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MOBIL RESEARCH AND DEVELOPMENT CORPORATION

RESEARCH DEPARTMENT

TECHNICAL MEMORANDUM NO. 67-37

ANALYTICAL LABORATORY METHODS  
(FINAL REVISION)

ANVIL POINTS OIL SHALE RESEARCH CENTER

Rifle, Colorado

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The primary object of the Anvil Points Oil Shale Research Center TECHNICAL MEMORANDUM is to advise authorized personnel employed by the Participating Parties<sup>(1)</sup> that various activities are in progress or that certain significant data have been obtained within the Research Center.

These TECHNICAL MEMORANDA have been prepared to provide rapid, on-the-spot reporting of research currently in progress at Anvil Points. The conclusions drawn by project personnel are tentative and may be subject to change as work progresses. The TECHNICAL MEMORANDA have not been edited in detail.

(1) Mobil Research and Development Corporation, Project Manager

Continental Oil Company  
Humble Oil and Refining Company  
Pan American Petroleum Corporation  
Phillips Petroleum Company  
Sinclair Research, Inc.

TECHNICAL MEMORANDUM NO. 67-37

These analytical laboratory methods have been issued as a technical memorandum so that (1) they will become part of the formal memoranda issued by the Anvil Points Oil Shale Research Center and, (2), they will be automatically distributed to all authorized personnel of the Participating Parties.

This is a revision and final updating of the material contained in Technical Memorandum No. 65-5.

Of necessity, copies of that memorandum were issued to the laboratory technicians in the Analytical Laboratory, who were employees of the Colorado School of Mines Research Foundation, Inc.

ANALYTICAL LABORATORY METHODS  
(FINAL REVISION)

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ANALYTICAL LABORATORY METHODS  
(FINAL REVISION)

I. INTRODUCTION

The purpose of this manual is (1) to present the details of the analytical methods used in this laboratory and (2) to report general information relative to the operation of the laboratory.

The procedural details are mainly for the laboratory technicians, but are also intended for those in other Analytical Laboratories who are, or will be, involved in oil shale and shale oil analyses.

In general, the apparatus used is described in detail. It is not necessarily the only equipment suitable, but it has been selected for the laboratory and found to be satisfactory. Much of the equipment left by the U. S. Bureau of Mines was used. Although some of it is not as good as other equipment commercially available today, it was satisfactory for our purpose.

The methods were written for use on routine samples originating from the Anvil Points research program; often, they were applied to special samples with little or no modification.

An explanation of the numbering of the methods is give below:

AP - Anvil Points (identifies procedure used in the Anvil Points Oil Shale Research Analytical Laboratory).

S - Shale (procedure used for raw and spent shale).

O - Oil (procedure used for crude shale oil or liquid product).

G - Gas (procedure used for recycle gas).

W - Water (procedure used for water).

The main goal of the laboratory was to provide accurate and precise analyses. Standard samples were used to check accuracy; a quality control program was used to obtain precision data. Precision figures were recalculated about every four months from data obtained by our continuous quality control program.

## II. SUMMARY

Methods applicable to the analytical requirements of the Anvil Points Oil Shale Research Center were adopted, adapted, or developed, and are reported in this memorandum.

Results for precision of these methods, as used by our analytical personnel, are given in Table 1.

For convenience of reference, a summary of sample treatment and result reporting data are shown in Table 2.

TABLE 1

## PRECISION OF LABORATORY ANALYSES

<u>Material</u>	<u>Method</u>	<u>Level</u>	<u>Standard Deviation</u>	<u>95% Confidence Limit</u>
Raw Shale	Fischer Assay	28 gal/ton	0.226	0.476
	Mineral CO <sub>2</sub>	17 Wt %	0.139	0.320
	Ash	69 Wt %	0.087	0.191
	Moisture	0.2 Wt %	0.014	0.034
	Carbon	16 Wt %	0.069	0.156
	Hydrogen	1.7 Wt %	0.028	0.063
Spent Shale	Mineral CO <sub>2</sub>	14 Wt %	0.114	0.254
	Ash	82 Wt %	0.047	0.111
	Moisture	0.15 Wt %	0.014	0.036
	Carbon	7 Wt %	0.031	0.070
	Hydrogen	0.3 Wt %	0.018	0.041
	Nitrogen	0.2 Wt %	--	0.012
Shale Oil	Carbon	84 Wt %	0.15	0.35
	Hydrogen	11 Wt %	0.25	0.55
	Nitrogen	2.2 Wt %	0.05	0.11
	Gravity	20 °API	--	0.1
	Ramsbottom Carbon	2 Wt %	--	0.1
	Ash	0.02 Wt %	--	< 0.01
	Viscosity, 130 F	123 SUS	--	24
	Viscosity, 210 F	46 SUS	--	1.6
	Pour Point	85 F	--	0
Distillation	Within limits given in ASTM method			
Gas	Carbon	10 lb/MSCFDG	0.22	0.48
	Hydrogen	0.3 lb/MSCFDG	0.06	0.13

TABLE 2

## SUMMARY OF SAMPLE TREATMENT AND REPORTING OF RESULTS

TEST	SAMPLE TREATMENT	REPORTING OF RESULTS
<u>RAW AND SPENT SHALE</u>		
Fischer Assay	Grind to minus 8-mesh	as rec'd., gal/ton S.G. oil oil Wt % water Wt % spent shale Wt % gas + loss Wt %
Mineral CO <sub>2</sub>	Grind to minus 48-mesh	as rec'd., Wt %
Ash	Grind to minus 48-mesh	as rec'd., Wt %
Moisture	Grind to minus 48-mesh	as rec'd., Wt %
Carbon	Grind to minus 48-mesh	as rec'd., Wt %
Hydrogen	Grind to minus 48-mesh	as rec'd., Wt %
Nitrogen	Grind to minus 48-mesh	as rec'd., Wt %
Benzene Extractables	Grind to minus 48-mesh or none	as rec'd., Wt %
Particle Size Distribution	Dry, if wet	"dry", Wt %
Density	Dry, if wet	"dry", gm/ml
Richness Distribution	Dry, if wet	Richness, gal/ton; or graph
<u>LIQUID PRODUCT</u>		
Carbon	Centrifuge to separate water and sediment	dry oil, Wt %
Hydrogen	Centrifuge to separate water and sediment	dry oil, Wt %
Nitrogen	Centrifuge to separate water and sediment	dry oil, Wt %
API Gravity	Centrifuge to separate water and sediment	dry oil, °API @ 60 F
Water in LP	None	as rec'd., Wt %
Sediment in LP	None	as rec'd., vol/wt %
Ramsbottom Carbon	Centrifuge to separate water and sediment; filter through 100-mesh screen	dry oil, Wt %
Ash	Gravity separated, use oil on top	as rec'd., Wt %
Viscosity @ 130 F	Centrifuge to separate water and sediment, filter through 100-mesh screen	dry oil, S.U.S.
Viscosity @ 210 F	Centrifuge to separate water and sediment, filter through 100-mesh screen	dry oil, S.U.S.
Pour Point	Centrifuge to separate water and sediment	dry oil, F
Distillation	Centrifuge to separate water and sediment; dry with CaCl <sub>2</sub> ; filter through 100-mesh screen	dry oil, Vol %

(Continued on next page)

TABLE 2 (CONTINUED)

SUMMARY OF SAMPLE TREATMENT AND REPORTING OF RESULTS

<u>TEST</u>	<u>SAMPLE TREATMENT</u>	<u>REPORTING OF RESULTS</u>
<u>GAS</u>		
Component Analysis	Oil condensed out, gas dried with $MgClO_4$	dry, Vol %
Total Carbon	Oil condensed out, gas dried with $MgClO_4$	dry, lbs/MSCF
Total Hydrogen	Oil condensed out, gas dried with $MgClO_4$	dry, lbs/MSCF
<u>WATER PRODUCT</u>		
Various components	Detailed in method	Wt %

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

Scope

This method is used to prepare raw and spent shale samples for various analyses performed in the laboratory.

Outline of Method

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.

