

ANALYTICAL LABORATORY TECHNIQUES FOR OIL SHALE

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Introduction

From 1964 to 1967, the U. S. Bureau of Mines oil shale facilities at Anvil Points near Rifle, Colorado were reactivated for a cooperative industrial oil shale research program. Mobil Oil Corporation acted as manager for this project with five other major oil companies actively participating. These were Humble Oil and Refining Company, Continental Oil Company, Pan American Petroleum Corporation, Phillips Petroleum Company, and the former Sinclair Research, Inc. Technical people from these oil companies, supported by personnel from the Colorado School of Mines Research Foundation (CSMRF), carried out an intensive retorting and mining research program at the then named Anvil Points Oil Shale Research Center. This paper describes the activities of the analytical laboratory which supported the research program. These activities would probably be typical of any such oil shale laboratory in a remote location. Information on the research program may be found elsewhere (1).

The primary purpose of the analytical laboratory was to serve the retorting and mining research program as opposed to doing analytical research. Some supplementary research work actually was found necessary and was done. However, the scope of this paper is limited to the role of the laboratory as a support group.

The Laboratory and Staff

The Bureau of Mines building, laboratory furniture, and much equipment were available and used. Where necessary and justifiable, new equipment was added to complete the physical part of the laboratory. Our major concern was obtaining equipment and instrumentation that had a short delivery time, was reliable, and was as simple as possible. No skilled laboratory instrument repair service was available onsite.

The staff was headed by a supervisor and a chemist, both professional analytical chemists from the participating companies. From four to seven laboratory technicians were required during the project. These were hired specifically for this limited project by the CSMRF and had limited or no laboratory experience.

Training in oil shale laboratory techniques was required for both the technical staff and the technicians. For the technical people, this came from visits to the Bureau of Mines Station in Laramie, Wyoming and to the CSMRF in Golden, Colorado. The technicians were trained onsite by the chemists.

Analytical Methods

A variety of methods was used to analyze the samples generated by the research program. These are listed in Table I. Many are or are similar to ASTM methods and are so noted. Others are described below.

Fischer Assay

One of the most important tests was the Fischer Assay on raw and spent shale. A semiautomated apparatus was designed using the basic principles of the methods reported by the Bureau of Mines (2), and the CSMRF (3).

One control unit of the six-unit apparatus is shown in Figure 1. This control circuit provided the desired heating rate with an upper temperature limit

cutoff and indicator. Temperature was monitored with the pyrometer, and heating power with the ammeter. All six control units were mounted on an aluminum panel 24 in by 66 in.

When an assay was started, the variable transformer was set a full power (normally about 13.5 amperes), and the high set point of the pyrometer at 510°C. When the temperature reached 500°C, the variable transformer was adjusted to a pre-determined setting to maintain the final 500°C temperature. After retorting was complete, the main switch was opened.

A complete description of the Fischer Assay method is found in the Bureau of Mines paper.

### Carbon and Hydrogen

Precision carbon and hydrogen determinations were made using the conventional high temperature oxidative combustion technique followed by weighing the CO<sub>2</sub> and H<sub>2</sub>O formed. The apparatus was specifically designed and assembled for our needs. Three furnaces were used around a 19 mm by 36 in Vycor combustion tube, packed according to Steyermark (4). Temperatures of the furnaces were:

- 4 in Sample Furnace - Oil and Organic Standards 700 ± 10°C  
Gas, Shale, and Inorganic Standards 950 ± 10°C
- 12 in Middle Furnace - 680 ± 10°C
- 8 in Exit Furnace - 190 ± 10°C

For all but gas samples, the sample furnace was motor driven to allow an hour for movement from its initial position to its final position next to the middle furnace. When the final position was reached, a timer was activated to give 45 minutes additional combustion time before an end-of-run alarm sounded.

For gas samples, the sample furnace was positioned next to the middle furnace. A roll of copper gauze was inserted in place of the combustion boat and a special adapter (Figure 2) added to the combustion tube inlet. A 25% brine solution was used to displace the gas sample from a 1-liter gas sample tube in about 40 minutes. The combustion tube was then oxygen purged for an additional 20 minutes.

