far conducted one sampling trip to the lysimeters at Paraho. We collected rainwater that had run across the bare bottom and side surfaces of the empty lysimeters. Analysis of this leachate will give us background information that we can use in assessing the true concentration of the trace elements that will result from passage of water through spent shale when the lysimeters are filled later this spring. We were able to prepare our x-ray targets at the site, thus avoiding all problems of storage and contamination.

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PROGRESS REPORT

TRACE ELEMENTS IN OIL SHALE

Availability of As, Se, B, Mo, and F to Plants Growing
on Revegetated Spent Shales of Western Colorado during 1976

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Future development of oil shale in western Colorado will disturb many land areas that will require revegetation as spent shale is redistributed to form new land surfaces.

The objective of this study was to see if trace elements such as As, Se, B, Mo and F are rendered more available to plants growing on processed spent shales. The high pH often associated with spent shales can be expected to increase the solubility and availability of these anionic trace elements.

The revegetation plots of Dr. W.A. Berg, located at Anvil Points and Piceance Basin in western Colorado, were used as the 1976 sampling sites. These plots were established in 1973 for vegetation stabilization studies of spent shales. The spent shales used were from TOSCO (the Oil Shale Corporation) and USBM (U.S. Bureau of Mines). Each site consisted of seven treatment plots for each type of spent shale. The treatments consisted of varying amounts of soil cover over the shales and different leaching treatments. Following construction of the plots they were fertilized, seeded with a mixture of native grasses and shrubs, mulched, and irrigated by sprinklers.

In July of 1976, vegetative samples were collected from both sites. Samples of western wheatgrass, Agropyron smithii var. "Arriba" were chosen because it comprised a dense cover over the plots at both sites, and was successfully established as the predominant vegetation. Four-wing saltbush, Atriplex canescens, was also chosen because as a salt accumulator, it offered special interest. Samples were composited from lines, transecting each treatment plot at three points: two feet from the crest; across the middle; and two feet from the bottom of the plots. Plant samples were clipped about 1 1/2" above ground and placed into clean cloth bags with labels.

In the laboratory, each sample was thoroughly washed to remove soil and dust adhering to the plant and separate other debris. The washed samples were placed in clean cloth bags, dried at 70° C for 48 hours and ground with a small Wiley mill with stainless steel head and screen. The ground sample was stored in a wax-lined paper bag.

Core samples from all treatment plots were also taken in August of 1976. These samples were screened and stored in soil test bags.

A portion of the ground plant samples was sent to Boulder for initial x-ray fluorescent analysis. Results were somewhat disappointing because of sensitivity and homogeneity problems. The results at this time are indicative only of expected ranges of the elements in the plant materials.

In conjunction with the analytical lab in Boulder, reliable procedures are being worked out to analyze the plant materials for the indicated elements. Some of the representative results are shown in Tables I and II.

The boron analyses are quite variable for plants sampled from the same treatments and will need further development work before proceeding with the analysis. Some samples would appear to show toxic levels of boron, and do present some concern for the uptake of boron from spent shale sites by vegetation growing on them. The molybdenum content of wheatgrass at the Piceance Basin was significantly higher on spent shale sites than on soil check. At Anvil Points there was no difference between the soil checks and the spent shale sites.

The fluorine analyses are incomplete at this time, but the results given in Table I are within the normal ranges expected in plants. The arsenic levels indicated by x-ray fluorescence were less than one ppm. These levels have been substantiated in our lab. Selenium analyses are underway and are scheduled for completion by June.

In Table III there is evidence that the molybdenum content of four-wing saltbush growing on revegetated spent shales in the Piceance Basin had elevated levels of molybdenum wherever the USBM materials were used. This was true whether or not there was a cover of soil over the spent shale. At Anvil Points there was no indication of greatly enhanced levels of molybdenum.

