

MOBIL OIL CORPORATION
Research Department
Rifle, Colorado

Anvil Points Oil Shale Research Center

ANALYTICAL LABORATORY RESEARCH AND
PERFORMANCE DURING THE ANVIL
POINTS OIL SHALE PROGRAM

67.73 AP

November 22, 1967

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File 108.04.04

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REPORT NO. 67.73 AP
ANALYTICAL LABORATORY RESEARCH AND PERFORMANCE DURING
THE ANVIL POINTS OIL SHALE PROGRAM

This is the second in a series of seven final summary-reports covering specific research programs performed under the auspices of the Initial Program at Anvil Points. A single final report containing a summary of the most important findings and conclusions related to the entire Initial Program will also be issued.

The Analytical Laboratory Section was a major participant in an intensive and continuing effort which successfully improved carbon balances from the retorts. These are important to establish better understanding of the retort operation and greater confidence in yield levels. A problem, which was uncovered during the carbon balance investigation, was the characterization of the recycle gas composition. This work contributed to the economic evaluation of recovery of components of the gas and helped to establish a maximum yield for the Gas-Combustion Retorting process.

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ANALYTICAL LABORATORY RESEARCH AND PERFORMANCE DURING THE ANVIL POINTS OIL SHALE PROGRAM

INTRODUCTION

The former U. S. Bureau of Mines facility at Anvil Points, near Rifle, Colorado, was reactivated starting in May 1964 and was operated during 1965, 1966, and 1967. A research and development program was conducted to investigate the technical feasibility of room-and-pillar mining with explosives, crushing and Gas-Combustion Retorting techniques for oil shale. Mobil Oil Corporation acted as Project Manager for the cooperative industry group at Rifle which included Continental Oil Company, Humble Oil & Refining Company, Pan American Petroleum Corporation, Phillips Petroleum Company, and Sinclair Research, Inc. as Participating Parties. Costs of the Rifle operation were shared equally by the six participants. Each Participating Party was represented by personnel on the technical staff. The Colorado School of Mines Research Foundation, Inc. acted as lessor-of-record and supplied nontechnical personnel for administrative and logistic support.

The planned research program at Rifle consisted of two 18-month stages: Stage I, to determine retorting feasibility in small-scale pilot plant equipment and to provide information as to whether or not to continue the Rifle program; Stage II, to operate large-scale pilot plant equipment to develop information for scale-up to commercial-size retort elements and to conduct mining and crushing research. Because of technical difficulties with the retorting process, Stage I, which was initiated in May 1964, was extended by six months. These technical difficulties were resolved and Stage II commenced in April 1966. Experimental work was concluded in September 1967.

The final reporting from the Anvil Points project has been structured in pyramidal fashion. Reporting for three levels of interest has been implemented:

- General Management Summary - a single volume summary report covering the entire project.
- Technical Management Summary - seven reports, each summarizing work in a specific area, i.e. mining, crushing, retorting, mechanical models, mechanical engineering, analytical laboratory, and economics.

- Technical Detail - the mass of data transmissions, Monthly Progress Memoranda, Technical Memoranda, Weekly Newsletters, Technical Advisory Committee and Technical Observer presentations.

This is the technical management summary report dealing with the Analytical Laboratory.

The report describes the various activities of the Analytical Laboratory Section during the research program. This included:

- Participation in the investigation of special problems encountered during various phases of the project, including the development of methods for properly sampling the heterogeneous materials encountered in oil shale retorting, such as shale, liquid product and mist-gas mixtures.
- Rehabilitation of analytical facilities at Anvil Points, and establishment of the means to supply analytical data for the program.
- Development of sample and data handling systems, including identification of samples, recording of identity and results, and dissemination of data.
- Training and supervision of Analytical Laboratory personnel, many of whom were untrained in scientific techniques.
- Generation of data on precision, limitations, and potential improvements of analytical test methods used for the project.

The information included in this report should be useful for application to future oil shale research programs.

SUMMARY

During the course of the Anvil Points research program, the Analytical Laboratory Section made major efforts, in conjunction with other sections, toward solutions of many diverse problems that arose in connection with the retorting, crushing, and mining programs.

One of these problems, that of unsatisfactory carbon balance in the retorting program, led to a critical reevaluation and correction of sampling and analytical procedures, and established the source of discrepancies in carbon accounting. The carbon balances were important for accurately evaluating the distribution of carbon in the process streams, for better understanding and evaluation of retort operation, and for establishing greater confidence in product yields. Correction of, or compensation for, these discrepancies resulted in greatly improved balances.

Another problem, somewhat related to carbon balance - but also bearing on retorting economics - was the characterization of retort recycle gas composition. Experimental work, supported by analytical data from Mobil's Paulsboro Laboratory and by engineering calculations made at Anvil Points, established the composition of the recycle gas. This work contributed to the economic evaluation of potential recovery of components of the gas, and, based on flash vaporization calculations, helped to establish the maximum yield for the Gas-Combustion Retorting process.

The Laboratory also functioned in the routine supply of analytical data needed to support the retorting, crushing, and mining programs. To accomplish this, the Section shared in the rehabilitation of facilities, purchased equipment, established the analytical methods to be used, set up data recording and transmittal systems, and hired and trained laboratory technicians.

Outlines of test procedures (1), with precision data, analysis times, and potential improvements, are given in Section B.

The general operation of the Analytical Laboratory is described herein in Section B. The Laboratory was operated with 2 chemists and from 4 to 7 technicians over a period of 3 1/2 years, at a total cost of about \$60,000 per year. It was placed on a stand-by basis at the end of the program.

(1) See references listed in Bibliography.

DETAILED REPORT

A. Examples of Special Research Problems Investigated by the Analytical Laboratory Section

In addition to its routine task of supplying analytical data for the project, the Analytical Laboratory Section participated in the investigation and solution of a variety of special problems related to oil shale.

Many of these problems were uncovered by the Retorting, Mechanical Engineering, Mining, and Engineering and Economic Analyses units - and were worked on and solved in cooperation with them.

Two important problems which were investigated were attaining accurate carbon balances around the retorting process, and determining the composition of recycle gas from the Gas-Combustion Retort.

Accurate carbon balances were necessary to properly understand the retorting process, to determine sources of yield loss, and to measure yield accurately. Because, at the beginning of the program, the amount of carbon measured coming out of the process was less than that going in, an intensive program was initiated to correct - or at least locate and define - feed and product discrepancies. This investigation involved accurate determination of carbon in the raw shale input and the spent shale, shale oil, and retort gas outputs.

The characterization of the recycle gas from the retorting process was needed for several reasons. The first was related to its importance in the carbon balance, since it was one of the carbon-containing products. A second was that the gas composition was necessary for a reliable estimation of its potential economic value. A third was that it could be used for a valid approximation of the gas heating value.

1. Efforts to Improve Carbon Balance

a. Introduction

Early in the research program, during late 1964, it was recognized that there was a problem in obtaining good material balances for retort runs (2). This applied particularly to carbon balances. Part of the problem was caused by inaccurate measurements of retort input and output streams; another part was caused by inaccuracies in sampling and analytical procedures. Consequently, a joint program (3) was started in order to investigate the factors that influenced these balances,

and to improve them. This was a recurring problem which had to be solved for each of the three retort systems used during the program. This section of the report will concentrate on some of the work done by the Analytical Laboratory Section in the continual effort to solve this problem.

b. Status of Carbon Balances at Different Stages in the Program

The status of carbon balances varied from time to time throughout the program. The usual pattern was that poor carbon balances were obtained whenever a new retort was started up, and as measurement problems were solved, the balances improved.

Near the start of experimentation on Retort No. 1, balances for 18 runs from this program were compared with 18 balances that had been previously obtained by the U. S. Bureau of Mines (4). The comparison, in Table 1, indicated that the balances (on a 100% ash basis) obtained during this program were about as good as those from the previous one. Obviously, however, the carbon balances, needed improvement.

TABLE 1

COMPARISON OF BALANCES OBTAINED BY THE U. S. BUREAU OF MINES AND THE ANVIL POINTS PROGRAM (100% ASH BALANCE BASIS) (4)

Balance, %	18 Runs by the U. S. Bureau of Mines		First 18 Runs by Anvil Points	
	Mean Value	95% Confidence Limits	Mean Value	95% Confidence Limits
Overall	101.4	±3	99.8	±5
Total Carbon	93.6	±16	95.7	±14

After a major effort at Anvil Points, during which both material input and output data, and analytical information (especially on carbon content of the vent gas) were made more accurate, the balances improved markedly. (Figure 1 shows sampling points on Retort No. 3; the systems for the other retorts were similar.) Data showing the comparisons of carbon balances for runs near the beginning and end of each retort's operation are given in Table 2.