### Gas Chromatography of Gas Samples

Retort gases were routinely analyzed for CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO, and H<sub>2</sub>. A Fischer Gas Partitioner Model 25V with two columns in series was used. Column 1 was 30 in of hexamethylphosphoramide on 60-80 mesh Columpak; Column 2 was 6.5 ft of 42-60 mesh activated 13X molecular sieve. A Sargent Model SR-25 recorder with a 1.0-mv range plug recorded the chromatographic peaks. Both instruments provided the remote laboratory with the high reliability required. Helium was used as carrier gas for determining all components except hydrogen; nitrogen was used for determining hydrogen. Analyzed standard gas mixtures were used for calibration.

To obtain a composite sample for an experimental retort run, a continuous sample was sent to a brine-displacement gas-holder at the laboratory. Approximately 3 cu ft of gas were collected via a heat-traced line. After a complete sample was obtained, it was then routed through a drying tube directly to a 0.5 ml sample loop at the chromatograph.

### Water Analysis

Retort water produced by the retorting of oil shale was analyzed because of interest in corrosion, pollution, disposal, and possible future utilization. Analyses were made for NH<sub>3</sub>, Cl<sup>-</sup>, CO<sub>2</sub>, solids, ash, and pH.

### Shale Richness Distribution

Shale richness, or assay, can be predicted from its density. Consequently the richness distribution of a sample can be determined from the density distribution. Seven solutions of carbon tetrachloride and tetrabromoethane were prepared to cover the density range of interest, 1.6 to 2.4. The volumes of measured shale

samples floating in graduates of the various solutions were normalized to 100% followed by application of a richness-density relationship (5).

#### Sampling

Obtaining representative samples of raw and spent shale, and liquid and gaseous retort products were always of major concern. Crushed shale, especially raw shale, shows variations in richness with particle size. Liquid product from retorts is a mixture of oil, water, and solids. Gaseous product from retorts has entrained oil, solids, and water.

The various phases of the liquid and gaseous samples were normally separated, measured, and then analyzed individually.

Sampling and sample size reduction of the raw shale were very important. The Fischer Assay and other tests on raw shale samples were the bases of material balances for each experimental retort run.

Several steps of size reduction take place from the tons of raw shale mined to the 100 grams of raw shale charged to the laboratory retort for Fischer Assay. However, the minus eight-mesh shale fed to the laboratory retort must be representative of the sample of interest. When raw shale is crushed, the leaner, more brittle material concentrates in the finer particles, while the richer, tougher material resists crushing and concentrates in the larger particles. To dramatize this effect, Fischer Assays were run on various particle sizes of a crushed sample. The results are shown in Table II.

All shale samples submitted to the laboratory needed to be reduced in quantity and particle size before analyses could be made. A rigorous splitting procedure was developed to reduce the initial quantity received to a basic 775 to 825 gram portion. This portion was crushed to pass an eight-mesh screen. Then another specific splitting and combining procedure was used to reduce this quantity to the amounts required for the individual tests.

#### Records

As previously noted, this project involved the U. S. Bureau of Mines, the CSMRF and six oil companies. Under these circumstances, accurate and complete records of samples and their analyses were essential. All samples received by the laboratory were sequentially numbered and recorded in bound notebooks. Their identity, date received, date analyses completed, and analyses made were also recorded. Bound calculation books were used and retained for each test, so that the original basic data were available if required.

Nine forms for data workup and reporting were developed for consistency and simplification. All of these were color coded for ease of identification.

Before the completed analyses on any sample were officially released from the laboratory, they were checked by one of the analytical chemists. The philosophy maintained by the laboratory was to report no result in preference to a questionable result.

#### Quality Control and Crosscheck Programs

A planned and effective quality control program was maintained throughout the research project. A schedule was posted for the technicians showing what tests each was to run on the quality control samples each week. At the end of the week they submitted a form with their results. These were recorded and any abnormal variations noted and investigated.