Apparatus

- a. Jaw Crusher - Denver Fire Clay Company, 4 1/2 inch.
- b. Pulverizer - Bico-Braun UA.
- c. Sieve Shaker - Braun-Porter, accommodates one to six standard 8-inch sieves with cover and pan.
- d. Sieves - 8 inch; 8 mesh, 48 mesh, pan and cover.
- e. Splitters - various sizes, 6 inch and up.
- f. Pans - for splitters.
- g. Plastic bags - Scientific Products Whirl-Pak bags; 18-oz. capacity, 6-oz. capacity.
- h. Jars - 4-oz. wide mouth, screw cap, glass.

Procedure

Using proper splitting technique\*, reduce the amount of the shale sample to 775 - 825 grams. With the jaw crusher, crush this entire sample so that it passes the 8-mesh sieve. Mix the resulting minus 8-mesh sample well.

Follow the splitting procedure outlined in Figure 1 to obtain samples for analysis. "A" is 775 - 825 grams of minus 8-mesh shale. The portions identified by a solid circle should be poured into an 18-oz. plastic bag as a retain sample. (Attach the original sample tag to this bag.)

\*See Discussion

When duplicate Fischer Assays are required (raw shale), portions "I" and "L" should each be poured into a 6-oz. plastic bag labeled with the laboratory number of the sample. These two samples will be used for Fischer Assay. Combine "P" and "Q" for Fischer Assay Moisture which is determined by AP-S-6.

When only a single Fischer Assay is required (spent shale), treat portions "I" and "L" as shown at the bottom of Figure 1. Pour portion "U" into a 6-oz. plastic bag labeled with the laboratory number of the sample. This sample will be used for Fischer Assay.

Grind portion "S" to minus 48-mesh according to the following directions:

Set the grinding plate adjustment knob on the Bico-Braun pulverizer so that practically all of the shale charge is crushed to -48 mesh in one pass. Handle all samples in a way that minimizes dust loss. Carefully brush shale dust from the pulverizer into the sample pan. Grind any material that remains on the screen in a mortar, add this material to the other portion, and mix thoroughly.

#### Discussion

The reasons for reducing the submitted shale sample to 775 - 825 grams are (1), that a four-fold reduction in size will provide a sample in the 95 - 105 gram range which is required for Fischer Assay, and (2), that the approximately 550 to 650 grams of retained sample not used for analyses, conveniently matches the capacity of the 18-oz. plastic bag.

Because of the heterogeneity of oil shale, extreme care must be used in splitting and grinding; this is necessary to insure that the smaller samples used for analyses are truly representative of the original large sample submitted to the laboratory.

Proper splitting technique to be used is as follows: A pouring pan, a splitter, and two receiving pans are used. The size of the splitter should be commensurate with the size of sample being split. The three pans should be of the same length as the splitter. Place one receiving pan on the "right" side of the splitter: place the other receiving pan on the "left". Pour the sample into the pouring pan, distributing it evenly throughout the pan. Raise this pan next to the splitter so that one side is parallel and directly adjacent to the splitter. Slowly tilt the pouring pan so that the shale is uniformly transferred from the pan into the splitter. (This step should be done slowly to minimize dust loss.) The sample should then be equally divided into the right and left receiving pans. While reducing the sample size, alternately discard the shale in the right and left receiving pans.

When the original sample has been reduced to about 2000-3000 grams, use the examples shown in Figure 2 as a guide to further reduce the sample to the 775 - 825 gram range.

Retain about 3 to 5 pounds of the uncrushed sample for possible future analyses.

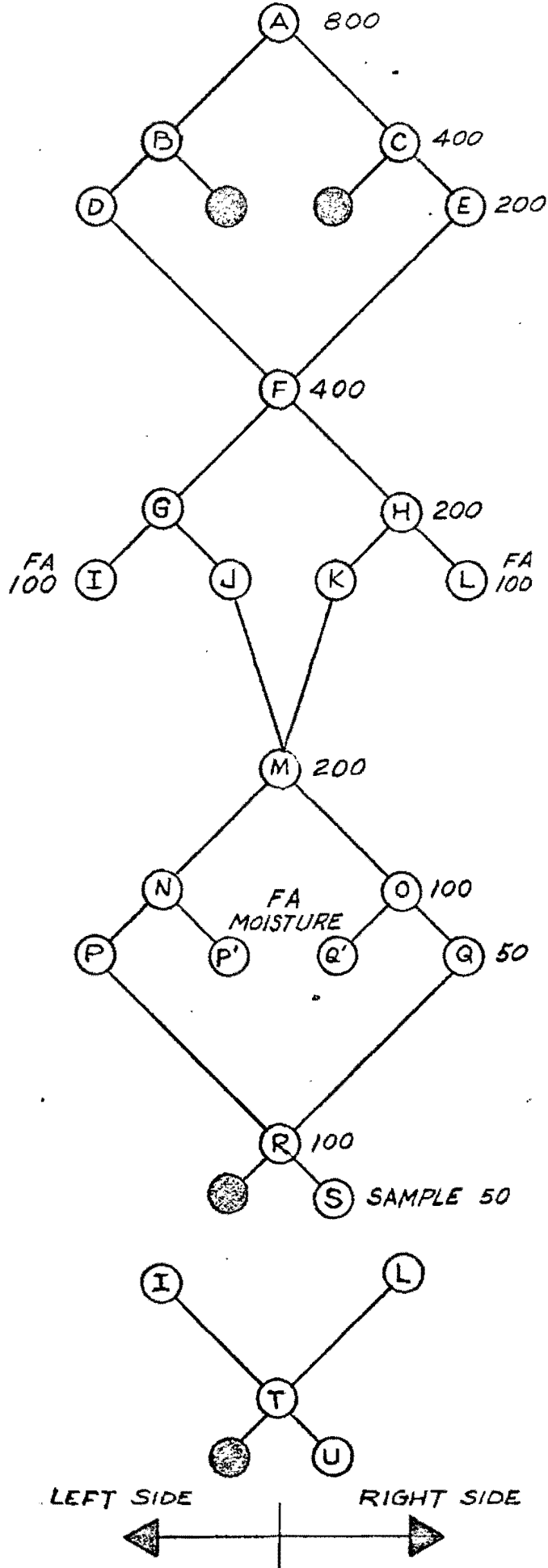
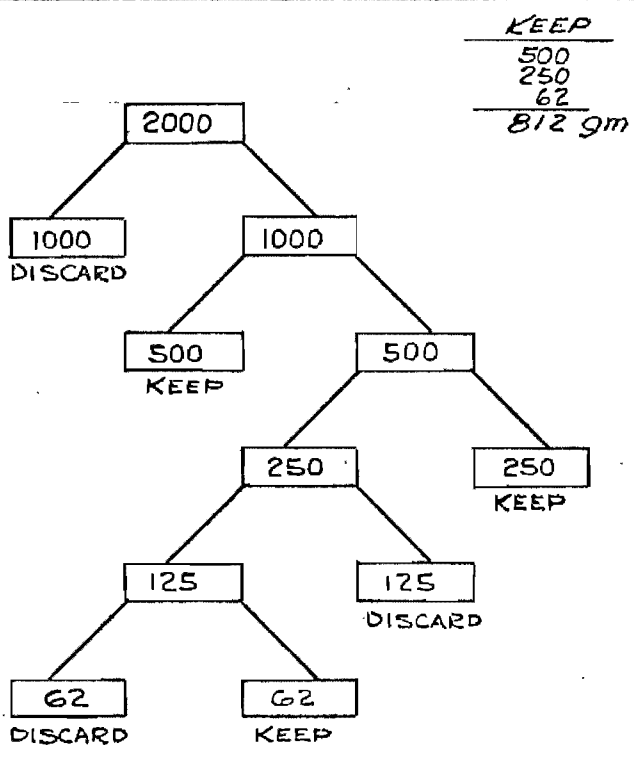