FIGURE 1

RETORT NO.3 - PROCESS FLOW DIAGRAM

SAMPLING POINTS

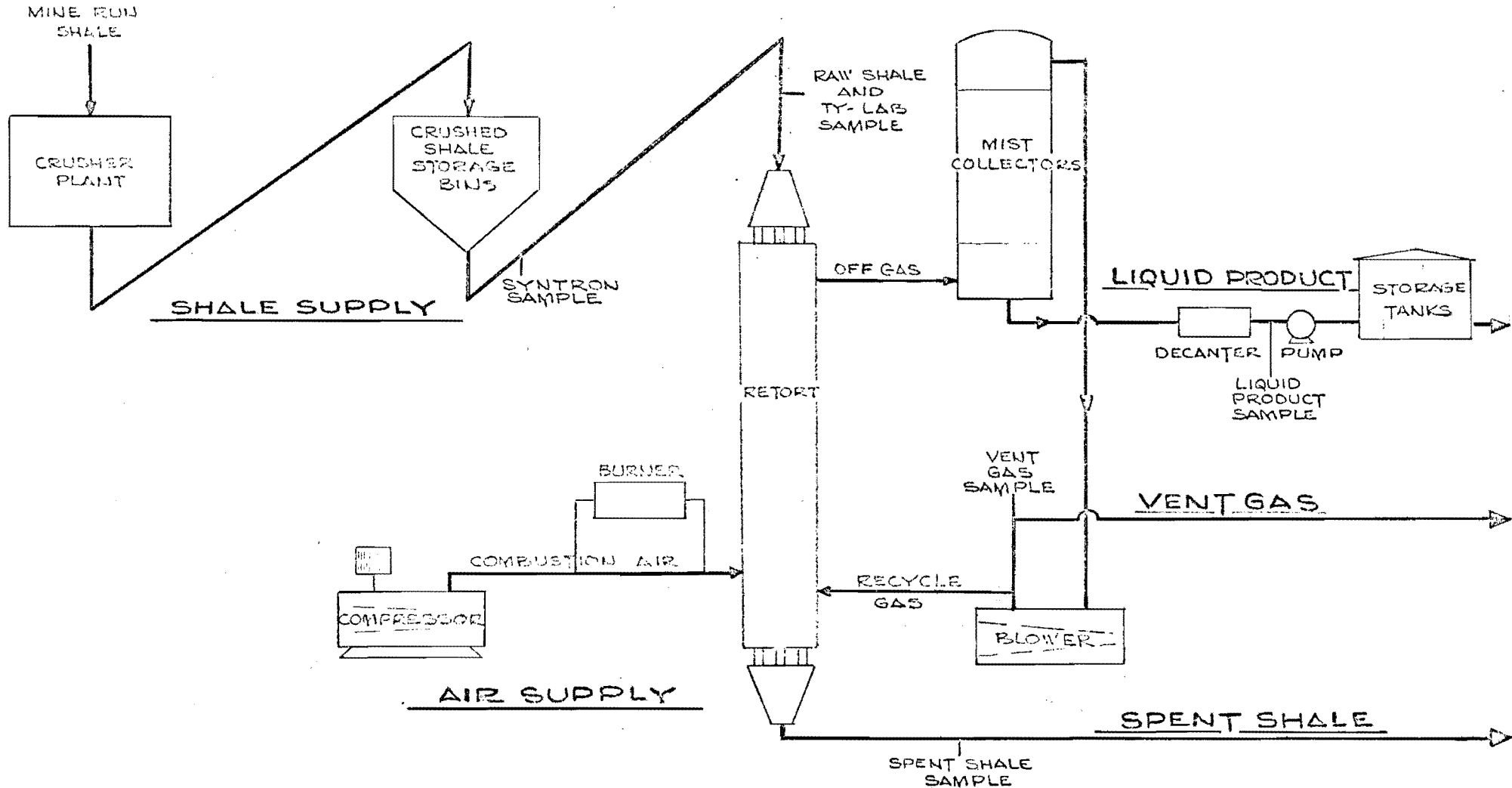


TABLE 2

COMPARISON OF CARBON BALANCES FOR RUNS NEAR THE BEGINNING
AND END OF OPERATION OF RETORTS NO. 1, 2, AND 3

	<u>Total Carbon Balance, %</u>		<u>Organic Carbon Balance, %</u>	
	<u>Balance</u>	<u>95% Confidence Limits</u>	<u>Balance</u>	<u>95% Confidence Limits</u>
Retort No. 1				
Beginning (1)	93.4	±18	--	--
End (2)	100.2	± 3.7	100.3	± 5.2
Retort No. 2				
Beginning (3)	96.7	± 4.7	95.5	± 6.2
End (4)	96.9	± 4.2	96.4	± 4.3
Retort No. 3				
Beginning (5)	101.4	± 8.7	102.1	±12.2
End (6)	99.3	± 4.4	98.2	± 5.8

- (1) Results on 18 runs - 222B through H, 334FA through FC, and 400A through 406.
- (2) Results on 24 runs - 549 through 573 (572 excluded).
- (3) Results on 24 runs - B670 through B696 (B671, B692, B695 excluded).
- (4) Results on 20 runs - B817A through B817U (B817L excluded).
- (5) Results on 24 runs - PTC988 through C988-13, and PTC990-1 through C990-11.
- (6) Results of 41 runs - C1027-1 through C1051-3.

c. Factors That Affect Total and Organic Carbon Balances

Material and heat balances are described in Technical Memoranda No. 65-3 (5) and No. 67-9 (6). These include the total and organic carbon balances which are important in properly defining the process.

The equations below (from Technical Memorandum No. 67-9) show the important analytical determinations that affect the balances. These determinations are the total and organic carbon in the raw shale, the spent shale, the shale oil, and the vent gas; the mineral CO₂ in the raw shale and spent shale; and the CO₂ in the vent gas (1).

$$TC = \frac{100.0 \text{ TOTCSS} + \text{ORGCOL} + \text{TOTCVG}}{\text{TOTCIN}}$$

Where,

$$\text{TOTCSS} = 0.01 (\text{SSRS}) (\text{CSS})$$

$$\text{ORGCOL} = 0.01 (\text{OIL}) (\text{COL})$$

$$\text{TOTCVG} = \text{ORGCVG} + \frac{12.0 [(\text{CO}_2\text{RS} - \text{CO}_2\text{SS})]}{44.0}$$

$$\text{ORGCVG} = (\text{CG}) (0.001) (\text{DRYGAS}) - \frac{[(\text{CO}_2\text{RS}) - (\text{CO}_2\text{SS})] (12.0)}{44.0} + (\text{ZZMIST}) (\text{COL}) (0.01)$$

$$\text{TOTCIN} = 20 \left[\text{CRS} + \frac{81.6\text{P}}{\text{RS}} \right]$$

$$\text{ORGC} = \frac{100.0 \text{ ORGCSS} + \text{ORGCOL} + \text{ORGCVG}}{\text{ORGCIN}}$$

Where,

$$\text{ORGCIN} = 20.0 \left[\text{CRS} - 0.273 (\text{CO}_2\text{RS}) + \frac{81.6\text{P}}{\text{RS}} \right]$$

The terms are defined below:

CG = Total carbon in the dry vent gas, lb per MSCF.

COL = Shale oil carbon content, weight %.

CO₂RS = Raw shale mineral CO₂ content, lb/ton raw shale.

CO₂SS = Spent shale mineral CO₂ content, lb/ton raw shale.

CRS = Raw shale total carbon content, weight %.

CSS = Spent shale total carbon content, weight %.

DRYGAS = Dry vent gas produced, SCF/Ton raw shale.

OIL = Shale oil produced, lb/ton raw shale.

ORCSS = % organic carbon in spent shale.

ORGC = % organic carbon balance, Organic carbon out/Organic carbon in.

ORGCIN = Total organic carbon in, lb/ton raw shale.

ORGCOL = Organic carbon in shale oil, lb/ton raw shale.

ORGCSS = Organic carbon in spent shale, lb/ton raw shale.

ORGCVG = Organic carbon in vent gas, lb/ton raw shale.

P = Propane burned in line burner. Input to program in SCFM, which is converted in program to lb/hour.

RS = Raw shale rate, lb raw shale/hour.

SSRS = Spent shale produced, lb spent shale/ton raw shale.

TC = % total carbon balance, carbon out/carbon in.

TOTCIN = Total carbon into retort, lb/ton raw shale.

TOTCSS = Total carbon in spent shale, lb/ton raw shale.

TOTCVG = Total carbon in vent gas, lb/ton raw shale.

ZZMIST = Shale oil in vent gas, lb/ton raw shale.

d. Investigation of the Effects of Variations In Sampling and Analytical Test Results On Carbon Balance

(1) Sampling at the Laboratory

During early stages of the program (near January 1965) about 2 pounds of shale, which had been crushed and

split from a 25-pound sample, was being submitted to the Laboratory. To prepare it for analysis, the sample was first crushed in a jaw crusher to pass 8 mesh, then was split into portions for Fischer Assay, carbon-hydrogen, ash, etc. The portion for analyses other than Fischer Assay was ground in a pulverizer, screening out 100-mesh material after each pass. The pulverizer was brushed out and all the material was transferred to a jar and mixed by shaking.

Replicate determinations run on different portions of several samples, split and ground as above, showed that carbon-hydrogen reproducibility was good for parts of the same portion but was poor for the different portions (7). In general, the carbon results were lower than would be expected from the Fischer Assay of the sample (based upon U. S. Bureau of Mines Fischer Assay versus Carbon curves).

The results, shown in Table 3, indicated that the splitting and grinding procedures were not adequate to insure accuracy. Therefore, a more rigid pattern of splitting was introduced and the grinding procedure was improved. The 50-g portion for carbon-hydrogen and other analyses was ground in the pulverizer for five minutes, with care being taken to brush all material down onto the pulverizer plates. The plates were then slowly opened to permit larger hard-to-grind particles to pass through. The material remaining on 48 mesh was ground manually with a steel mortar and pestle. The whole portion was again passed through the pulverizer to mix it thoroughly. After that it was transferred to a jar and mixed again.

Results designated by (3) on Table 3 were on different portions of samples prepared by the new procedure. The results, in practically all cases, showed an increase in carbon-hydrogen levels and, as they should, a decrease in ash content. In addition, the precision among different portions of the same sample were much improved.

In July-August 1965, the new sampling-splitting-grinding procedure was again verified by analyzing several sets of duplicates for Fischer Assay (8). These were obtained by first splitting out a set of duplicates, then mixing all discards and splitting out another set. The results presented in Table 4, showed that the sampling, splitting, and crushing procedures were satisfactory for regular samples and could also be used for samples of larger particle sizes.