Every three months standard deviations for all tests in the quality control program were updated. Final statistics for some of the key tests in the program are shown in Table III. The number of quality control tests run depended upon the

frequency of each test normally requested and its importance. They averaged about 5% of the normal work load. Fischer Assays were run most frequently.

The internal quality control program took care of the precision of the tests. However any laboratory, especially a remote and relatively inexperienced laboratory, is also concerned about the absolute accuracy of its results. Standards and synthetic samples were used where possible. In addition, during the program several samples were crosschecked with other laboratories. Most of the comparisons were made with the Bureau of Mines at Laramie. Data were also exchanged with the CSMRF, Mobil, and Humble. Some of the typical crosscheck data are shown in Table IV. The Fischer Assay data are averages of several determinations. Agreements were from satisfactory to excellent.

Participating oil company laboratories were also requested to perform analyses for which this laboratory was not equipped. Examples of these were mass spectrometer gas analyses, and detailed analyses of oil and distillation fractions.

#### Correlations Among Analyses

During the course of analyzing several hundred samples, some correlations among the results from several methods were developed. Most of these were with the Fischer Assay of raw shale. A computer regression analysis program developed the equations for the relationships, as well as the correlation coefficient and standard deviation. These data are given in Table V.

These relationships compared well with those previously obtained by the Bureau of Mines, and were very useful to internally check analytical results for consistency.

#### Termination of Program

The Anvil Points Oil Shale Research Center Laboratory was in operation three years, and satisfactorily performed its function as a support group. At the end of the program, all equipment and supplies were appropriately deactivated, stored, or otherwise disposed of. All notebooks and records were filed and a final summary report was prepared. With this experience and newer instrumentation available, a laboratory today could be significantly improved. Undoubtedly much of the success of the laboratory was due to the high staff ratio of two analytical chemists to four-to-seven technicians for mostly routine analyses. The chemists were able to closely supervise the routine work and develop and improve methods. In addition, they were still able to keep familiar with and contribute to the research program.

#### Acknowledgment

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References

- (1) Lawson, J. E., et.al., "Gas Combustion Retorting Performance in a Large Demonstration Retort" This Symposium.
- (2) Hubbard, A. B., "Automated Modified Fischer Retorts for Assaying Oil Shale and Bituminous Materials, U. S. Bureau of Mines Report of Investigations No. 6676, (1965).
- (3) Reeves, W. H., "Investigation of Methods for the Determination of Crude Shale Oil in Oil Shales," Colorado School of Mines Research Foundation, Report No. 64-1, (1964).
- (4) Steyermark, A., Quantitative Organic Microanalysis, pp. 221, Academic Press, New York, 2nd edition, (1961).
- (5) Smith, J. W., "Applicability of a Specific Gravity-Oil Yield Relationship to Green River Oil Shale," Ind. Engr. Chem, 3, 306 (1958).

TABLE I

ANALYTICAL METHODS

<u>Name</u>	<u>Procedure</u>
Ash Content of Oil	ASTM D 482
Ash Content of Shale	950°C with air
Benzene Extractables in Shale	ASTM D 473 s
C and H (total) in Shale, Oil, or Gas	See Text
Density of Shale	Loose, packed, solid
Distillation of Oil (10 mm.)	ASTM D 1160
Fischer Assay of Shale	See Text
Gas Analysis by Gas Chromatography	See Text
Gravity of Oil	ASTM D 287
Mineral CO <sub>2</sub> Content of Shale	ASTM D 1756 s
Moisture Content of Shale	Volatiles at 105°C
Nitrogen (Kjeldahl) in Shale and Oil	ASTM E 258 s
Particle Size Distribution of Shale	Sieve analysis
Pour Point of Oil	ASTM D 97
Ramsbottom Carbon Residue of Oil	ASTM D 524
Saybolt Viscosity of Oil	ASTM D 88
Shale Richness Distribution	See Text
Water Analysis	See Text
Water in Oil	ASTM D 95
Water and Sediment in Oil	ASTM D 1796 s

s - method used similar to ASTM method

TABLE II

VARIATION OF RICHNESS OF RAW SHALE WITH SIZE

<u>Size (mesh)</u>	<u>Gal/Ton (Fischer Assay)</u>
+4	31.8
-4, +8	30.6
-8, +20	28.6
-20, +48	28.0
-48, +100	23.9
-100, +200	20.8
-200	19.6