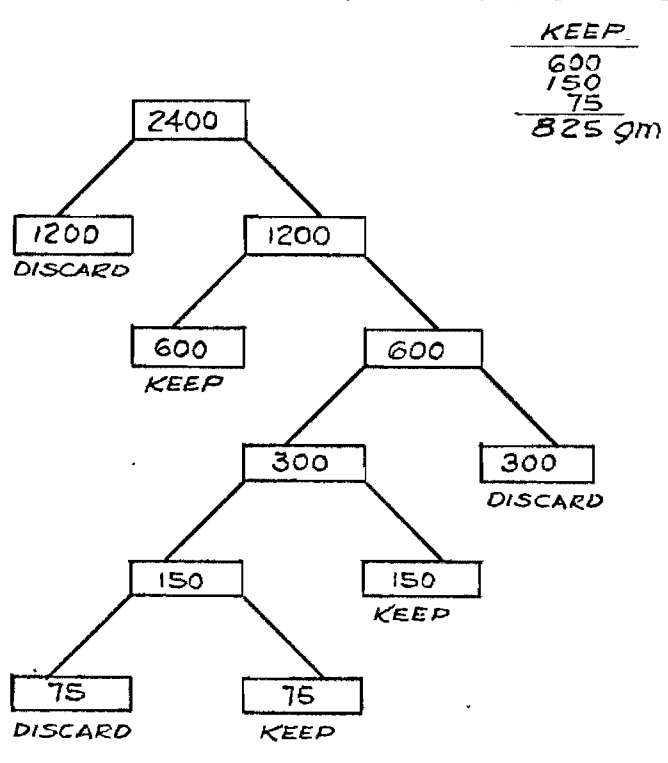
FIGURE 1.

SPLITTING PROCEDURE FOR MINUS 8 MESH SAMPLE

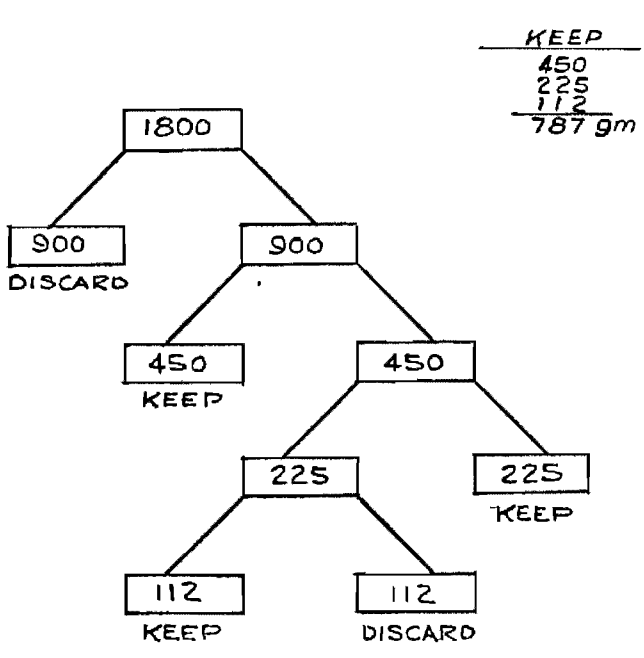
EXAMPLE 1 - WEIGHT - 2000 GM



EXAMPLE 2 WEIGHT 2400 GM



EXAMPLE 3 - WEIGHT 1800 GM



EXAMPLE 4 - WEIGHT 3000 GM

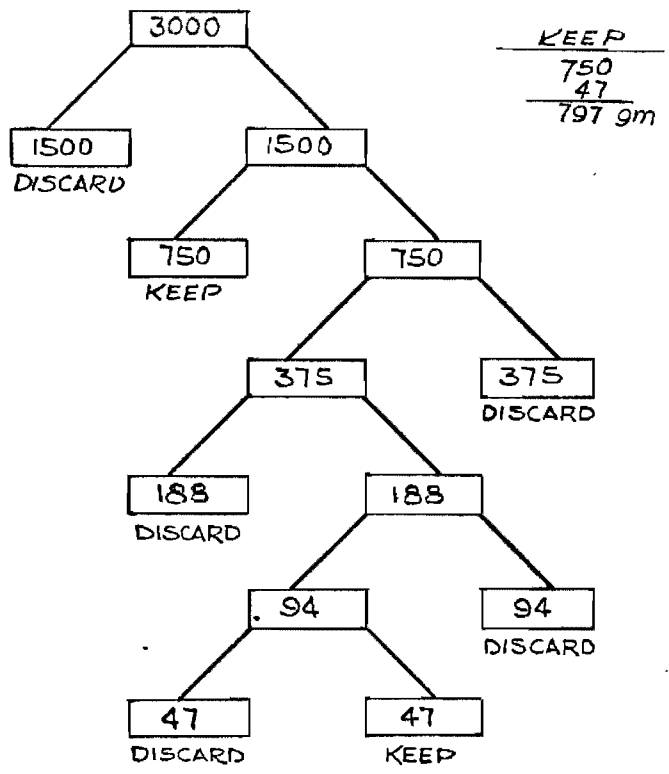


FIGURE 2  
 EXAMPLES OF SPLITTING SAMPLES TO 775-825 GRAMS

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

Scope

This method describes the treatment of liquid product (crude shale oil + water + sediment) before various analyses, such as specific gravity, water-and-oil, and ash, are made.

Apparatus

- a. Malt Mixer - such as the Hamilton Beach No. 18.
- b. Centrifuge - International Size 2, EXD, with head, cups, and Neoprene cushions to fit centrifuge tubes in (c) below.
- c. Centrifuge tubes - 100 ml, pear shape, 3-ml stem, Kimble No. 45245, calibrated before using (see Centrifuge Tube Calibration below).
- d. Water Bath - 80 C, with holder for six centrifuge tubes.
- e. Jars - 1 pint, glass, wide-mouth, with screw cap, (to fit sampler at the retort).

Procedure

Liquid product samples, which are collected from various parts of the retort product recovery system, are usually submitted to the laboratory in pint jars.

Warm the sample in an oven at about 140 F for 10 to 15 minutes, then mix it well with the malt mixer for about 30 seconds.

Immediately transfer 50 to 80 g into a preweighed flask for determination of water in oil by distillation, and about 50 ml into a centrifuge tube to use for specific gravity, C-H, and N determinations. If the ash content, Ramsbottom carbon, viscosity, pour point, or distillation of the oil are to be determined, transfer enough liquid product to a centrifuge tube(s) for the required analyses.

Heat the centrifuge tube(s) in the 80 C bath for five minutes, wipe dry, and centrifuge for 10 minutes. Remove the supernatant oil for the analyses.

Centrifuge Tube Calibration

Clean the centrifuge tube with cleaning solution, rinse well with distilled water, and air dry.

Add 5 ml of shale oil and, successively, 0.1, 0.3, 0.5, 0.8, 1.2, 1.5, 2.0, 2.5, and 3.0 ml of water from the retort product. After each addition, warm the tube in the water bath and centrifuge for 10 minutes. Read the water level at the bottom of the meniscus.

On graph paper, plot the amount of water added versus that read. Prepare a chart with the corrections to be made for each reading at 0.1 ml intervals up to 3.0 mls.

Revised October 2, 1967

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, ColoradoAnalytical LaboratoryFischer Assay of Raw and Spent Shale  
(AP-S-3)Scope

This method is the modified Fischer Assay Procedure developed by the U. S. Bureau of Mines, and is used to determine the oil content of raw and spent shale.

Outline of Method

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 yield, in gallons per ton, is calculated.

Apparatus

A six-unit Fischer Assay apparatus has been designed and constructed in the laboratory. Each unit can be operated individually. In this section, the components and assembly for one unit are described; in addition, a description of the components common to all six units is included.

1. Components For One Unit

- a. Aluminum retort\* - with plug, vent tube, 4 discs, and outlet tube. Casting available from Winner Foundries, Inc., 5655 Marshall Street; Arvada, Colorado.
- b. Transite heater\* - with 4 Chromalox strip heating elements (No. PT-502, 120v., 250 watts) and 1 Chromalox Ring Heating Element (No. A-20, 120v., 500 watts).
- c. Silicone stoppers - Size 6, 1-hole for outlet tube; Size 3, 1-hole for condenser top; Size 1, 1 hole for drying tube.
- d. Adapter - See Drawing No. RE 23; available from Scientific Glassblowing Company, Houston, Texas. (Design from Colorado School of Mines Research Foundation, Golden, Colorado)

\*"Automated Modified Fischer Retorts for Assaying Oil Shale and Bituminous Materials", by Arnold B. Hubbard, Bureau of Mines Report of Investigations, RI 6676.