(2) Determination of Carbon-Hydrogen Content

(a) In Shale and Shale Oil

When the combustion method for carbon-hydrogen was first put into operation, organic standards

TABLE 3

COMPARISON OF ANALYTICAL DATA ON RAW SHALE FOR THE INVESTIGATION OF THE CARBON-BALANCE PROBLEM

Lab No.	Run No.	Total Carbon, wt %						Hydrogen, wt %					
		1 ⁽¹⁾	2	3	4	5	6	1	2	3	4	5	6
908	454L	15.2	15.4	15.9 ⁽³⁾				1.56	1.54	1.73 ⁽³⁾			
		15.3		16.1 ⁽³⁾				1.67		1.68 ⁽³⁾			
		15.3						1.60					
		15.3						1.62					
		15.3 ⁽⁵⁾						1.67 ⁽⁵⁾					
		15.3 ⁽⁶⁾						1.62 ⁽⁶⁾					
914	454M	15.3	15.1	16.3 ⁽³⁾	16.3 ⁽³⁾	16.2 ⁽³⁾	16.2 ⁽³⁾	1.61	1.61	1.74 ⁽³⁾	1.76 ⁽³⁾	1.70 ⁽³⁾	1.67 ⁽³⁾
		15.6						1.65					
		15.3						1.56					
		15.6 ⁽⁵⁾						1.72 ⁽⁵⁾					
		15.3 ⁽⁶⁾						1.60 ⁽⁶⁾					
932	454O	15.2	16.2	16.7 ⁽³⁾	16.6 ⁽²⁾	16.4 ⁽³⁾		1.60	1.74	1.71 ⁽³⁾	1.78 ⁽²⁾	1.76 ⁽³⁾	
		15.2		16.3				1.58		1.66			
		15.4						1.62					
		15.1 ⁽⁴⁾						1.57 ⁽⁴⁾					
		15.2 ⁽⁵⁾						1.74 ⁽⁵⁾					
		15.3 ⁽⁶⁾						1.62 ⁽⁶⁾					
938	454P	16.4	16.0	16.5 ⁽³⁾	16.3 ⁽³⁾	16.3 ⁽³⁾		1.74	1.68	1.76 ⁽³⁾	1.75 ⁽³⁾	1.72 ⁽³⁾	
		16.3	15.7					1.72		1.58			
971	460	16.1	16.5 ⁽³⁾	16.4 ⁽³⁾	16.3 ⁽³⁾			1.70	1.76 ⁽³⁾	1.75 ⁽³⁾	1.75 ⁽³⁾		

See page 11 for foot notes.

TABLE 3 (Continued)

COMPARISON OF ANALYTICAL DATA ON RAW SHALE FOR THE INVESTIGATION OF THE CARBON-BALANCE PROBLEM

Lab No.	Run No.	Ash, wt %				Mineral CO ₂ , wt %				Fischer Assay, gal/ton		
		1	2	3	4	1	3	5	6	1	2	3
908	454L	69.4 69.5 69.4(6)	69.4	68.2(3)		17.0 16.8(6)	17.5(3)			26.0	26.2	25.6(6)
914	454M	69.4 69.3 69.6(6)	69.8	68.2(3)	68.2(3)	17.2 16.9(6)	17.6(3)	17.1(3) (100 mesh)	17.1(3) (48 mesh)	27.1	26.5	26.2(6)
932	454O	69.7 69.8 69.9(6)	68.2	67.6(3) 67.8(3)	68.3(3) 68.2(3)	16.8 16.7(6)	17.3(3)			26.8	27.3	26.4(6)
938	454P	68.3 68.2	68.7	68.1(3)	68.2(3)	17.0	17.5(3)			27.2	27.4	
971	460	68.4	68.0(3)	68.1(3)	68.0(3)	17.5	17.4(3)			26.5	26.5	

- (1) These numbers, 1, 2, 3, etc., refer to different 50-gm portions of sample.
- (2) Calculated from analyses on two components of the sample; 95.1 wt % fines and 4.9 wt % hard coarse material. The fines contained 16.3 wt % C and 1.75 wt % H; the coarse material 21.5 wt % C and 2.50 wt % H.
- (3) Split and ground by the new method.
- (4) An additional 45-minute combustion and purge gave 15.1 wt % C and 1.63 wt % H on this sample.
- (5) Analyses by Humble Service Laboratories, Baytown.
- (6) Analyses by U. S. Bureau of Mines, Laramie.

TABLE 4

FISCHER ASSAYS ON DIFFERENT PORTIONS SPLIT FROM THE SAME
SAMPLE OF RAW SHALE

<u>Lab No.</u>	<u>Sampling Location</u>	<u>Fischer Assay (gal/ton)</u> <u>(Sets of duplicates)</u>				
2226	Retort	30.6	30.8	31.0	30.8	30.4
		30.9	31.1	30.8	30.1	30.9
2233	Ty-Lab ⁽¹⁾	30.7	30.1	28.9		
		30.8	29.8	29.1		
2234	Crusher	27.5	27.7			
		27.4	27.5			
2235	Retort	28.2	28.8			
		28.0	28.8			
2236	Crusher	28.0	28.4			
		28.1	28.1			
2237	Ty-Lab ⁽¹⁾	27.0	27.6			
		27.1	27.4			
2244	Ty-Lab ⁽¹⁾	28.4	28.4	28.3		
		28.6	28.6	28.1		

(1) The Ty-Lab samples were submitted to the laboratory as 3/4 to 1 1/2 inch pieces; the other samples had been crushed to minus 8-mesh at the sampling locations. All Fischer Assays were run on minus 8-mesh material.

were analyzed in order to verify the accuracy of the procedure. During the period November 1964 to January 1965, the method was checked again by cooperative analyses with other laboratories. Two types of samples were analyzed. The first type comprised typical samples of raw shale and spent shale and shale oil. The second type comprised inorganic standards containing carbonate-carbon as does oil shale.

The cooperative results shown in Table 5, for the raw shale, spent shale, and shale oil were generally in excellent agreement (2). One result was discarded because an inappropriate method was inadvertently used. The U. S. Bureau of Mines' result for carbon in shale oil did not agree very well with the other two. It is probably incorrect, because it does not agree with the averages of results for 70 samples of shale oil analyzed subsequently at Anvil Points (9). These averages were 84.1 wt % carbon and 11.1 wt % hydrogen.

TABLE 5

COMPARISON OF CARBON AND HYDROGEN RESULTS
FROM DIFFERENT LABORATORIES

	<u>Anvil Points</u>	<u>Humble</u>	<u>U. S. Bureau of Mines</u>
<u>Raw Shale</u>			
Carbon, wt %	16.3	(discarded)	16.2
Hydrogen, wt %	1.70	1.72	1.70
<u>Spent Shale</u>			
Carbon, wt %	6.77	6.77	6.78
Hydrogen, wt %	0.30	0.28	0.27
<u>Shale Oil</u>			
Carbon, wt %	83.9	84.0	84.8
Hydrogen, wt %	11.1	11.4	11.6

Results for the two samples which contained carbonate-carbon, are shown below (10). The excellent recovery of the carbon showed that the combustion procedure completely decomposed the carbonates, which is necessary for accurate results on carbonate-containing raw and spent shales.

<u>Material</u>	<u>Carbon, wt %</u>		<u>Hydrogen, wt %</u>	
	<u>Present</u>	<u>Found</u>	<u>Present</u>	<u>Found</u>
Basic Magnesium Carbonate	9.9	10.0	2.20	2.30
Argillaceous Limestone	9.76	9.81 9.64	--	--

(b) In Retort Gas

Early in the program, it was recognized that an accurate analysis of carbon in the retort gas was required (2, 4). In an effort to determine the total carbon and hydrogen in the gas, the Laboratory developed a combustion method (Anvil Points Analytical Method AP-SOG-7). However, the extremely difficult problem of obtaining a representative sample of the gas remained. Not only did gas and mist exist simultaneously in the process lines, making it necessary to sample a heterogeneous mixture, but condensation of some of the gas occurred as it was transported through sample lines to the storage and analysis area. These problems prevented the realization of accurate results for gas analysis during the initial period of retort operation.

An improved gas sampling system was installed on Retort No. 2. In this system, a condenser and trap were used to collect easily condensible materials before the gas was transported through very short lines to a sampling point (11). This arrangement allowed more confidence to be placed in the gas carbon-hydrogen results.

After the new gas sampling system was put into use (also after improvements in air measurement and after reduction of air leakage were made), the carbon balances improved, as shown by the summary of results from low and high-yield operation, both before and after the changes were put into effect (Table 6).

TABLE 6 (3)

IMPROVEMENT IN CARBON BALANCE ON RETORT NO. 2

	<u>Yield, vol % RSFA</u>		<u>Organic Carbon Balance, %</u>	<u>Organic Carbon Distribution, wt % Organic Carbon</u>	
	<u>Tank</u>	<u>Mist and Condensate</u>		<u>Gas Spent</u>	<u>Shale</u>
<u>Low Yield</u>					
Before	78	0.2	92	19	13
After	79	2.0	101	26	16
<u>High Yield</u>					
Before	90	0.2	101	23	12
After	88	0.7	102	25	12

The improvement is most noticeable for the low-yield operation where the organic carbon balance increased from 92% to 101%, primarily because of the increased amount of mist and condensate recovered from the gas.

An even better sampling system on Retort No. 3 allowed measurement of the water and some of the organics that were condensed near the retort (12). After these materials were removed, the gas was pumped to a Laboratory Annex next to the unit, where the gas could be stored over brine and later analyzed.

(3) Determination of Carbonates (as Mineral CO₂)

In November-December 1964 (2), both Anvil Points and the U. S. Bureau of Mines at Laramie analyzed a sample of raw shale and spent shale for mineral CO₂. The results, shown below, were in good agreement, although both Anvil Points' results were slightly higher than the U. S. Bureau of Mines' results.