TABLE III  
INTERNAL QUALITY CONTROL PROGRAM STATISTICS

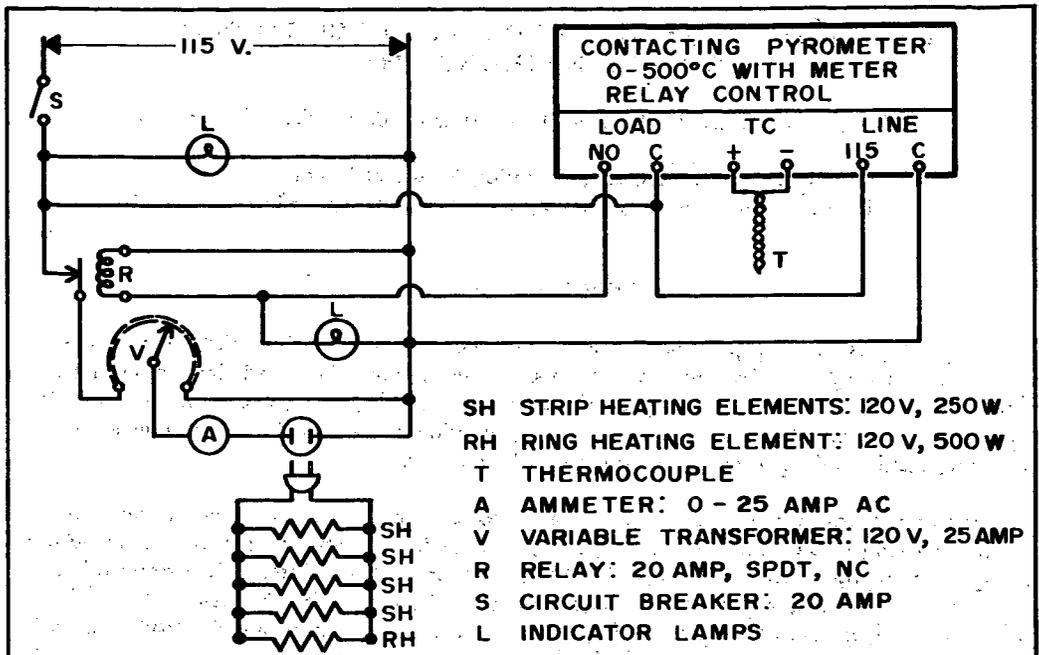
<u>Material</u>	<u>Test</u>	<u>Level</u>	<u>95% Confidence Limit</u>
Raw Shale	Fischer Assay	28 gal/ton	0.48
	Mineral CO <sub>2</sub>	17 Wt%	0.32
	Ash	69 Wt%	0.19
	Moisture	0.2 Wt%	0.034
	Carbon	16 Wt%	0.16
	Hydrogen	2 Wt%	0.063
Shale Oil	Carbon	84 Wt%	0.35
	Hydrogen	11 Wt%	0.55
	Nitrogen	2 Wt%	0.11
Retort Gas	Carbon	10 lb/MSCF	0.48
	Hydrogen	0.3 lb/MSCF	0.13