- e. Centrifuge tube - "1.5 ml": 100-ml, oil, pear shape, Kimax; stem graduated up, from 0 to 1.5 ml by 0.1 ml; body graduated at 2 ml., from 2 to 5 ml by 0.5 ml, from 5 to 10 ml by 1 ml, from 10 to 25 ml by 5 ml, and at 50 and 100 ml.
- f. Centrifuge tube - "3.0 ml": 100 ml, oil, pear shape, Kimax; stem graduated up, from 0 to 3 ml by 0.1 ml; body graduated from 3 to 10 ml by 0.5 ml, from 10 to 25 ml by 5 ml, and at 50 and 100 ml.
- g. Tape - Permacel, 3/4", MMS-J517A, P2650 - 10 ml.
- h. Condenser - Allihn, Pyrex, 300 mm. jacket length; top - adapter for No. 3 rubber stopper; bottom - 24/40  $\text{\textcircled{S}}$  with drip tip.
- i. Asbestos tape - 2-inch width.
- j. Drying tube - straight form, single bulb, Pyrex, 150 mm.
- k. Glass Wool.
- l. Drierite - indicating, 8-mesh.
- m. Thermocouple - Bayonet, Type 2# TE 2A0121P Iron-Constantan, Immersion length 2" to 2 5/8" (with light spring, 2 lbs.) Type E coupling for lead wires; Adapters #1500-2, 3/8" - 24 thread, screw driver slot. Available from Thermo-Electric Company, Inc., Saddle Brook, New Jersey.
- n. Pyrometer - Contacting, Model No. 461-C, Cat. No. 4625 for Iron-Constantan Thermocouple (ISA Calibration J); Dial-Standard 0-1000 F, 0-500 C. single high set point, zero left, standard type set-point adjustment; with meter relay control package MFP Unit for "Alarm or Shutoff-Single (High Set Points)". Available from Assembly Products, Inc., Chesterland, Ohio.
- o. Ammeter - Triplet AC Ammeter, 0-25 amperes, Model 330-M.
- p. Variable Transformer - STACO, Type 2500 BU, 3.5 KVA, 120 volts, output 0-132/0-120 volts, 25.0 amperes.
- q. Relay - 20 ampere, single pole-double throw, normally closed.
- r. Switch - 20 ampere circuit breaker.

s. Indicator Lights - 1 red, 1 yellow, 120 volts.

2. Components Common to the Six Units

- a. Instrument Panel - 1/8"-aluminum, 24" X 66", bottom 42" from floor, supported by 1-1/4" angle iron.
- b. Circuit Breaker - 200 amperes.
- c. Cooling Bath - for centrifuge tubes, galvanized metal, 45" length by 4" width by 7 1/2" height, with 1/4-inch copper inlet tubes, and two 1/2-inch I.D. outlet pipes.
- d. Cooling Bath Supports - (2), Laboratory Big Jack.
- e. Refrigeration Bath\*\* - insulated, approximate 35 gallon capacity.
- f. Compressor - #EKD-331 Sealed Unit 1/3 hp. Cap. Start. Refrigerant #F-12, with #F210-4, 1/4" SAE Filter Dryer and #A302S03 Cold Control (Ronco): available from McCombs Supply Company, Denver, Colorado.
- g. Coolant - 1:2 Prestone-water, maintained at  $0 \pm 5$  C.
- h. Circulating Pump\*\* - 115 volts, 1/4 hp.
- i. Exhaust fan and manifold\*\*.
- j. Centrifuge - Universal No. 2, EXD, with suitable head, cups, and cushions.
- k. Water Bath - 80 C, with holder for six centrifuge tubes.
- l. Retort Plug Puller - See Drawing No. RE 21.
- m. Solvent - 1:1 Acetone - Trichloroethylene.
- n. Graphite - powdered.
- o. Support Structure\*\* - for retorts, water, cooling bath, etc.

\*\*These items (among others) were left in the laboratory by the U. S. Bureau of Mines. A complete description of these items has not been included since many designs of these pieces of equipment are acceptable.

### Preparation of Apparatus

The final assembly of the apparatus for one unit is shown in Figure 1. The identifications in the figure refer to those described in the "Apparatus" section, parts 1 and 2. The layout of a single unit on the control panel is shown in Drawing No. RC-8-A (not included). The circuit diagram for a single unit is shown in Drawing No. RE 22.

The refrigeration system consists of a reservoir of coolant and a circulator. By means of the circulating pump, the solution is pumped in parallel to the bottom of the condensers which are wrapped with asbestos tape, and then out the top to the inlets of the cooling bath. The height of the outlets in the cooling bath is such that the solution covers the centrifuge tube up to its widest point. The solution then flows by gravity back into the reservoir in the refrigeration bath.

Fill the drying tube in the conventional manner with glass wool at either end and indicating drierite in the middle. Insert a Size 1, 1-hole rubber stopper in the large end and rubber tubing on the small end.

### Procedure

Use the 95-105 gram portion of minus 8-mesh shale in the 6 oz. plastic bag as obtained by the procedure, "Preparation of Raw and Spent Shale Samples".

Record all data and make all calculations on OSRC-13, "Fischer Assay".

Weigh an empty retort with its four discs, vent tube, plug, and rubber stopper, to the nearest 0.1 gram. Record this weight, Retort. Slowly pour (to prevent dust loss) the entire contents of the 6-oz. bag into the retort in five layers separated by the four discs about the vent tube. (Be careful not to pour any sample down the distillate tube.) Tap the plug in place with the retort plug-puller. (See Drawing) Weigh the filled retort to the nearest 0.1 gram. Record this weight, Retort + Sample.

Use a "3.0 ml" centrifuge tube. Weigh a clean, dry, empty centrifuge tube (receiver) and adapter together to the nearest 0.01 gram. Record this weight, Rec. and Adp.

Refer to Figure 1 for assembly of the apparatus. Place the filled retort within the heater and close the lid. Be sure the thermocouple is making good contact with the retort. Attach the centrifuge tube and adapter to the distillate tube; attach the condenser to the adapter. All connections must be gas tight. The centrifuge tube should be well immersed in the

coolant. Be sure the coolant is flowing through the condenser and out of the cooling bath. Turn on the power switch and set the variable transformer at full power. Adjust the high set point of the pyrometer to 510 C. When the temperature reaches 500 C, adjust the variable transformer so that the 500 C temperature is maintained. After 25 minutes at 500 C,\* turn off the power switch. Open the heater lid. After about five minutes, move the retort to the cooling rack. Attach a filled drying tube to the outlet tube. Meanwhile, raise the condenser and remove the centrifuge tube and adapter together. Rinse the coolant from the centrifuge tube with water, and dry. Allow the centrifuge tube and adapter to come to room temperature, and then weigh them together to the nearest 0.01 gram. Record this weight, Rec. + Adp. + Dist. Place the centrifuge tube and adapter in the 80 C water bath for 10 minutes. Remove the adapter, and centrifuge the oil and water in the centrifuge tube for 10 minutes. Read the volume of water to the nearest 0.05 ml. Record this volume, Water Vol. (Wt).

If the water-oil interface is not sharp, insert a small wire into the sample and scrape around the tube to sharpen the interface. Then reheat the centrifuge tube in the water bath for five minutes, re-centrifuge for five minutes, and then read the water volume.

Determine the specific gravity of the oil as described in "API Gravity of Crude Shale Oil". Record the weight of the pipet plus oil, Weight (Pipet + Oil). Convert to specific gravity at 60 F by use of the prepared tables. Record this value, S.G. 60/60 F. If there is insufficient oil for a specific gravity determination, use a value of 0.914 for further calculation.

After the retort is cool, remove the drying tube and weigh the retort to the nearest 0.1 gram. Record this weight, Retort + Sp. Shale. Use the retort plug-puller to remove the plug from the retort. Pour out the spent shale, and clean the inside of the retort, plug, four discs, and vent tube with a dry brush. Swab the outlet tube with the 1:1 acetone-trichloroethylene solvent, and dry. After emptying the centrifuge tube and adapter, clean them with the solvent, and dry.