TABLE 7

COMPARISON OF MINERAL CO₂ RESULTS

<u>Sample</u>	<u>Anvil Points</u>	<u>U. S. Bureau of Mines</u>
Raw Shale Mineral CO ₂ , wt %	16.5	16.2
Spent Shale Mineral CO ₂ , wt %	14.9	14.5

The precision of the method for mineral CO₂ was good, as indicated by the results given in Table 3. These were on multiple analyses of raw shale.

The mineral CO₂ which remained as gaseous carbon dioxide in liquid product and in water from the process, was found to have an insignificant effect on the carbon balance.

(4) Determination of Ash

In November-December 1964, Anvil Points and the U. S. Bureau of Mines at Laramie analyzed portions of a sample of raw and a sample of spent shale for Ash. The results, shown below, were in excellent agreement.

TABLE 8

COMPARISON OF ASH RESULTS

<u>Sample</u>	<u>Anvil Points</u>	<u>U. S. Bureau of Mines</u>
Raw Shale Ash, wt %	68.2	68.4
Spent Shale Ash, wt %	82.7	82.8

Additional data, which showed the excellent precision of the method, are given in Table 3.

In January-February 1965, results for 34 sets of duplicates for ash in raw shale gave 95% confidence limits of ± 0.35 wt % in the range of 67 to 71 wt % ash (7).

(5) Moisture in Shale

In October-November 1965, work was started on determining the moisture in the 3/4 to 1 1/2-inch raw shale going into the retort (13), because any difference in the moisture contents of the raw shale feed and the crushed sample delivered to the laboratory for analysis, would appear as a discrepancy in carbon balance.

Samples of raw shale feed were taken on Retort No. 2, at about the same time, at several points which were progressively closer to the retort. One portion of sample was taken at the Syntron feeder (see Figure 1), which was near the shale supply bins. Another portion was removed at the Ty-Lab sampling point, where a sample was normally taken for the determination of shale size distribution. A third portion was taken at the retort standpipe, which was where the shale entered the retort.

The weighed samples were dried at 220 F for increasing lengths of time until, after 12 hours, the total moisture lost was practically constant (14). The data, in Table 9, showed that the moisture content of the shale going into the retort was different from that of the crushed sample submitted to the laboratory. Moisture determined on the Ty-Lab sample and the Syntron sample was about the same as that for shale going into the retort. Since the Ty-Lab sample was easy to obtain, it was used for all subsequent moisture determinations for retort raw shale feed.

The average difference between the prepared laboratory sample and the other samples was about 0.9 wt %. This moisture was lost during crushing of the laboratory samples. Use of correct moisture, from the Ty-Lab sample, increased several computer results; the overall balance by about 0.7%, the overall carbon balance on an "as is" or raw shale basis by about 1.2%, and yield by about 0.9%. The overall carbon balance on a spent shale basis was unchanged.

Heating at 220 F for 48 hours was necessary to drive off about 90% of the moisture (15, 16) from large (1 to 2 1/2-inch) shale. Therefore, the loss in weight in 48 hours divided by 0.9 was used as the shale moisture content. A

TABLE 9

MOISTURE CONTENTS OF RETORT FEED
 SAMPLED FROM DIFFERENT LOCATIONS
 (3/4 to 1 1/2-Inch Oil Shale)

<u>Date Sampled</u>	<u>Run No.</u>	<u>Sample Location</u>	<u>Moisture Content, wt %</u>			
			<u>Sample Taken</u>	<u>Lab Sample</u>	<u>Difference</u>	
11/12/65 (1)	B753 PT	Syntron	1.3	0.40	0.9	
11/15/65 (2)	B757	Syntron	1.1	0.49	0.6	
11/18/65	No Test	Syntron	1.2	--	--	
11/18/65	No Test	Standpipe	1.2	--	--	
11/19/65	B759 PT	Syntron	1.4	0.47	0.9	
11/19/65	B759 PT	Syntron	1.2	0.47	0.7	
		(Duplicate)				
11/30/65	765	Ty-Lab	1.2	0.43	0.8	
11/30/65	766	Ty-Lab	1.4	0.44	1.0	
12/1/65	767	Ty-Lab	1.4	0.12	1.3	
12/2/65	768	Ty-Lab	1.3	0.26	1.0	
12/3/65	769	Ty-Lab	1.2	0.40	0.8	
12/4/65	770	Ty-Lab	1.1	0.44	0.7	
12/5/67	771	Ty-Lab	1.2	0.35	0.8	
12/9/65	772	Ty-Lab	1.1	0.34	0.8	
12/10/65	773	Ty-Lab	1.1	0.38	0.7	
12/11/65 (3)	774	Ty-Lab	1.5	0.60	0.9	
12/12/65	775	Ty-Lab	1.1	0.35	0.7	
12/13/65	776	Ty-Lab	1.2	0.40	0.8	
12/13/65 (4)	776	Standpipe	1.6	0.40	1.2	
			Average Difference			0.9

- (1) Relative humidity, approximately 80%.
- (2) Slight drizzle.
- (3) Rainy day.
- (4) Taken in open area, in driving snow.

separate moisture, on the raw shale sampled for Fischer Assay determination, was also reported so that analyses could be calculated on a moisture-free basis.

(6) Miscellaneous Studies (11)

To investigate further possibilities of carbon loss in the retorting system, many miscellaneous studies were made. Among these were investigations of:

(a) Loss of Carbon From Spent Shale

One hypothesis proposed, was that some of the carbon on hot spent shale oxidized before it was analyzed at the Laboratory. Experiments on Retort No. 1 showed that when the hot spent shale flowed from the retort to the spent shale belt, its surface cooled quickly, and there was no significant loss of carbon. Since the part of the spent shale that was crushed for a laboratory sample cooled quickly, it did not oxidize appreciably.

However, when the shale was stored in the spent shale bin, where its internal heat caused the temperature to rise to about 400 F, a substantial amount of carbon could be oxidized and result in low balances. A nitrogen purge system was installed on the spent shale weigh bin in order to alleviate this problem.

(b) Spent Shale Dust Problems

When spent shale is conveyed from place to place, it is partially abraded to a fine dust. If this dust has a higher carbon content than the average on the spent shale, the carbon determined by analysis would be low. Samples of dust taken from Retort No. 1 did not indicate a high carbon content in the spent shale dust. However, samples of dust taken from the Rotoclone stack on Retort No. 2, showed an appreciably higher carbon content on the dust compared to the normal spent shale (13). The difference of about 3 wt % carbon in spent shale could have accounted for a 0.5% deficit in carbon balance.

Extra precautions were taken to avoid dust losses while splitting the sample at the Laboratory.

(c) Spent Shale Sample Size

About a 1% sample of the total spent shale was taken from Retort No. 1 operations at the beginning of the program. A statistical study by the Engineering and Economics Group showed that a 3% sample was desirable. Therefore, the sample size was increased so that it would be more representative of the total from the retort.

2. Retort Gas Characterization

Sporadic efforts were made, during much of the program at Anvil Points, to characterize the retort offgas composition. The work, which was started at the Laboratory early in 1965 (17), received increased impetus in 1966 (18). It resulted in the determination of the C₃-and-heavier hydrocarbon composition of the gas after removal of the shale oil mist.

Results are reported in Technical Memorandum No. 67-4 (19).

In brief, the memorandum stated that the equilibrium retort gas contained about 2.5 lbs/MSCF Dry Gas of C₃-and-heavier hydrocarbons, which is equivalent to between 5 and 25 volume % of raw shale Fischer Assay. A typical composition of equilibrium retort gas, which was derived from cold-trapping experiments and from routine gas analyses by the analytical laboratory, was given as:

<u>Component</u>	<u>Mol %</u>
H ₂	4.97
N ₂	60.96
CO	3.59
CO ₂	26.07
C ₁ 's	1.89
C ₂ 's	0.90
C ₃ 's	0.50
C ₄ 's	0.20
C ₅ 's	0.12
C ₆ 's	0.31
C ₇ 's	0.16
C ₈ 's	0.22
C ₉ 's	0.06
C ₁₀ 's	0.05
	<u>100.00</u>

Details of experimental work, and of hydrocarbon-type distribution, are also given in the memorandum.

Various means of processing the gas, in order to recover the hydrocarbons were investigated. The conclusion was that recovery was not economically feasible at the present time.

B. General Operation of the Analytical Laboratory

1. Laboratory Facilities, Personnel, and Activities

When the Initial Program at Anvil Points began in May 1964, the facilities had been idle for about eight years. To

resume operations, all facilities, including the Laboratory, had to be rehabilitated. Services and usable equipment on hand were restored. New apparatus and equipment for the program were purchased. Laboratory Technicians were hired and trained to do the work required.

As the program progressed, the laboratory services and personnel were adjusted to the demands of the retort program and other investigations.

a. Physical Plant and Facilities

The Laboratory had a 95 by 41 foot floor area and was divided into 4 laboratory rooms, an analytical furnace room, a glassblowing room, and 2 offices. A partial basement contained a sample crushing room and some storage rooms. Utilities such as electricity, steam, air, vacuum, and gas were supplied to the Laboratory.

To increase the efficiency of the Laboratory, apparatus for tests that could be run simultaneously by one Technician, was grouped together.

b. Personnel

During the first part of the program, the Laboratory was staffed by two chemists and four technicians. As the demands on the laboratory increased, the number of technicians was gradually increased to seven men.

The additional men were needed for several reasons. Retort material balance periods were shortened temporarily to eight hours, with a consequent 50% increase in sample analysis requirements. New tests were added. More samples were generated by an increased level of bench-scale work. More investigations that required analytical services were made by various sections into aspects of retorting, product separation, sampling, etc.