From the present results, it appears that molybdenum and boron concentrations in plants growing on spent shale are sufficiently high to warrant further investigation. Since the plant materials are very difficult to sample and analyse because of variability between individual plants, re-sampling of the same plots would be desirable to provide a broader base of data.

Table I Representative results of trace element contents of western wheatgrass from revegetated spent shale plots.

Location	Treatment	Slope	Rep	B ppm	Mo ppm	F ppm
Piceance Basin	Soil Check	North	A		0.93	
			B	25	0.65	
		South	A	0	0.68	2.0
			B	0	0.90	2.4
	TOSCO S.S.	North	A	118	3.0	
			B	124	3.4	
		South	A	97	3.2	4.3
			B		3.8	2.6
	USBM S.S.	North	A	14	3.0	
			B		4.5	
		South	A	93	2.4	3.5
			B	28	5.5	
Anvil Points	Soil Check	North	A	19	3.2	
			B	2	6.0	1.6
		South	A		3.3	3.4
			B	115	2.5	
	TOSCO S.S.	North	A		3.5	
			B		2.5	5.1
		South	A	150	4.0	
			B	250	5.7	
	USBM S.S.	North	A	71	3.0	3.0
			B	27	4.4	5.0
		South	A	44	4.0	
			B			3.9

Table II Arsenic contents of western wheatgrass grown on spent shale.

Location	Treatment	Slope	Rep	As ppm
Piceance Basin	Unleached TOSCO w/12" soil cover	South	A	0.11
			B	0.12
	Unleached USBM w/24" soil cover	South	A	0.14
			B	0.13
	TOSCO S.S.	South	A	0.19
			B	0.20
	USBM S.S.	South	A	0.32
			B	0.26

Table III The molybdenum content of four-wing salt bush
(*Atriplex Canesens*) growing on revegetated spent
shales in western Colorado in 1976.

Treatment	Slope	Piceance Basin (ppm)	Anvil Points (ppm)
Soil Check	South	6.5	3.0
	North	5.8	2.8
TOSCO to Surface	South	6.7	2.3
TOSCO with 6" soil cover	North	4.0	_____
TOSCO with 12" soil cover	South	3.8	_____
USBM to Surface	South	23.5	6.3
	North	31.5	4.9
USBM with 6" soil cover	South	28.2	6.2
USBM with 24" soil cover	South	23.2	_____
	North	33.8	_____

ANALYTICAL FACILITIES

The analytical facilities consist of two separate laboratories. The chemistry facility is concentrating on the methods of sample preparation and wet chemical analyses of the samples submitted by the investigators. The nuclear physics facility is applying the x-ray fluorescence technique for routine multi-element analysis. During the development phase of the analytical work many samples are being analysed by both chemical and x-ray techniques. This procedure is used to evaluate accuracy and to determine the most efficient method of analysis. The two facilities are working together to develop methods that exploit the advantages of these two complementary analytical techniques. The following report, in two sections, will describe the work being performed in these two laboratories.

PROGRESS REPORT
TRACE ELEMENTS IN OIL SHALE

Analytical Chemistry

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INTRODUCTION

The primary function of the central analytical laboratory of the Environmental Trace Substances Research Program is to supply accurate chemical analyses for the project investigators. The methods used for these analyses are primarily those described in the current literature. While the literature contains several methods for the analysis of boron, arsenic, selenium, fluoride, and molybdenum, these methods have required considerable modification to accommodate the special analytical problems associated with the samples collected for the study. Two factors have slowed the progress of the project considerably. First, the samples are unique in many ways, and they present chemically complex matrices that are different from the matrices encountered in the published methods. Secondly, the five elements to be determined are among the most difficult to determine accurately. This difficulty is compounded by the fact that many of the samples submitted have concentrations near the detection limits of existing methods. For these reasons, a substantial expenditure of time has been required for the development of reliable and accurate methods. The following report will summarize some of the progress that has been achieved in detection techniques, sample preparation, and assessment of accuracy.