### Calculation and Report

Complete OSRC-13 as shown on the sample form.

\*For very rich shales (>50 gallons per ton) more than 25 minutes at 500 C may be required to retort all of the oil. Do not terminate heating the retort until five minutes after the last drop has fallen into the centrifuge tube and adapter.

Report: Gallons per ton to the nearest 0.1

S.G. 60/60 F to the nearest 0.001

Wt % Oil to the nearest 0.1

Wt % Water to the nearest 0.1

Wt % Spent Shale to the nearest 0.1

Wt % Gas + Loss to the nearest 0.1

### Coking Tendency

Report coking tendency on the shale as described below (from Bureau of Mines RI 4825, Properties of Colorado Oil Shale, p 13);

<u>Coking Tendency</u>	<u>Condition of Spent Shale from Assay</u>
None	The spent shale poured from the retort similar to sand without any evidence of conglomeration.
Slight	The spent shale adhered but could be removed completely from the retort by stirring with a light spatula or rod.
Moderate	The spent shale was partially fused but contained some unfused particles. It was difficult to remove from the retort.
Heavy	The spent shale was completely fused and the original form of all visible particles was completely altered. The residue was very difficult to remove from the retort.

### Discussion

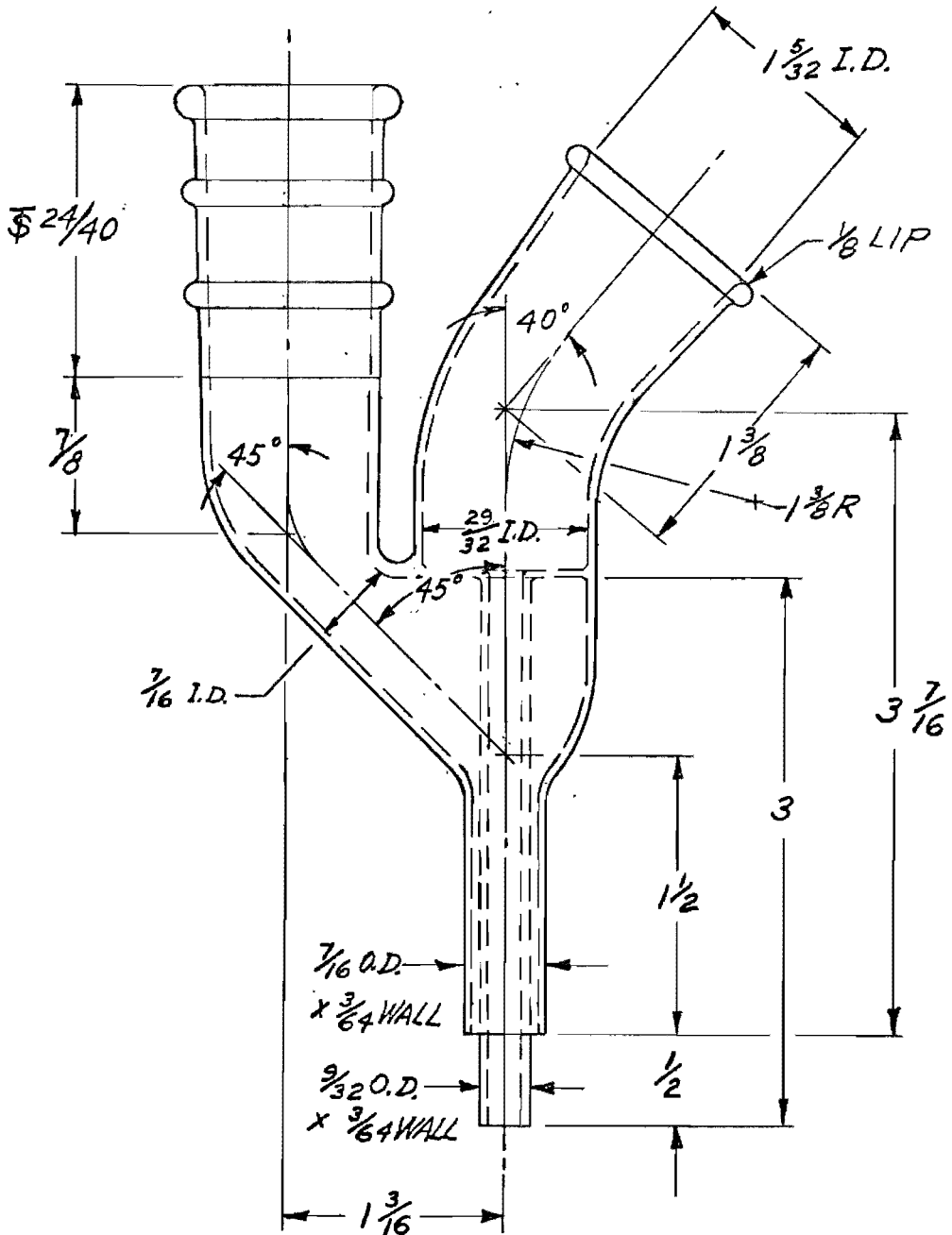
With the 1500 watts of heating elements operated at 110 volts, the ammeter will normally read about 13.5 amperes at full power of the variable transformer. If the heating elements are not drawing this much current, a defective element is indicated. It should be replaced, since the final temperature of 500 C will be reached more slowly than required. Normally, the 500 C is reached in about 40 minutes.

If necessary, lubricate the retort plug with the powdered graphite.

The condensers should occasionally be rinsed with the solvent.

The factor 239.6 on Form OSRC-13 converts ml/gram to gallons per ton. Density and specific gravity are assumed to be the same number.

NOTE: ALL WALL THICKNESSES SHALL BE  $\frac{3}{64}$  MIN. UNLESS OTHERWISE SPECIFIED.



NO.	DATE	PRINT ISSUED TO

<p><b>OIL SHALE RESEARCH CENTER</b>  <b>ANVIL POINTS</b>  <b>RIFLE, COLO.</b></p>			
<p>PROJECT MANAGER - SOCONY MOBIL OIL CO., INC.</p>			
<p>APPROVED</p>	<p>PROCESS</p>	<p>DESIGN</p>	<p>SAFETY</p>
<p>JOB NO.</p>	<p>CHARGE</p>		

<p>SCALE</p>	<p>FULL SIZE</p>
<p>DRAWN BY</p>	<p>Joe H. ...</p>
<p>STARTED</p>	<p>5-28-65</p>
<p>COMPLETED</p>	<p>6-1-65</p>
<p>DIMENS. CHECKED</p>	<p> </p>

<p>LOCATION</p>	<p>ANALYTICAL LAB.</p>
<p>DRAWING NO.</p>	<p>RE 23</p>
<p>ADAPTER</p>	

3397 (8-55)