Most of the men chosen and trained as laboratory technicians, had had no previous experience in this field. However, they were generally above average in intelligence, and once trained, proved to be excellent technicians.

c. Activities

The Analytical Laboratory Section performed in two major functions:

- The initial primary function was to supply accurate analytical data rapidly so that the retorting operation could be controlled and studied. In order to do this, appropriate

analytical methods had to be adapted, adopted, or developed for the required jobs. Analytical technicians had to be hired, trained, and supervised. A constant surveillance of the applicability and accuracy of methods had to be maintained. Means of obtaining and keeping accurate records had to be developed.

- A second function, which turned out to require a large portion of the Analytical effort, was the study of peripheral aspects of retorting, such as agglomerate and clinker formation, and the investigation of retorting improvements which included participation on the Retort Operability Task Force (20).

d. Application of Tests

Analytical tests were performed for three main purposes:

- To determine the properties of material going into and out of the retorts, to define:
 - Product yield
 - Balances, such as material balances, total and organic carbon balances, heat balances, etc.
- To describe the properties of the liquid product in order to detect effects of process changes and for predicting transport and refining problems.
- To identify the composition of special samples, such as deposits, clinkers, water produced, etc., obtained during the course of retorting research.

e. Costs

The approximate cost of supplying analytical service, which also includes a substantial amount of research participation, is shown below:

	<u>Stage I</u> <u>(24 Months)</u>	<u>Stage II</u> <u>(18 Months)</u>
Total Analytical Salaries and Wages	\$ 95,000	\$ 86,000
Total Analytical Materials, Supplies, and Equipment	\$ <u>20,700 (est.)</u>	\$ <u>15,500</u>
Total Analytical Operating Costs	\$ 115,700	\$ 101,500

	<u>Stage I</u> (24 Months)	<u>Stage II</u> (18 Months)
Total Project Salaries and Wages	\$1,263,000	\$1,611,000 (est.)
Total Project Materials, Supplies, and Equipment	<u>\$ 522,000</u>	<u>\$ 814,000 (est.)</u>
Total Project Operating Costs	\$1,785,000	\$2,425,000
Total Project Cost	\$2,720,000	\$4,500,000

Total Analytical Operating Costs were about 6.5% of Total Project Operating Costs for Stage I, and about 4.2% for Stage II. Rehabilitation costs are not included.

2. System of Operation

a. Sample Submittal, Verification of Results, Reporting, and Correction of Errors

Samples were taken usually by the Retort Section and were delivered to the Laboratory. The samples were identified by type of material (i.e. raw shale, spent shale, liquid product), retort run number, date, time, etc.

It was prearranged, between the Retort and Analytical Sections, that certain analyses would be made on each type of sample unless the Retort Section instructed otherwise. On the basis of this understanding, the Analytical Technicians made out the appropriate Laboratory Analysis Sheets (1).

Tests that were needed for a rapid determination of retort yield were completed first. Results were forwarded, as quickly as possible, on a "Quick-Yield Sheet".

So that progress could be followed in an organized manner, each technician initialed the Laboratory Analysis Sheet next to the analyses on which he was working.

When analyses were completed, the results were examined by supervisory personnel before being sent to the sample submitter. The analytical correlations, described in Section B-6 of this report were used to determine if the results were reasonable. When anomalous results were encountered, the calculations were checked. If the anomaly persisted, the sample was re-analyzed in duplicate; where necessary a fresh portion of sample was taken for analysis.

Any errors that were found were corrected on the Laboratory Sample Sheets. If an error was discovered and

corrected after the sample sheet was returned to the submitter, or if additional analyses were completed after that time, the results were reported on a Supplemental Analytical Laboratory Report form.

b. Records and Log Books

Information for each sample, including instructions on unusual analytical requests, was entered into a Laboratory Sample Log Book.

As the technicians worked on the samples, they entered all raw data, such as weights, and calculations in Test Log Books supplied for each test.

All completed sample sheets are in Anvil Points Oil Shale Research Center files.

c. Sample Storage

Portions of all samples for which there was an excess, except for gas and water samples, were put into containers, labeled, and stored in the basement store room. Liquid samples were stored in jars and solid samples in plastic bags.

3. Sampling and Sample Preparation

Oil shale retorting presents especially difficult sampling problems because both input and output materials are heterogeneous.

Raw shale presents particular difficulty because it consists of two materials which are unevenly distributed and vary in composition from place to place in the oil shale deposits. The shale is composed of a waxy material, kerogen, laminated with a dolomitic marlstone. Typical composition of 28 gallon-per-ton raw shale is given below:

Ash	66.3 wt %
Total Carbon	17.4 wt %
Mineral Carbonates (as CO ₂)	17.7 wt %
Total Hydrogen	1.9 wt %
Nitrogen	0.4 wt %
Sulfur	0.6 wt %

It was found that great care must be exercised, not only to take a sample of sufficient size, but to take it in such a way that it is representative of the whole. Technical Memorandum No. 67-13 describes the difficulties of shale sampling and presents proper sampling methods (21).

At the Laboratory, where the shale samples are crushed and split to give sample sizes adequate for analysis, great care had to be used to maintain sample homogeneity during the procedure. Early in the program, improper grinding and splitting procedures were revealed in a cooperative program on Fischer Assay analyses. Correction of the methods used, led to excellent repeatability of results, as shown in Table 10.

The gas generated in the retort is a mixture of fixed and condensible gases, and shale oil mist. It is extremely difficult to obtain a representative sample of gas from this mixture. The method used during this program was to separate the mist and some condensibles, and then collect a sample of the remaining gaseous phase. Each of these portions were measured separately.

The liquid product from the retort is another heterogeneous mixture, consisting of shale oil, water, and some sediment. To determine the relative amounts of water and oil, the sample must be well homogenized before sampling.

Effective sampling procedures in the laboratory are described in Technical Memorandum No. 67-37 (1).

4. Potential Improvements on Analytical Tests

The methods and apparatus used during the Anvil Points project were chosen for simplicity, convenience, and short pay-out time. For a project of longer duration, different choices would undoubtedly have been made. A rapid combustion method would have been chosen for carbon-hydrogen determinations. A more accurate curve area-integrating gas chromatography unit would undoubtedly have been purchased. Fully-automated Fischer Assay equipment would have been used. All of these improvements are more complicated and require more expensive equipment than the methods used. More details on potential improvements in methods and equipment for selected tests are outlined below:

a. Recycle Gas

Sampling of recycle gas definitely requires improvement. The problem of sampling resolves itself into obtaining a stable sample of gas from a process line where gas, vapor, and mist exist simultaneously. This involves separation and careful measurement of several components. It was accomplished on Retort No. 3 to some extent (12). The system there, was to try to sample isokinetically, to cool and condense and demist in order to remove unstable fractions, and then transport the gas a short distance to a laboratory annex for storage and analysis.

TABLE 10

PRECISION AND ANALYSIS TIME REQUIREMENTS FOR ANALYTICAL TEST METHODS

Method	Level	Standard Deviation	Total Time For Analyses (Hours)					
			Single		Group			
			Elapsed	Working	Elapsed	Working	No.	
AP-S-1 Shale Preparation	--	--	1	0.7	2	1.5	3	
AP-O-2 Liquid Product Treatment	--	--	1	0.5	1.5	0.7	3	
AP-S-3 Fischer Assay	(RS) (1)	28 gal/ton	0.23	4	3	5	4	6
	(SS)	0-5 gal/ton	0.1 (2)	4	3	5	4	6
AP-S-4 Mineral CO ₂	(RS)	17 wt %	0.14	2	0.5	2.5	1	4
	(SS)	14 wt %	0.11	2	0.5	2.5	1	4
AP-S-5 Shale Ash	(RS)	69 wt %	0.087	3.5	0.2	3.5	0.5	4
	(SS)	82 wt %	0.047	3.5	0.2	3.5	0.5	4
AP-S-6 Shale Moisture	(RS)	0.2 wt %	0.014	3.5	0.2	3.5	0.5	4
	(SS)	0.15 wt %	0.014	3.5	0.2	3.5	0.5	4
AP-SOG-7 Carbon	(RS)	16 wt %	0.069	3	0.3	4	1.2	3
	(SS)	7 wt %	0.031	3	0.3	4	1.2	3
	(GAS)	10 lb/MSCF	0.22	1.7	1.4	--	--	--
Hydrogen	(RS)	1.7 wt %	0.028	3	0.3	4	1.2	3
	(SS)	0.3 wt %	0.018	3	0.3	4	1.2	3
	(GAS)	0.3 lb/MSCF	0.06	1.7	1.4	--	--	--
AP-SO-8 Nitrogen	(O)	0.2 wt %	0.05	4	1	5	3	6
AP-O-9 API Gravity	(O)	20° API	0.1 (2)	0.5	0.5	1	1	6
AP-O-10 Water and Sediment	(LP)	--	--	0.7	0.4	1.2	1	3
AP-O-11 Ramsbottom Carbon	(O)	2 wt %	--	1.7	0.3	2.2	0.5	3
AP-O-12 Shale Oil Ash	(O)	0.02 wt %	<0.01	4.5	0.5	5	1	3
AP-O-13 Saybolt Viscosity, 210 F	(O)	46 SUS	0.6	1	0.4	1.7	1	3
AP-O-14 Pour Point	(O)	85 F	--	1	0.5	1.5	0.7	3
AP-O-15 Distillation	(O)	--	--	4	3	--	--	--
AP-O-16 API Gravity	(VP)	40° API	0.1 (2)	1	0.4	2	0.5	2
AP-G-17 Gas-Combustion Analysis	(GAS)	--	--	1.5	1.5	1.5	4	3
AP-S-18 Benzene Extractables	(S)	--	--	--	0.5	--	2	6
AP-S-19 Particle Size Distribution	(S)	--	--	0.8	0.5	1.5	1.2	3
AP-S-20 Shale Density	(S)	--	--	1	0.7	2.2	2	3
AP-O-21 Water in Liquid Product	(LP)	--	--	1.5	0.3	2	1	6
AP-W-22 Retort Water Analysis	(W)	--	--	8	3	--	--	--
AP-S-23 Shale Richness Distillation (S)	--	--	--	8	1.5	--	--	--

(1) Definitions of abbreviations: RS - Raw Shale, SS - Spent Shale, O - Shale Oil, VP - Vent Purge Product, LP - Liquid Product, W - Water

(2) Estimated.