TABLE IV  
SUMMARY OF CROSSCHECK DATA

<u>Test</u>	<u>Laboratory</u>		
	<u>Anvil Points</u>	<u>B of M</u>	<u>Humble</u>
Fischer Assay	26.7	27.0	-
	30.7	30.4	-
Specific Gravity (Oil)	0.917	0.917	-
Carbon (Raw Shale)	16.3	16.2	-
(Spent Shale)	6.77	6.78	6.77
(Oil)	83.9	84.8	84.0
Hydrogen (Raw Shale)	1.70	1.70	1.72
(Spent Shale)	0.30	0.27	0.28
(Oil)	11.1	11.6	11.4
Mineral CO <sub>2</sub> (Raw Shale)	16.5	16.2	-
(Spent Shale)	14.9	14.5	-
Ash (Raw Shale)	68.2	68.4	-
(Spent Shale)	82.7	82.8	-

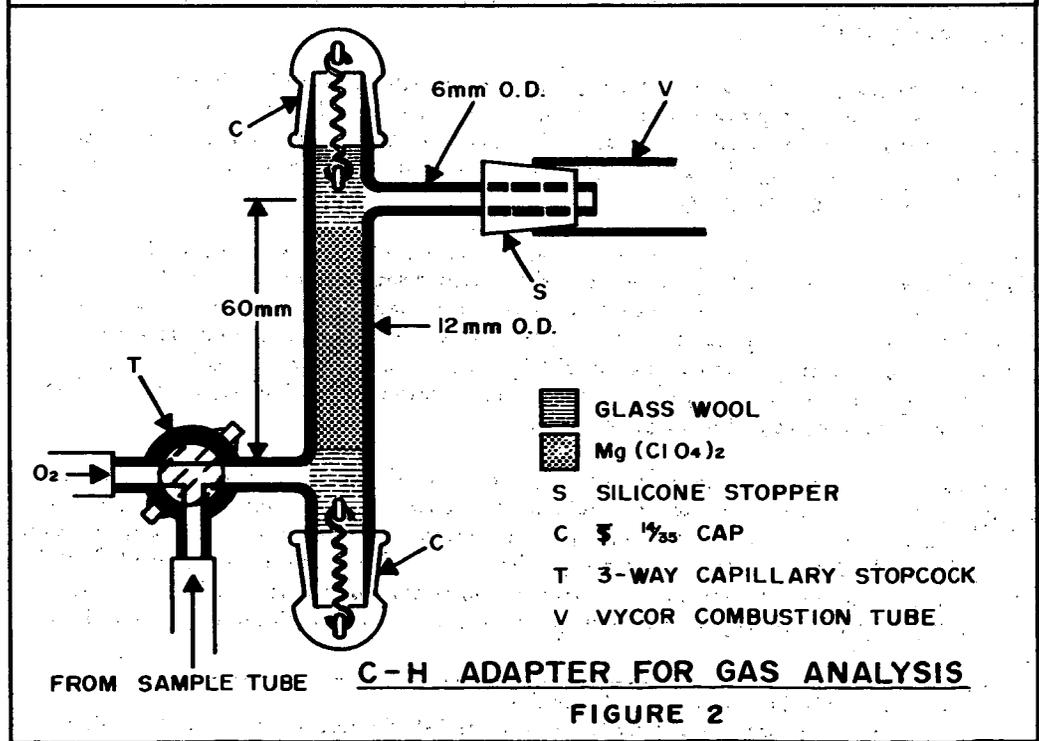
TABLE V  
CORRELATIONS AMONG ANALYSES

<u>Equations of Relationships</u>		<u>Correlation Coefficient</u>	<u>Standard Deviation</u>
<u>(R - Raw Shale)</u>	<u>S - Spent Shale)</u>		
R	Total Carbon = (0.404)(FA) + 5.58	0.97	0.15
R	Organic Carbon = (0.444)(FA) - 0.25	0.97	0.16
R	Hydrogen = (0.0499)(FA) + 0.39	0.93	0.03
R	Ash = (-0.372)(FA) + 77.70	0.92	0.24
R	Ignition Loss - CO <sub>2</sub> = (0.511)(FA) + 1.085	0.92	0.33
S	Mineral CO <sub>2</sub> = (-0.809)(Ash) + 82.20	0.99	0.23



**FISCHER ASSAY CONTROL CIRCUIT**

**FIGURE 1**



**FIGURE 2**