METHODS DEVELOPMENT

Two major areas of development are underway: adaptation of available measurement techniques, and development of sample preparations. Many techniques published in the literature are generally applicable to aqueous solutions of the sample. The approach taken in this laboratory has been to adapt the available methods to our instrumentation and facilities. We have attempted to validate these techniques by first applying the methods to aqueous standards. We are now confident that we can reproducibly and accurately measure all of the target elements in simple aqueous media. This is an important prerequisite for the evaluation

of our sample handling and preparation techniques. With this capability we can isolate specific interferences associated with the analysis of real samples. The second, and most difficult aspect, of methods development has been the sample preparation.

In most cases, if the sample can be completely dissolved in an aqueous medium, the chemistry can be adequately controlled so that the measurement can be performed with confidence. Geological samples have presented the most complex problems since the vigorous treatments required to completely dissolve silicates often causes the loss of the more volatile elements. Arsenic and selenium are among the most easily lost during sample treatment. Conventional high temperature fusions and acid digestions are therefore not applicable. A second complication is introduced by the presence of large quantities of organic material (as in the shales). Even more moderate chemical treatments lead to substantial losses of As and Se when high concentrations of organic compounds are present during the sample preparation. Boron and fluoride also present special difficulties since the use of conventional borosilicate glassware leads to contamination of samples and the loss of fluoride through adsorption. These difficulties have required that we use separate sample preparations for each element.

Four major types of sample matrix are being examined:

1. Geological Samples: including rocks, soils, shales, and spent shales.
2. Biological Samples: plant matter and animal tissue.
3. Waters : natural waters, waters from laboratory and field tests, and sample solutions from all sample preparations.
4. Shale oil.

We are attempting to reduce the number of sample preparations from one per element per matrix. The analytical procedures in which we have confidence are shown in Table I. A brief description of the detection technique used for each element follows. The various sample preparations which have been successful are also briefly described below.

TABLE I

Status of Methodology for the Target Elements in Various Sample Matrices

Element	Sample Type			
	Geological	Biological	Water	Oil
Arsenic	+	+	+	+
Boron	(+)	(+)	+	?
Fluoride	?	(+)	+	?
Molybdenum	+	+	+	+
Selenium	?	?	+	?

+ = Treatment and detection validated

(+) = Method near validation

? = Work in progress, provisional method only

Boron

A spectrophotometric method is the most widely used technique for the analysis of boron in aqueous media. This technique requires the formation of an organic (2-ethyl-1,3-hexandiol) complex of boron which may be extracted into an organic solvent (chloroform). This extraction effects a separation of the analyte from potential interferents. An aliquot of the extract is then chemically treated to release borate which can form a colored complex with carcumine. This yellow complex is soluble in ethyl alcohol and may be used to quantitatively determine the elemental content. This procedure is relatively simple but very poor reproducibility is obtained. Plant samples are ashed at 450°C and dissolved in aqueous hydrochloric acid for subsequent separation and measurement. The acid solutions of the alkaline fusion product of geological samples are similarly treated.

A new detection procedure is currently being evaluated. This method uses the flame emission spectrometric technique. This method is much less sensitive than the colorimetric method but is much more reproducible. This method will probably become operational within the next few weeks. Atomic absorption analysis for boron is not sufficiently sensitive for our needs.

Arsenic and Selenium

Aqueous samples containing As and Se are analyzed by generation of volatile hydrides. The hydride gases are carried into a hydrogen-argon-air flame and the elements are detected by atomic absorption spectrophotometry. The liberation of gaseous hydroxides avoids the matrix effects that would exist with graphite-furnace atomic absorption. The detection limit for arsenic by this technique is sufficiently low for the analysis of most of the samples submitted by the project investigators. However, the selenium detection limit of this technique is not low enough to permit the accurate analysis of many of the samples submitted. Several alternate detection methods exhibiting better sensitivity are currently under development. Complexation with 2,3 diaminonaphthalene followed by fluorescence measurement is one procedure that can be adapted to our use most quickly.