The principle of this system was very good, but improvements are needed in the equipment and in the measurement of the condensed products, for greater accuracy in determining the retort gas composition at different run conditions.

b. Fischer Assay

A semi-automated Fischer Assay apparatus was used during this project. However, a fully-automated apparatus, designed by Arnold Hubbard of the U. S. Bureau of Mines at Laramie, is available (22). The automatic equipment obviates the need for the attention of a technician during the analysis.

A simplification that should be applicable to the Fischer retort, is one that is used by the Colorado School of Mines at Golden. At that laboratory, a thick-walled copper tube, instead of perforated aluminum plates and tube, is used as a heat transfer element in the Fischer retort. Preliminary work here at Anvil Points could show no difference between results obtained with the two systems.

An improvement made at Anvil Points on the Fischer retort proved satisfactory and should be used on retorts fabricated in the future. This was the welding of an aluminum tube to the retort body instead of attaching a stainless steel tube with a gland and nut. This innovation eliminated leaks at the joint.

c. Total Carbon and Hydrogen in Raw Shale, Spent Shale, Crude Shale Oil, and Recycle Gas

At Anvil Points, carbon-hydrogen analyses were made by an old, but effective, packed-combustion-tube technique. There are presently available, rapid, automatic carbon-hydrogen analysis systems that would surely be applicable to shale oil, and would probably be applicable to raw and spent shale.

The reliability of gas analyses would be improved by more precise gas chromatographic equipment using automatic peak area integration.

Finally, because carbon balances are important for accurately defining the process, a system should be developed for continuous onstream analysis of gas carbon content.

d. Ash Content of Raw and Spent Shale

To determine ash content, shales were heated at about 1750 F for two hours. Furnaces are available that can attain much higher temperatures. If it becomes necessary to

reduce the elapsed time for an ash analysis, heating the shale at a higher temperature for a shorter time (perhaps 1500 F for 3/4 hour) would probably be suitable.

5. Test Precision and Analysis Times

In order to keep analytical methods and techniques under constant surveillance, an internal quality control program was maintained during the operation of the Laboratory. The program generally required that each laboratory technician perform each of the important tests on standard samples. The level for each test and the precision of the data obtained are shown in Table 10.

Estimates of the amount of time necessary to perform the various tests - both singly, and in groups - are also shown in Table 10.

Table 11 shows the effects on carbon balances and yield, of increasing certain of the key analytical results by an amount equal to the approximate 95% confidence limits of the analyses. These figures give clues to the methods which most need improving in order to give more meaningful engineering data.

Even though the precision data for the tests showed that they were adequate for the purposes of this program, improvements described below could give significantly more precise balances and yields.

a. Fischer Assay

One of these tests is the Fischer Assay. The 95% confidence limits for a single analysis, about ± 0.46 gallon per ton, result in an uncertainty of about $\pm 1.4\%$ in yield. During this program, the Fischer Assays for retort runs were always run in duplicate. This reduced the uncertainty to about ± 0.35 gallon per ton, which was still about $\pm 1\%$ in yield.

b. Carbon-Hydrogen Determination

Although the carbon determination is relatively precise, the 95% confidence limits of ± 0.14 wt % total carbon in raw shale are equivalent to about $\pm 1.1\%$ in organic carbon balance. Averaging multiple determinations by a rapid method would probably be the easiest way to improve this precision.

6. Analytical Test Correlations

A series of correlations was developed early in the operation of the laboratory in order to be able to check the

TABLE 11

EFFECT OF INCREASING CERTAIN ANALYTICAL RESULTS, BY THE AMOUNT OF THEIR 95% CONFIDENCE LIMITS, ON COMPONENT BALANCES AND YIELD

<u>Analysis</u>	<u>95% CL</u>	<u>Change In Balance, %</u>				<u>Change In Yield, %</u>
		<u>Overall</u>	<u>Organic C</u>	<u>Total C</u>	<u>Organic H</u>	
Fischer Assay (RS) ⁽¹⁾	±0.46 gal/ton	0	0	0	0	-1.44
Fischer Assay (SS)	±0.01 wt %	0	0	0	0	0
Mineral CO ₂ (RS)	±0.28 wt %	0	-0.03	0	+1.6	0
Mineral CO ₂ (SS)	±0.22 wt %	0	-0.01	0	-0.99	0
Ash (RS)	±0.17 wt %	+0.17	+0.1	+0.07	-0.15	0
Ash (SS)	±0.094 wt %	-0.07	-0.05	-0.04	+0.04	0
Carbon (RS)	±0.14 wt %	0	-1.09	-0.80	0	0
Carbon (SS)	±0.06 wt %	0	+0.39	+0.28	0	0
Carbon (GAS)	±0.44 lb/MSCF	0	+1.15	+0.83	0	0

(1) Definition of abbreviations:

RS - Raw Shale
 SS - Spent Shale

consistency of certain analyses. One of these, a relationship between organic carbon and Fischer Assay, was very similar to one that was derived from U. S. Bureau of Mines data (23) in 1951.

The correlations used for raw shale, including the one described above, in the range of about 24 to 33 gallons per ton Fischer Assay (FA), are shown below. All derived quantities are in weight percent.

	<u>Correlation Coefficient</u>	<u>Standard Deviation</u>
Total Carbon = (0.404) (FA) + 5.58	0.97	0.15
Organic Carbon = (0.444) (FA) - 0.25	0.97	0.16
Hydrogen = (0.0499) (FA) + 0.39	0.93	0.03
Ash = (-0.372) (FA) + 77.70	0.92	0.24
Ignition Loss - CO ₂ = (0.511) (FA) + 1.085	0.92	0.33

These correlations are all highly significant.

For spent shale containing no unretorted kerogen, the following correlation was applicable:

Mineral CO₂ = (-0.809) (Ash) + 82.20 Correlation Coefficient = 0.99
Standard Deviation = 0.23

Still another relationship was used to check the analytical results. This was the total of Ash + C + H + O + N in raw shale and in spent shale. The acceptable averages and their 95% confidence limits are given below (24). These data were obtained between about March and July, 1965.

<u>Raw Shale</u>		<u>Spent Shale</u>	
<u>Total, %</u>	<u>95% Confidence Limits</u>	<u>Total, %</u>	<u>95% Confidence Limits</u>
100.4	±0.54	100.9	±0.38

7. Outlines of Test Procedures

The test procedures used at Anvil Points during the period May 1964 to September 1967 (1) are outlined below. Some of the methods are official U. S. Bureau of Mines methods (25) or adaptations of them, some are ASTM methods, and some are methods which have been developed at Anvil Points during the Initial Program. The detailed methods are given in Technical Memorandum No. 67-37 (1).

a. Preparation of Raw and Spent Shale Samples (AP-S-1)

The sample is first split to about 800 grams, then crushed to pass an 8-mesh screen. A portion for Fischer Assay and a portion to be used for other analyses are then split out. The latter portion is ground to pass a 48-mesh screen.

b. Treatment of Liquid Product Samples (AP-O-2)

The sample is well homogenized in a malt mixer. Individual portions are withdrawn for analyses such as specific gravity, water-and-oil, and ash.

c. Fischer Assay of Raw and Spent Shale (AP-S-3)

Approximately 100 grams of minus 8-mesh shale is heated in an aluminum retort. Retorted oil and water are collected in a cooled receiver. The weights of the resulting oil, water, spent shale, and gas + loss (by difference), and the specific gravity of the oil are determined. Oil content, in gallons per ton, is calculated.

d. Mineral Carbon Dioxide in Raw and Spent Shale (AP-S-4)

The ground sample is treated with hydrochloric acid which decomposes mineral carbonates. The carbon dioxide released (Mineral CO₂) is absorbed by Ascarite and weighed. The percent mineral CO₂ is calculated from this weight.

e. Ash Content of Raw and Spent Shale (AP-S-5)

The ground sample is ignited for two hours in a muffle furnace at 1750 F to burn organic material and to decompose carbonates. The inorganic material remaining is the ash, and is free of volatile matter. The weight percent of material remaining is reported as the ash content.

f. Moisture Content of Raw and Spent Shale (AP-S-6)

The ground sample is heated in an oven at 105 C (221 F) for two hours to remove any moisture present. The percent loss in weight is the moisture content of the sample.

g. Total Carbon and Hydrogen in Raw and Spent Shale, Crude Shale Oil, and Recycle Gas (AP-SOG-7)

The sample is burned in a stream of oxygen in a packed combustion tube. The products of combustion of carbon

and hydrogen (carbon dioxide and water) are collected in caustic on asbestos, and magnesium perchlorate, respectively. Interfering products, such as sulfur gases, are removed by the packing. The increases in weight of the carbon dioxide and water absorbers are used to calculate the carbon and hydrogen in the sample.

h. Nitrogen in Raw and Spent Shale and Crude Shale Oil (AP-SO-8)

The sample is decomposed by digestion with concentrated sulfuric acid and a catalyst (Hg); the nitrogen is thereby converted to ammonium sulfate. After the resulting solution is made alkaline, ammonia is distilled off into a boric acid solution. The borate formed is titrated acidimetrically with standard sulfamic acid to a methyl purple end point. The total nitrogen, in weight percent, in the original sample is calculated.

i. API Gravity of Crude Shale Oil (AP-O-9)