NO.	DATE	PRINT ISSUED TO

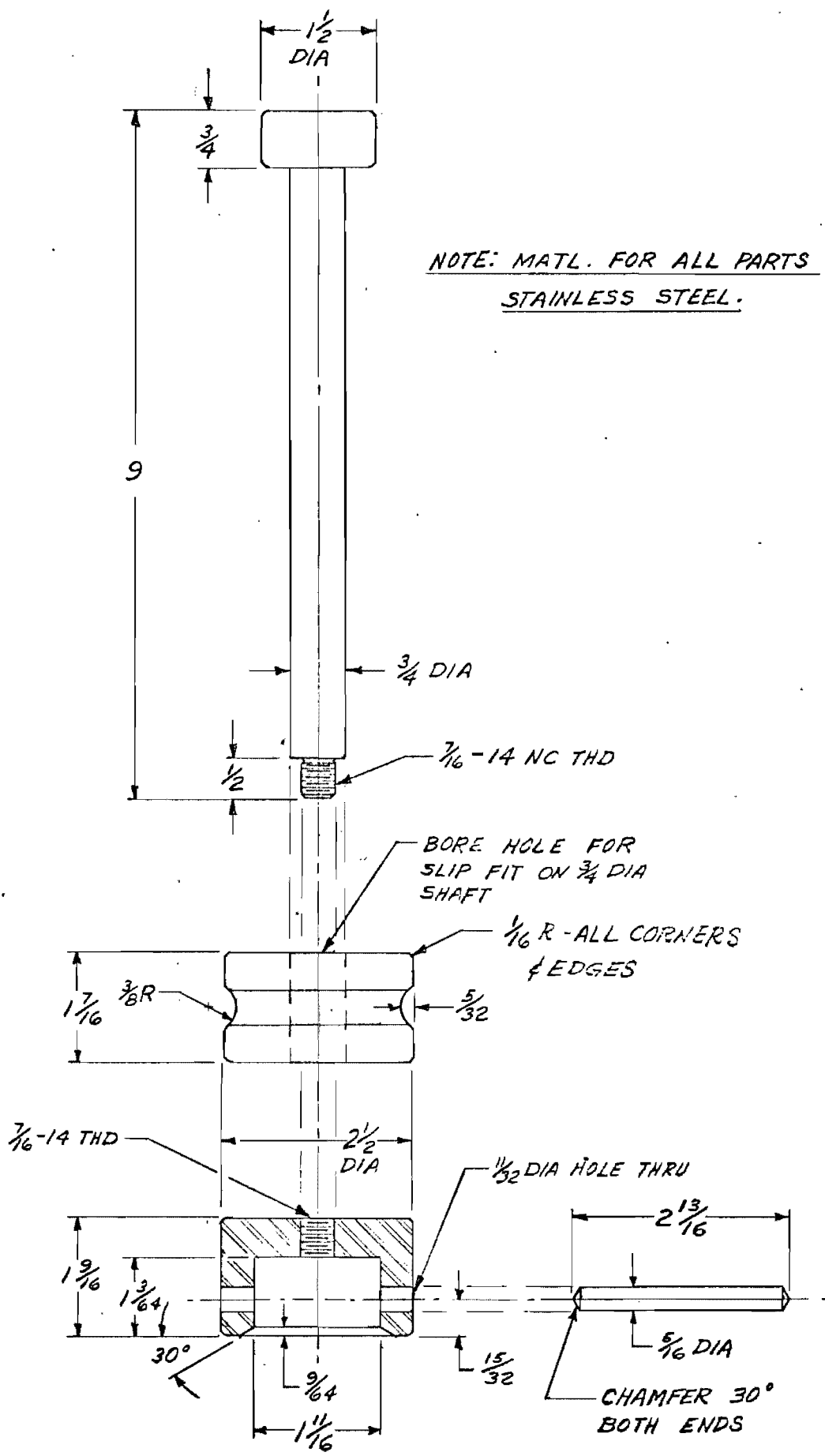
**OIL SHALE RESEARCH CENTER**  
**ANVIL POINTS**  
**RIFLE, COLO.**  
**PROJECT MANAGER - SOCONY MOBIL OIL CO., INC.**

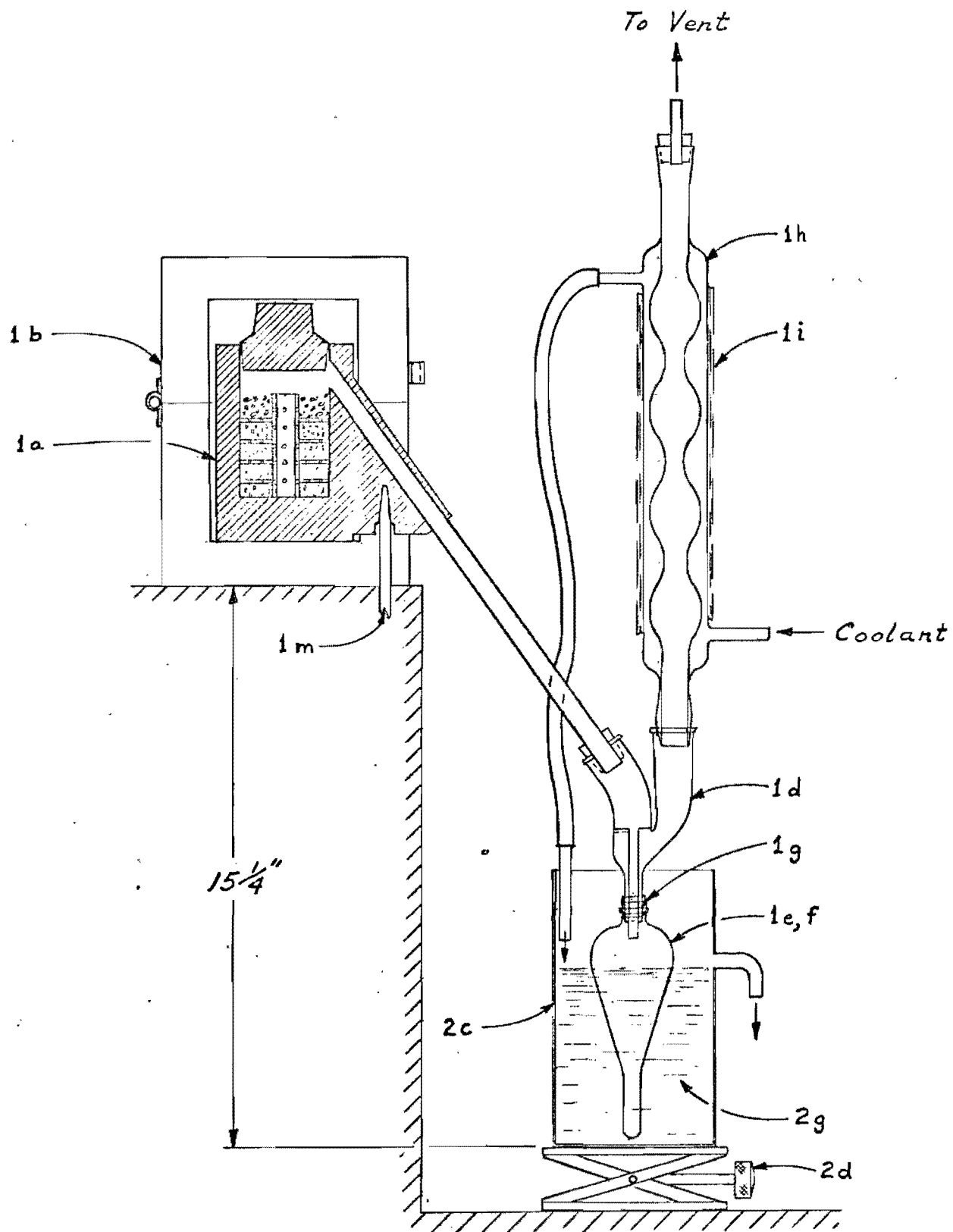
JOB NO. \_\_\_\_\_  
 APPROVED \_\_\_\_\_  
 PROCESS \_\_\_\_\_  
 DESIGN \_\_\_\_\_  
 SAFETY \_\_\_\_\_  
 CHARGE \_\_\_\_\_

SCALE: 1/2" = 1"  
 DRAWN BY: [Signature]  
 STARTED: 5-28-65  
 COMPLETED: 5-28-65  
 DIMENS. CHECK: [Signature]