Geological samples are fused with sodium peroxide. The aqueous solutions of the fusion product are used for the detection of the elements. Plant samples are digested in sulfuric, nitric acid mixture in the presence of hydrogen peroxide. A similar digestion procedure may be used for the dissolution of the shale oil. A short description of the reliability and accuracy of these treatments is discussed in a later section of this report.

Molybdenum

The spectrophotometric detection of the Mo thiocyanate complex is used for aqueous extracts of plant digests and geological samples. Plants are ashed at 450°C prior to acid dissolution of the sample. Geological samples are treated with sulfuric, nitric, and hydrofluoric acid prior to analysis. In addition, two fusion techniques are also available for the decomposition of silicate materials. Unfortunately, the vigor of these treatments leads to the loss of As and Se. Therefore, separate fusion techniques are required for these elements. For samples above 10 ppm in Mo the sodium peroxide fusion is applicable to As, Se, and Mo. This method results in a considerable saving of time when applicable.

Fluoride

Fluoride in aqueous solution is detected by using a fluoride selective electrode. This method is severely limited in its applicability by the presence of many interferences. Aqueous solutions of biological and geological samples present several matrix interferences. At the present time it is necessary to use the method of standard additions to analyze such samples. This is highly undesirable because the time required per analysis is about three times as long as is required for direct analysis. These problems are presently the subject of extensive examination.

ACCURACY

One of the most difficult tasks facing the analyst is the determination of the accuracy of his results. No absolute measure of accuracy is possible. The analyst must make a judgement about probable accuracy by comparing his results to the value obtained by other competent analysts using perfected techniques and methods. The analyst's competence and the perfection of this techniques are usually determined by performing several accuracy and precision tests. Three of the testing procedures used in this laboratory are:

1. Analysis of Standard Reference Materials (SRM's) when available.
2. Elemental Spike Recovery from real sample matrices.
3. Replicate analyses by independent detection techniques.

The analysis of Standard Reference Materials (SRM's) provides a useful test of the reliability of an analytical procedure. When available, SRM's can faithfully reproduce the kinds of chemical and physical problems that are encountered in the analysis of real samples. However, in some cases the elemental content of the available SRM's are

sufficiently different from the concentrations expected in our samples that evaluation is less meaningful. In spite of this limitation, analysis of several different SRM's for the volatile elements can provide a valuable check of the recovery of the element after our rather vigorous sample treatments. The following table (Table II) lists the analyses and comparisons that have been completed. Additional SRM's are now in preparation for analysis. These include coal, bovine liver, and fuel oil. Boron, fluoride, and molybdenum have not yet been reported by the National Bureau of Standards for these samples.

Table II

Analysis of Standard Reference Materials

		<u>This Lab</u> (mg/g)	<u>NBS</u> (mg/g)
Orchard leaves SRM 1571	As	9.5 ± .9	11 ± 2
	B	29 ± 3	33 ± 3
	F	4.2 ± .4	(4)
	Mo	0.2 ± .1	0.3 ± .1
	Se	≤ .2	0.08 ± .01
Fly ash SRM 1633	As	60 ± 6	61 ± 6
	B	_____	_____
	F	_____	_____
	Mo	_____	_____
	Se	_____	9.4 ± .5

Spike Recovery studies have been helpful in determining the effectiveness of the sample treatments. One difficulty associated with Spike recovery studies is that the chemical form in which the element is added to the experimental matrix does not necessarily duplicate the naturally occurring form. In most cases this means that the substance is more readily released from the experimental matrix. However, Spike Recovery studies for the more volatile elements such as As and Se can provide a valuable test for the retention of the elements during vigorous sample treatment. Two artificial matrices have been used to test our sample treatment methods:

- (a) An artificial silicate material has been prepared from aqueous sodium silicate solution. The aqueous solution was spiked at four concentrations of the five target elements. The excess water was slowly evaporated at 70°C until a silicate glass was formed. The solid silicate was then pulverized and subjected to analysis, Na_2O_2 scintering at 450°C. This is the same technique used for geological sample preparation. So far only As has been analyzed accurately. The recoveries are shown in Table III. The detection limit for As is about 0.5 mg/g. All spikes were recovered quantitatively.
- (b) The analysis of oil from the more volatile elements has been quite difficult since a vigorous acid digestion at high temperatures can lead to a loss of As and Se when organics are present. In order to test our digestive procedure, an artificial oil matrix was prepared using commercially available CONOSTAN OIL. This oil consists of pure mineral to which 15 elements have been added as organometallic compounds. Five samples were prepared containing 0 to 17 mg/g of As. The samples were refluxed under a water cooled condenser with fuming nitric acid and sulfuric acid. Following this preliminary oxidation 30% hydrogen peroxide was added and the samples were refluxed until the destruction of organic matter was complete. Arsenic analysis was performed by AAS (a completely satisfactory method for selenium spiking has not yet been found). The As Spike Recoveries are also shown in Table III.

The final type of accuracy test being done is a comparison of analyses performed by independent detection techniques. Comparisons between the spectrophotometric and atomic absorption determinations of Mo show excellent agreement for all sample matrices. A comparison of these techniques with the results obtained for As, Se, and Mo by x-ray fluorescence are also in good agreement. Comparison of x-ray fluorescence analysis of pulverized shale samples with atomic absorption results agree

Table III

Arsenic Spike Recovery Studies
for Matrix Types

	<u>Spike</u> (mg/g)	<u>Recovery</u> (mg/g)	<u>% of</u> <u>Recovery</u>
Silicate	0	.6 ± .4	
	1.2	2.0 ± .4	167*
	6.5	7.0 ± .4	108
	12.7	12.8 ± .4	101
	62.9	62.5 ± .8	99
Oil		0.1 ± .1	
	1.4	1.2 ± .2	86*
	5.0	5.0 ± .2	100
	10.0	10.0 ± .5	100
	17.0	18.5 ± 1.0	109

* At detection limit of the element the uncertainty of the method restricts the usefulness of these calculated recoveries.

within the experimental errors associated with the two techniques. Similar comparisons for Se analyses by the two techniques are also quite good for samples above the detection limit of about 2 mg/g in the solid sample. The more sensitive optical fluorescence technique also shows good agreement between the techniques. Since most of the samples submitted are at or near the detection limit of both XRF and AAS it appears that we will have to adopt the optical fluorescence technique for these samples until a better, more rapid technique can be developed.

Table IV summarizes the number and types of analyses performed in the chemistry facility from June 1, 1976 to the present.

Table IV

Summary of Chemical Analyses
June 1, 1976 to February 18, 1977

<u>Type of Sample</u>	<u>Number of Analyses</u>
Geological	306
Biological	178
Waters	179
Oil	<u>4</u>
TOTAL	667

PROGRESS REPORT

TRACE ELEMENTS IN OIL SHALE

X-Ray Fluorescence Analysis

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INTRODUCTION

The philosophy of the investigators on the oil shale project has been to have the capability of measuring every element of interest by at least two independent methods. Because x-ray fluorescence is a versatile method which can measure all elements from potassium to uranium, it provides considerable "second measurement" capability.

A unique x-ray fluorescence analysis facility has been developed at the Nuclear Physics Laboratory of the University of Colorado.¹ The special features of this system, together with their advantages and disadvantages will be discussed below.

The x-ray fluorescence method consists of irradiating a carefully measured mass or volume of a sample with a filtered beam of x-rays from an x-ray tube and simultaneously observing the fluorescent x-rays emitted by the sample. The energy of each x-ray from the sample is uniquely characteristic of the element from which it was emitted. The number of x-rays from each element is proportional to the amount of that element present in the sample, assuming that the absorption of x-rays leaving the sample is negligible.