The oil sample is heated to 100 F (37.8 C), and a 2-ml pipetful is weighed. From the density at 100 F, suitable corrections are applied, and the API gravity at 60 F is calculated.

j. Water and Sediment in Liquid Product (Centrifuge Method) (AP-O-10)

The weighed sample is heated, and then centrifuged to separate the oil, water, and sediment. The amounts of water and sediment are then measured, and the weight percent and volume per weight percent sediment calculated.

k. Ramsbottom Carbon Residue of Crude Shale Oil (AP-O-11)

Clean crude shale oil is charged to a pre-weighed Ramsbottom coking bulb and heated in a furnace for a specified time. After a period of time, the bulb is removed and weighed. The coke remaining in the bulb is a measure of the Ramsbottom Carbon Residue. The method is, essentially, ASTM D 524.

l. Ash Content of Crude Shale Oil (AP-O-12)

A weighed amount of crude shale oil is weighed into an evaporating dish and burned. The carbonaceous residue is ashed. The weight percent ash is calculated from the weight of the ash.

m. Saybolt Viscosity of Crude Shale Oil (AP-O-13)

The time for a known amount of oil, at a certain temperature, to flow through an orifice, is measured. The method is ASTM D 88.

n. Pour Point of Crude Shale Oil (AP-O-14)

The crude shale oil is cooled stepwise, until it no longer flows during a set period of time. The lowest temperature at which movement occurs is the pour point. The method is ASTM D 97.

o. Distillation of Crude Shale Oil (AP-O-15)

The crude shale oil is distilled at 10mm pressure as in ASTM D 1160. The fractions collected at different temperatures are reported.

p. API Gravity of Vent Purge Oil (AP-O-16)

A hydrometer reading on the dry oil is made as in ASTM D 287. This is reported as ^oAPI at 60 F.

q. Analysis of Recycle Gas (AP-G-17)

The method consists of (1) collecting a composite sample in a gas holder over the duration of a retort run and (2) transferring a portion to a gas chromatograph, where the individual gases are separated and their peaks recorded. The concentrations of the gases are calculated from these peaks.

r. Benzene Extractables in Raw and Spent Shale (AP-S-18)

The method used is similar to "Sediment in Fuel Oil by Extraction", ASTM D 473-59; the apparatus used is identical.

The sample, in an alundum thimble, is extracted with hot benzene. The amount of material extracted, as determined by the loss of weight of the sample, is calculated as the benzene extractables.

s. Particle Size Distribution of Raw and Spent Shale (AP-S-19)

The dry shale sample is segregated by particle size on a series of standard sieves. The weight percent held by each sieve is calculated.

t. Density of Raw and Spent Shale (AP-S-20)

Loose Density - the volume of a weighed amount of loosely packed dry shale is measured.

Packed Density - the volume of a weighed amount of tightly packed dry shale is measured.

Solid Density - the difference in volume between a known volume of toluene and the volume of a mixture of a weighed amount of dry shale plus the toluene is measured.

The density, in grams per milliliter, is calculated.

u. Water in Liquid Product by Distillation (AP-O-21)

The liquid product is heated with toluene which is azeotropically distilled over with the water. The amount of water collected is reported as weight percent in the sample.

v. Analysis of Retort Product Water (AP-W-22)

The sample is divided into several portions which are treated soon after sampling in order to preserve certain transient components. Determinations are made for pH, chloride, carbonate, residue, ash, etc.

w. Shale Richness Distribution (AP-S-23)

Portions of the ground shale are added to graduated cylinders containing liquids of different densities. The volume of material that floats is plotted versus the liquid density, on probability graph paper, to show the density - and thus richness - distribution of the shale. This analysis is based on Mobil Method 512, Density Distribution of Catalyst.

8. Cooperative Analytical Programs and Interlaboratory Comparisons

Several cooperative analytical programs were completed during the operation of the Research Center. The laboratories that participated in these programs were:

- Anvil Points -- Anvil Points Oil Shale Research Center, Rifle, Colorado
- Laramie -- U. S. Bureau of Mines Laboratory, Laramie, Wyoming
- Golden -- Colorado School of Mines Research Foundation, Inc., Golden, Colorado

and, each on one occasion,

- Humble - Baytown -- Humble Refinery Service Laboratories, Baytown, Texas
- Core Lab -- Core Laboratories, Inc., Rifle, Colorado

The purpose of the cooperative work was to ascertain that the Anvil Points results were comparable to those of more experienced, longer-established laboratories. The various programs are described below:

a. Fischer Assay

(1) Laramie - Golden - Anvil Points (August 1964)

Near the beginning of Stage I, a preliminary cooperative program on the Fischer Assay of raw shale was initiated (26). Seven samples of shale, of which two were sets of duplicates, were submitted to two other laboratories and were also analyzed at Anvil Points. The two outside laboratories were Laramie and Golden. The Laramie Laboratory was considered to provide definitive Fischer Assay results.

Analysis of the results from the different laboratories divulged the fact that the splitting procedure was faulty, and that biased samples had been submitted. Subsequent repeat runs by the three laboratories were in good agreement on the average, as shown in Table 12. However, agreement between several individual results was not very good.

(2) Laramie - Anvil Points (December 1965)

In November and December 1965, an extensive cooperative program on Fischer Assay was completed by Laramie and Anvil Points (14, 18). This program included a simultaneous test of both sample splitting and analytical procedures.

Three separate 15-pound samples were crushed to minus 8-mesh at Anvil Points, and were then shipped to Laramie, where three sets of duplicates were split out of each sample and analyzed. The remaining amounts of the samples were shipped back to Anvil Points, where they were split and analyzed. The analyses at Laramie were made on the same day by one analyst; those at Anvil Points, on several days by different analysts. The resulting data should be judged accordingly.

The data were evaluated statistically by Mobil's Central Research Division. Results are given in Table 13.

TABLE 12

COMPARISON OF FISCHER ASSAY RESULTS BY ANVIL POINTS,
LARAMIE⁽¹⁾, AND GOLDEN⁽²⁾ LABORATORIES (AUGUST 1964)

<u>Sample</u>	<u>Fischer Assay, gal/ton</u>	
	<u>Laramie and Golden (Pooled Data)</u>	<u>Anvil Points</u>
A	28.4	26.5
	27.1	27.6
B	28.4	27.6
	27.3	28.0
	27.9	28.5
	28.7	27.9
C	33.0	32.5
	32.3	32.8
D	26.8	27.4
	25.5	26.0
	26.9	26.2
	25.5	25.9
E	25.5	27.1
	<u>25.5</u>	<u>27.1</u>
Grand Averages	27.95	28.00

(1) U. S. Bureau of Mines Laboratory, Laramie, Wyoming.

(2) Colorado School of Mines Research Foundation, Inc., Golden,
Colorado.

TABLE 13

COMPARISON OF FISCHER ASSAY RESULTS BY LARAMIE (L)⁽¹⁾ AND ANVIL POINTS (AP) (DECEMBER 1965)

Lab No.	Split	Portion	Oil, wt %		Water, wt %		Spent Shale, wt %		Gas + Loss, wt %		Specific Gravity		Oil, gal/ton	
			L	AP	L	AP	L	AP	L	AP	L	AP	L	AP
3350	A	1	11.3	11.5	1.2	1.2	85.4	85.2	2.1	2.1	0.908	0.913	29.8	30.3
		2	11.3	11.6	1.1	1.2	85.2	85.0	2.4	2.1	0.908	0.917	29.7	30.2
	B	1	11.2	11.5	1.0	1.2	85.8	85.2	2.0	2.1	0.910	0.914	29.4	30.2
		2	11.3	11.4	1.2	1.2	85.6	85.3	1.9	2.0	0.910	0.912	29.6	29.8
	C	1	11.4	11.6	0.8	1.2	85.1	85.0	2.7	2.2	0.910	0.912	30.1	30.5
		2	11.6	11.4	1.1	1.2	85.0	85.2	2.3	2.2	0.910	0.912	30.4	30.0
3359	A	1	11.0	11.5	1.1	1.1	85.6	85.3	2.3	2.1	0.912	0.913	29.0	30.2
		2	11.3	11.3	1.0	1.1	85.5	85.5	2.2	2.1	0.913	0.913	29.6	29.5
	B	1	11.5	11.5	1.0	1.2	85.4	85.0	2.1	2.3	0.913	0.916	30.1	30.0
		2	11.2	11.5	0.9	1.2	85.2	85.1	2.7	2.2	0.913	0.914	29.5	30.1
	C	1	11.2	11.4	1.5	1.2	85.7	85.3	1.9	2.1	0.912	0.912	29.5	30.0
		2	11.0	11.4	1.3	1.2	85.6	85.7	2.1	1.7	0.911	0.914	29.0	29.8
3380	A	1	12.2	12.2	1.0	1.2	84.4	84.3	2.4	2.3	0.909	0.912	32.1	32.1
		2	12.0	12.3	1.0	1.2	84.6	84.4	2.4	2.1	0.910	0.914	31.7	32.2
	B	1	12.1	12.1	0.9	1.2	84.6	84.2	2.4	2.4	0.910	0.914	31.8	31.8
		2	12.1	12.1	1.0	1.1	84.5	84.2	2.4	2.6	0.911	0.915	31.8	31.6
	C	1	12.0	12.0	1.0	1.1	84.7	84.6	2.3	2.3	0.912	0.910	31.5	31.6
		2	12.1	12.1	1.0	1.1	84.5	84.5	2.4	2.3	0.911	0.912	31.7	31.9
Intralab Standard Deviations (18DF)			0.13	0.08	0.11	0.02	0.11	0.13	0.19	0.12	0.0005	0.0014	0.28	0.25
95% Confidence Limits			0.28	0.17	0.23	0.05	0.24	0.28						
Grand Averages			11.54	11.69	1.06	1.17	85.13	84.94	2.28	2.18	0.9107	0.9133	30.35	30.66
Difference Between Averages			0.15		0.11		0.19		0.10		0.0026		0.31	

(1) U. S. Bureau of Mines Laboratory, Laramie, Wyoming.