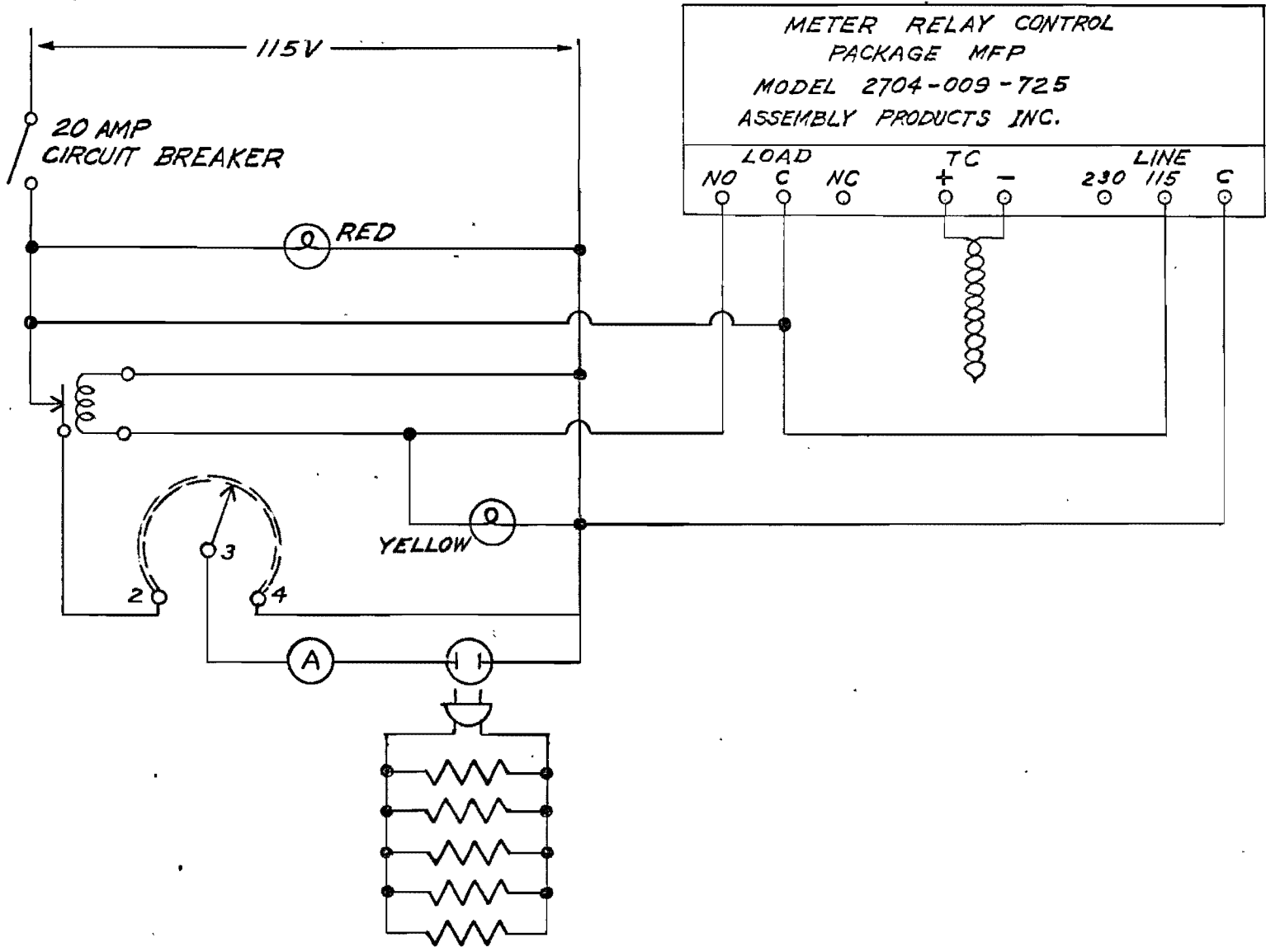
**RETORT PLUG PULLER**

LOCATION ANALYTICAL LAB.  
 DRAWING NO. **RE 21**



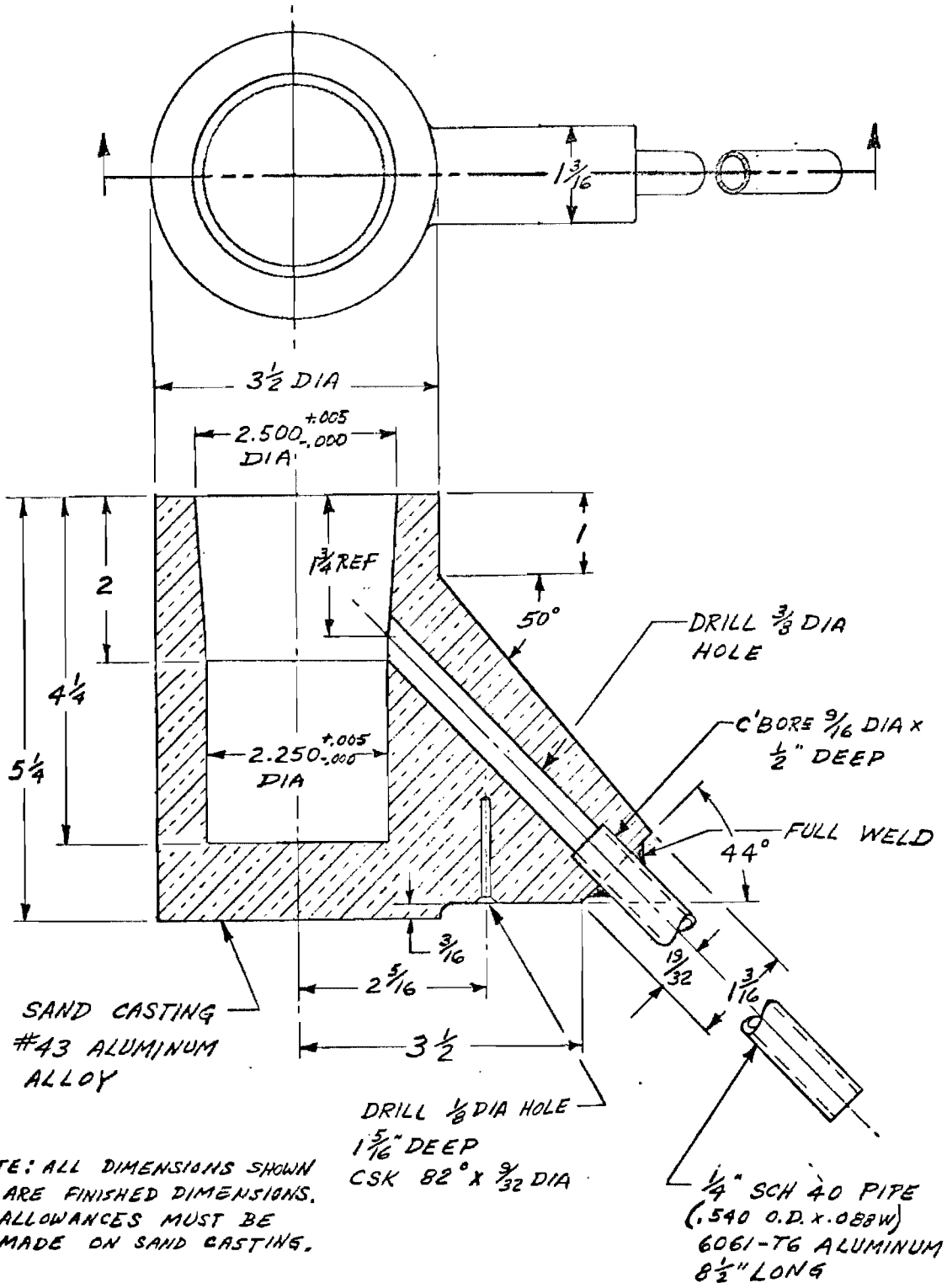
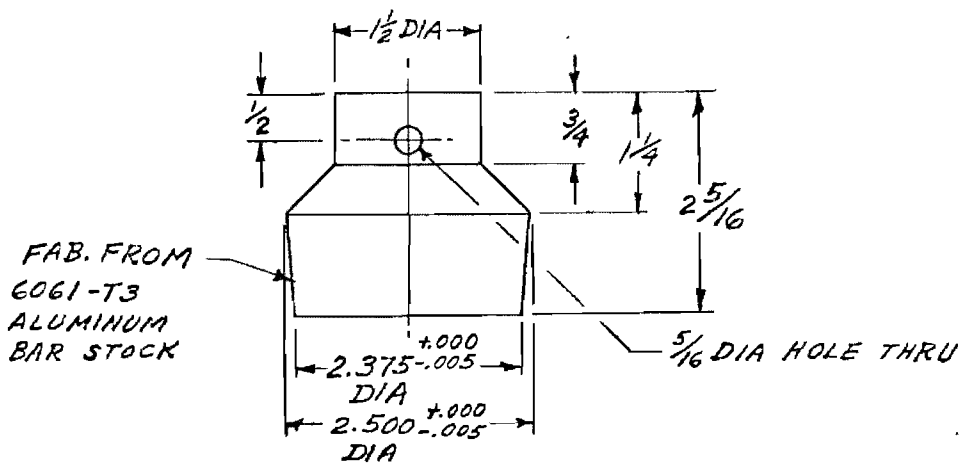


ASSEMBLY OF FISCHER ASSAY APPARATUS  
 (SIDE VIEW)  
 Figure 1.