The facility developed here has emphasized high sensitivity and small sample size. Samples from 10 to 3,000 micrograms are analyzed, with most solid samples being about 250 micrograms. The major advantage of small sample size is that corrections for the absorption of x-rays leaving the sample become small or negligible. This is a great advantage when analyzing a wide variety of samples, each of which would have different absorption correction problems. Our data is corrected for absorption, but because the corrections normally are small, uncertainty in the correction is not usually a major problem. The major disadvantage of small sample size is the possibility that a small sample may not be representative of the parent material. This problem is unimportant for liquid samples, such as leachates, where the liquid is homogenous. It is more serious in less homogenous materials, such as ground oil shale. However, the magnitude of the problem is measurable by simply analyzing multiple samples from the parent material and observing the standard deviation for the set of samples. Data on this point is presented later, however, we can say that for most elements (with a few notable exceptions, such as barium) the homogeneity

1. "Medical Applications of a Small Sample X-Ray Fluorescence System", A.C. Alfrey, L.L. Nunnelle, H. Rudolph, and W.R. Smythe, *Advances in X-Ray Analysis* 19 (1976), 497-510.

of the oil samples seems to be quite adequate.

Another feature of the existing system is a data storage and retrieval system. The x-ray fluorescence system is operated by a digital equipment corporation PDP-8E computer. When the samples to be analyzed (up to 32 at one time) are loaded into the XRF analyzer, the relevant information pertaining to each sample is entered into the computer by typewriter. The computer then controls the operation of the XRF system, ultimately storing the x-ray spectrum on magnetic tape, together with all of the information about the target. Throughout the the computer analysis of the data the sample information remains with the analytical results, both being ultimately filed on magnetic tape. A computer program known as "SERCH 2" is available for searching the tape, collecting runs of a particular type, searching for various types of correlations, and when correlations are found, it can produce printed plots of the data so that the significance of the correlation may be examined by the experimenter. It is also possible to perform both paired and unpaired Student T-Tests, to determine, for example, the degree to which the differences in concentration of elements from the two groups of samples are significant.

Table I shows the breakdown of the samples run from June 1, 1976 to February 8, 1977 by sample type. In addition to the runs shown, there were a number of pellet targets run in conjunction with oil shale pellet target development effort, which have not been included.

OIL SHALE LEACHATES

A simple, reliable method of analyzing oil shale leachates has been developed. Single or multiple ten microliter drops of the leachate are deposited with an Eppendorf pipette on a thin Formvar foil and evaporated to dryness. A second foil is placed on top to prevent loss of the residue. Arsenic, selenium, and molybdenum have been measured by this method. The group working with the leachates now prepares the target themselves to avoid any problem with storage and transfer of the leachates. In the future we will be reporting all of the elements detected in the leachates.

OIL SHALE STANDARD SAMPLES

The XRF analytical methodology for oil shale is being developed concurrently with the validation of nine proposed standard oil shale samples prepared by Dr. Thomas Wildeman. Our past experience in XRF has been primarily with small samples (approximately 300 mg) of human tissue. The use of the same samples size was attempted for analysis of the powdered oil shale. Approximately 300 mg of oil shale was weighed

Table I

A Summary of XRF Analyses from
June 1, 1976 to February 8, 1977

<u>Type of Sample</u>	<u>XRF Runs</u>
Oil Shale & Oil Shale Leachates	218
Oil Shale Solutions & Fly Ash Standard Solutions	74
Plants Grown on Spent Oil Shale	81
Lab Water Purity Tests	20
Oil Shale Pellet Targets	5
TOTAL	398

on an analytical balance and then spread out on a thin Formvar foil. A drop of polystyrene glue is put on the powder and another foil placed on top to complete the target.