DLiederman
11/17/67

The 95% confidence limits given for weight percent oil, water, and spent shale are for a single determination, although the laboratory normally analyzed retort samples of raw shale in duplicate for Fischer Assay.

The analysis indicated that a difference in the measurement of water existed between Laramie and Anvil Points. There was no significant difference between the two laboratories for oil or spent shale measurements; nor was there a significant difference for different portions of shale split from the same sample.

In order to investigate the discrepancy for water between the two laboratories, Anvil Points ran a series of known mixtures of oil and water (18). The mixtures were heated and centrifuged in pear-shaped centrifuge tubes with 1.5-ml stems, then submitted blind to the laboratory technicians.

The precision and accuracy of the results shown in Table 14, indicated that the Anvil Points method was satisfactory. The largest error was equivalent to only 0.2 gallon of oil per ton.

Volumes were also measured in pear-shaped tubes with 3.0-ml stems. The results showed that measurements of the larger volumes could be made more accurately in the tubes with the 3.0-ml stems; the error was less than half at the water levels normally encountered in the Fischer Assay. These were used in subsequent analyses.

(3) Core Lab - Anvil Points (October 1965)

In the course of determining if another laboratory could give reliable Fischer Assays in case of overload or breakdown of equipment, some of the Anvil Points Quality Control samples were submitted to Core Lab (13). The results are shown in Table 15.

The only unacceptable data from the Core Lab were those for Control Sample No. 1. This sample, analyzed in two sets of duplicates on separate days, gave 30.8 and 30.8 gallons per ton for one set of duplicates and 29.0 and 29.4 gallons per ton for the other set. This was not a result only of the samples being analyzed on different days, since Control Sample No. 2 was also analyzed in duplicate on two different days, and results are excellent. The Core Lab analyses for Control Sample No. 3 were made on the same day. Results for the Anvil Points Laboratory were averages of single analyses by different analysts on different days.

TABLE 14

MEASUREMENT OF WATER FOR THE
FISCHER ASSAY DETERMINATION

Centrifuge Tube Stem Volume, ml	Water Volume, ml						
	Added	Analyst 1	2	3	4	5	6
1.5	0.59	0.61	0.60	0.60	0.60	0.60	0.60
	0.95	1.00	1.00	1.00	1.00	1.00	1.00
	1.28	1.30	1.31	1.32	1.30	1.32	1.31
	1.82	1.90	1.80	1.90	1.90	1.80	1.85
3.0	1.75	1.78	1.77	1.77	1.78	1.79	--
	2.68	2.70	2.70	2.70	2.70	2.70	--

TABLE 15

COMPARISON OF FISCHER ASSAY RESULTS BY CORE LAB⁽¹⁾ AND
ANVIL POINTS (OCTOBER 1965)

<u>Fischer Assay Quality Control Sample</u>	<u>Fischer Assay, gal/ton</u>	
	<u>Core Lab</u>	<u>Anvil Points</u>
1	30.8	
	30.8	
	29.0	
	29.4	
	Average	30.00
	SD = 0.74	SD = 0.35
2	27.7	
	27.6	
	27.8	
	27.7	
	Average	27.70
	SD = 0.03	SD = 0.25
3	28.5	
	29.6	
	29.3	
	29.2	
	Average	29.15
	SD = 0.46	SD = 0.27

(1) Core Laboratories, Inc., Rifle, Colorado.

(2) Average of 16 determinations.

(3) Average of 15 determinations.

(4) Average of 11 determinations.

Standard deviations were calculated, for simplicity, assuming single analyses by both laboratories.

It can be concluded from the data, that Core Lab is generally precise enough to act as an emergency source of analyses, but that it is out of control enough so that any single result is suspect. Therefore, if Core Lab's services were required, multiple samples should be submitted for greater confidence.

(4) Laramie - Anvil Points (May 1966)

A final cooperative program for Fischer Assay was completed in May 1966 (27, 28). Six samples of a Fischer Assay Quality Control Sample were analyzed by both Laramie and Anvil Points. The results are given in Table 16. No significant differences appeared in the results by the two laboratories. This was a good indication that the Anvil Points Laboratory maintained good control on this analysis.

b. Specific Gravity of Shale Oil

In July 1965 (29), specific gravity on shale oil was determined by Laramie, Golden, and Anvil Points. The results are given in Table 17.

TABLE 17

RESULTS OF COOPERATIVE PROGRAM ON SPECIFIC GRAVITY

<u>Oil Sample</u>	<u>Specific Gravity, 60/60 F</u>		
	<u>Anvil Points</u>	<u>Laramie</u>	<u>Golden</u>
1	0.917	0.917	0.916
2	0.914	0.915	0.914
3	0.920	0.921	--

The agreement among the different laboratories was excellent.

c. Cooperative Analyses of Raw Shale, Spent Shale, and Shale Oil for Carbon-Hydrogen, Mineral CO₂, and Ash

During November 1964, in connection with the carbon-balance problem previously described, samples of raw shale, spent shale, and shale oil were analyzed for carbon and hydrogen by Laramie, by Humble - Baytown, and by Anvil Points (2). Laramie and Anvil Points also analyzed the samples for mineral CO₂ and Ash. The results are given in Table 18.

TABLE 16

COMPARISON OF FISCHER ASSAY RESULTS BY LARAMIE⁽¹⁾
AND ANVIL POINTS (MAY 1966)

		Fischer Assay Oil, gal/ton	Specific Gravity, 60/60 F	H ₂ O, wt %	Oil, wt %	H ₂ O + Oil, wt %	Spent Shale, wt %	Gas + Loss, wt %
Anvil Points	1	26.7	0.925	1.2	10.3	11.5	86.4	2.1
	2	26.6	0.920	1.3	10.2	11.5	86.3	2.2
	3	26.4	0.922	1.2	10.2	11.4	86.4	2.2
	4	26.8	0.925	1.3	10.4	11.7	86.4	1.9
	5	26.7	0.920	1.3	10.3	11.6	86.5	1.9
	6	26.9	0.923	1.3	10.3	11.6	86.3	2.1
	Averages -	26.68	0.922	1.25	10.28	11.55	86.38	2.07
Standard Deviation -	0.17	0.0023	0.055	0.074	0.105	0.075	0.147	
Laramie	7	26.7	0.916	1.2	10.2	11.4	86.2	2.4
	8	26.9	0.915	1.0	10.3	11.3	86.7	2.0
	9	26.7	0.915	1.1	10.2	11.4	86.6	2.1
	10	26.5	0.915	1.0	10.1	11.1	86.4	2.5
	11	27.5	0.913	1.2	10.5	11.7	86.0	2.3
	12	27.5	0.913	1.0	10.5	11.5	86.1	2.4
	Averages -	26.97	0.914	1.08	10.30	11.40	86.33	2.28
Standard Deviation -	0.43	0.0013	0.099	0.167	0.200	0.280	0.19	
Difference in Averages -- Laramie Minus Anvil Points		0.29	-0.008	-0.17	0.02	-0.15	-0.05	0.21
Calculated "t" Value		1.53	7.3	3.7	0.26	1.62	0.42	2.16
5% Critical "t" Value (10DF)		= 2.23						
1% Critical "t" Value (10DF)		= 3.17						

(1) U. S. Bureau of Mines Laboratory, Laramie, Wyoming.

TABLE 18

COMPARISON OF RESULTS ON CARBON-HYDROGEN, MINERAL CO₂, AND ASH

Carbon and Hydrogen

<u>Sample</u>	<u>Anvil Points</u>	<u>Humble - Baytown (1)</u>	<u>Laramie (2)</u>
Raw Shale (AP-RS)			
Carbon, wt %	16.3	(omitted)	16.2
Hydrogen, wt %	1.70	1.72	1.70
Spent Shale (AP-SS)			
Carbon, wt %	6.77	6.77	6.78
Hydrogen, wt %	0.30	0.28	0.27
Shale Oil (AP-LP)			
Carbon, wt %	83.9	84.0	84.8
Hydrogen, wt %	11.1	11.4	11.6

Mineral CO₂ and Ash

<u>Sample</u>	<u>Anvil Points</u>	<u>Laramie</u>
Raw Shale (AP-RS)		
Mineral CO ₂ , wt %	16.5	16.2
Ash, wt %	68.2	68.4
Spent Shale (AP-SS)		
Mineral CO ₂ , wt %	14.9	14.5
Ash, wt %	82.7	82.8

(1) Humble Refinery Service Laboratories, Baytown, Texas

(2) U. S. Bureau of Mines Laboratory, Laramie, Wyoming

The results are in generally good agreement. The result obtained by Humble - Baytown for carbon in the raw shale, was omitted because of inadvertent use of a method in which sulfur interfered. The only other slight inconsistency is Laramie's relatively high result for carbon in the shale oil sample.

9. Recommendations For Future Oil Shale Analytical Data Acquisition and Utilization

Serious consideration should be given to the acquisition, transmittal, and utilization of analytical data for future oil shale research programs and commercial applications of that research.

Studies are currently being made in linking automated process variable measuring transducers to computers and data transmittal devices. Results of these studies will be applicable generally and, in this case, specifically to the shale oil segment of the energy industry.

The great advantage of these systems is the rapid communication of process variables, to decision-making personnel. Their ultimate sophistication lies in the ability to furnish closed-loop control. This capability enables these systems to control the process as well as describe it.

Use of these computerized techniques can offer many advantages. The techniques increase decision-making effectiveness by reducing data lag time and minimizing data transmittal errors. These and other advantages make it desirable to consider these systems as an integral part of any future research or commercial project planning.

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