The analysis results for two samples are shown in Table II. These are preliminary results because the absorption corrections for oil shale samples have not yet been accurately worked out. Six targets were made from each of two samples to see if the results were reproducible for this small sample size. The homogeneity of the powdered oil shale is seen to be reasonably good for some elements but poor for others, particularly zirconium and barium. The three elements of most interest (arsenic, selenium, and molybdenum) have a standard deviation of approximately ten percent. Better precision is desirable but would require either a larger sample mass or a method for homogenizing the oil shale such as putting it into solution.

A technique is currently being developed that increases the mass of targets that we can analyze. The oil shale is pressed into a pellet using a high purity alumina punch and die to avoid contamination. The pellets can be made with a mass of three to ten milligrams which should improve the sampling precision.

The larger target mass results in much more absorption of the fluorescent x-rays in the sample and a careful correction for this must be made. A modified version of the absorption correction program is presently being developed and soon a suitable analysis method for powdered oil shale should be available.

An alternative method for alleviating the sampling problem is to homogenize the oil shale by putting it into solution and then making drop targets for analysis by XRF. Dr. Robert Meglen at the Analytical Chemistry Lab is currently developing a method for doing this in connection with his oil shale analysis by atomic absorption. The oil shale first undergoes a sodium peroxide fusion and is then dissolved in hydrochloric acid. We have analyzed his solutions by XRF to see if they would be suitable for our use. Unfortunately, when the drop targets dried, large salt crystals covered about one third of the sample area and made absorption corrections very difficult. The results obtained were not satisfactory. We will continue to analyze other solution methods in the future to see if they are suitable for our use.

PLANT SAMPLES

We received several samples of plants grown on spent oil shale plots from Dr. Willard Lindsay at Colorado State University. Standard 300 mg targets were made from the plant samples and results for arsenic, selenium, and molybdenum were reported. Two targets were made from each of seven samples to check for sample homogeneity. The molybdenum values were about 5 ppm but the variation between two targets of the same sample was sometimes large. The arsenic and selenium values were near our minimum detection

limit of 1 ppm for this type of target, so a comparison for these elements is difficult.

It is felt that future analyses of plant samples might best be accomplished with pellet targets to avoid the homogeneity problem. Alternatively, a suitable method of putting the plants into solution would permit the use of liquid drop targets.

Table II

XRF Analysis of Two Standard Oil Shale Samples.

Six targets of 300 mg each were made from each sample.

Raw Oil Shale OS-1 GU 00001 6 Targets								
Elements	Mean (ppm)	Range (ppm)	S.D.	% S.D.	Mean (ppm)	Range (ppm)	S.D.	% S.D.
Mn	130	100-142	17	14	160	150-185	13	8
Fe	12500	11500- 1300	500	4	15000	1400- 1700	850	6
Ni	22	21-24	0.9	4	26	24-29	1.3	5
Cu	37	33-41	3.7	10	38	37-41	1.6	4
Zn	59	44-73	9.8	17	63	57-68	4.4	7
Ga	3.6	3.0-4.2	0.4	11	3.9	2.8-4.5	0.6	2
As	59	54-68	5.2	9	72	63-82	7.3	10
Se	3.0	2.6-3.6	0.3	11	2.8	2.5-3.2	0.3	10
Rb	63	60-65	1.9	3	71	70-73	1.0	1
Sr	580	520-760	91	16	900	870-970	42	5
Y	8.0	7.4-8.8	0.5	6	9.5	9.1-10.0	0.3	3
Zr	48	41-65	8.8	18	57	44-78	14	24
Nb	4.2	3.9-4.6	0.2	6	4.2	3.9-5.0	0.4	9
Mo	28	25-30	1.8	6	31	28-38	3.8	12
Ba	5900	800- 20,000	8000	135	5200	2500- 11000	3400	64
Pb	27	23-29	2.1	8	27	25-29	1.4	5