NO.	DATE	PRINT ISSUED TO	ANVIL POINTS OIL SHALE RESEARCH CENTER RIFLE, COLO.				SCALE NONE	FISCHER RETORT HEATING CIRCUIT	LOCATION ANALYTICAL LAB.	DRAWING NO. <b>RE 22</b>
			PROJECT MANAGER-SOCONY MOBIL OIL CO., INC.				DRAWN BY <i>J. HAMILTON</i>			
			JOB NO.	CHARGE			STARTED 6-4-65			
			APPROVED	PROCESS	DESIGN	SAFETY	COMPLETED 6-4-65			
							DIMENS. CHECK			

AP-S-3



NOTE: ALL DIMENSIONS SHOWN ARE FINISHED DIMENSIONS. ALLOWANCES MUST BE MADE ON SAND CASTING.

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**ANVIL POINTS**  
**OIL SHALE RESEARCH CENTER**  
 RIFLE, COLO.  
 PROJECT MANAGER-SOCOMY MOBIL OIL CO., INC.  
 CHARGE

APPROVED \_\_\_\_\_  
 PROCESS \_\_\_\_\_  
 DESIGN \_\_\_\_\_  
 SAFETY \_\_\_\_\_

SCALE 1/2" = 1"

DRAWN BY J. H. HARRIS JR.

STARTED 2-10-66

COMPLETED 2-10-66

DIMENS. CHECK

LABORATORY RETORT

LOCATION

DRAWING NO. RE SK 73

Anvil Points Oil Shale Research Center

Sample No. XX - XXXXX Date 5/20/65  
 Retort No. 1 Receiver No. C Adapter No. 6

Retort + Sample	<u>2550.8</u>	gm	Retort + Sp. Shale	<u>2536.5</u>	gm
Retort	(-) <u>2449.5</u>		Retort	(-) <u>2449.5</u>	
Sample Weight	<u>101.3</u>	gm	Spent Shale	<u>87.0</u>	gm
Dist. + Sp. Shale	(-) <u>99.2</u>		Dist. Weight	(+) <u>12.2</u>	
Gas + Loss	<u>2.1</u>	gm	Dist. + Sp. Shale	<u>99.2</u>	gm
Rec. + Adp. + Dist.				<u>119.78</u>	gm
Rec. + Adp.	(-) <u>107.57</u>				
Distillate Weight				<u>12.21</u>	gm
Water Vol. (wt.)	(-) <u>1.45</u>				
Oil Weight				<u>10.76</u>	gm

OIL	<u>10.76</u>	gm	<u>10.6</u>	wt. % OIL
WATER	<u>1.45</u>	gm	<u>1.4</u>	wt. % WATER
SPENT SHALE	<u>87.6</u>	gm	<u>85.9</u>	wt. % SPENT SHALE
GAS + LOSS	<u>2.1</u>	gm	<u>2.1</u>	wt. % GAS + LOSS
SAMPLE WEIGHT	<u>101.31</u>		<u>100.0%</u>	

SPECIFIC GRAVITY OF OIL

Pipet No. N  
 Weight (Pipet + Oil) 10.986 gm  
 S. G. 60°/60°F 0.911

(Oil Weight) (239.6)  
 (S.G. 60°/60°) (Sample Weight)  
( 10.76 ) (239.6)  
( 0.911 ) ( 101.3 )  
27.9 GALLONS/TON

COOKING TENDENCY SLIGHT

COMMENTS NONE

Analyst ABC

Checked By XYZ

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

Scope

This method is used to determine from 0 to 20 percent mineral CO<sub>2</sub> in raw and spent shale.

Outline of Method

The ground sample is treated with hydrochloric acid which decomposes mineral carbonates. The carbon dioxide released (mineral CO<sub>2</sub>) is absorbed by Ascarite and weighed. The percent mineral CO<sub>2</sub> is calculated from this weight.

Apparatus

The apparatus is shown in Figure 1, and is made up of the following components connected with rubber tubing:

- a. Knorr Alkalimeter - Pyrex.
- b. Absorption Bulb - Nesbitt (2 needed).
- c. Drying Tube - 200 mm.
- d. Rotameter - Brooks Instrument Company, Inc., Hatfield, Pennsylvania. Tube Size 1-15-6, Glass Ball.

Reagents and Materials

- a. Carbon dioxide absorbent - Ascarite, 8-20 mesh
- b. Magnesium Perchlorate - anhydrous.
- c. Indicating Drierite - 8-mesh.
- d. Hydrochloric Acid - Reagent-grade, conc., sp gr 1.19.
- e. Aerosol(R) OT Solution - 10%, available from Fisher Scientific Co. (So-A-292).

### Preparation of Apparatus

a. Packing the Nesbitt CO<sub>2</sub> Absorber

Pack the absorber as follows: Place a 1/2-inch thick pad of moderately-packed glass wool at the bottom. Follow this with a 2 1/2-inch layer of loosely-packed Ascarite, 1/4-inch of glass wool, 1/2-inch of magnesium perchlorate, and finally 1/2-inch of glass wool. This absorber should be replaced when it is 1/2 exhausted as indicated by the Ascarite changing from brown to white. Discard the white spent Ascarite; retain the good Ascarite.

b. Packing the Nesbitt H<sub>2</sub>O Absorber

Pack the absorber as follows: Place a 1/2-inch thick layer of moderately-packed glass wool on the bottom. On top of this, add a 2 1/2-inch layer of magnesium perchlorate and a 1/2-inch layer of glass wool.

c. Filling the Guard Tubes

Fill these by putting a layer of glass wool into the vessels and then filling 1/2 the tube with Ascarite and 1/2 with indicating Drierite. The Drierite, which turns pink when exhausted, can be regenerated to its blue form by heating at 120 C in an oven.

### Procedure

With the whole system connected as shown in Figure 1, apply vacuum to the exit tube, and purge by drawing air through the apparatus at  $100 \pm 10$  ml per minute for 15 minutes (the rate is adjusted with the needle valve). At the end of this time, shut off the flow at the vacuum end, then close the ports of the CO<sub>2</sub> absorber. Remove it and weigh it to the nearest 0.0001 g. (Just before weighing, open the Nesbitt absorber ports momentarily to equalize its pressure to atmospheric.) Replace the absorber. Remove the Erlenmeyer sample flask and weigh (to the nearest 0.0001 g) into it  $2.0 \pm 0.2$  g of sample ground to -48 mesh. Add 4 - 5 drops of Aerosol OT Solution and  $50 \pm 5$  ml of deionized water. Close the stopcock on the separatory funnel and add 25 ml of concentrated hydrochloric acid to it. Reassemble the apparatus, turn on the vacuum and the water to the condenser. Immediately allow the acid to flow into the flask at a rate that keeps the bubbling in the Bubble Tube approximately the same as during the purge step. Heat the contents of the flask to boiling (If the contents of the flask begin to back up into the separatory funnel, reduce the heating rate momentarily.) Remove the heat and allow the system to purge for 60 minutes,

then turn off the vacuum. Close the Nesbitt absorber, allow it to equilibrate near the balance for about 15 minutes, then vent it and reweigh it to the nearest 0.0001 g.

Determine a blank by the same procedure used for a sample, except omit the sample.

Calculation and Report

$$\% \text{ Mineral CO}_2 = \frac{(W-B)(100)}{S}$$

Where,

W = the increase in weight of the Nesbitt absorber for the sample, in grams.

B = the increase in weight of the Nesbitt absorber for the blank, in grams.

S = the weight of the sample, in grams.

April 28, 1965

Precautions to Observe on Mineral CO<sub>2</sub> Method

1. Be sure to vent the absorbers after a 15-minute equilibration time at the balance.
2. Purge the apparatus for at least 15 minutes when first using the apparatus.
3. Add the acid slowly so that no CO<sub>2</sub> is forced back up the funnel.
4. Heat the acid at a moderate rate so that no gas or liquid is forced back up the funnel.
5. Be certain that all absorbers are properly filled, that is, with absorbents in good condition and filled to the proper levels.

This is a very important test since it is used in the carbon balance. It requires skill and care in order to obtain accurate results.

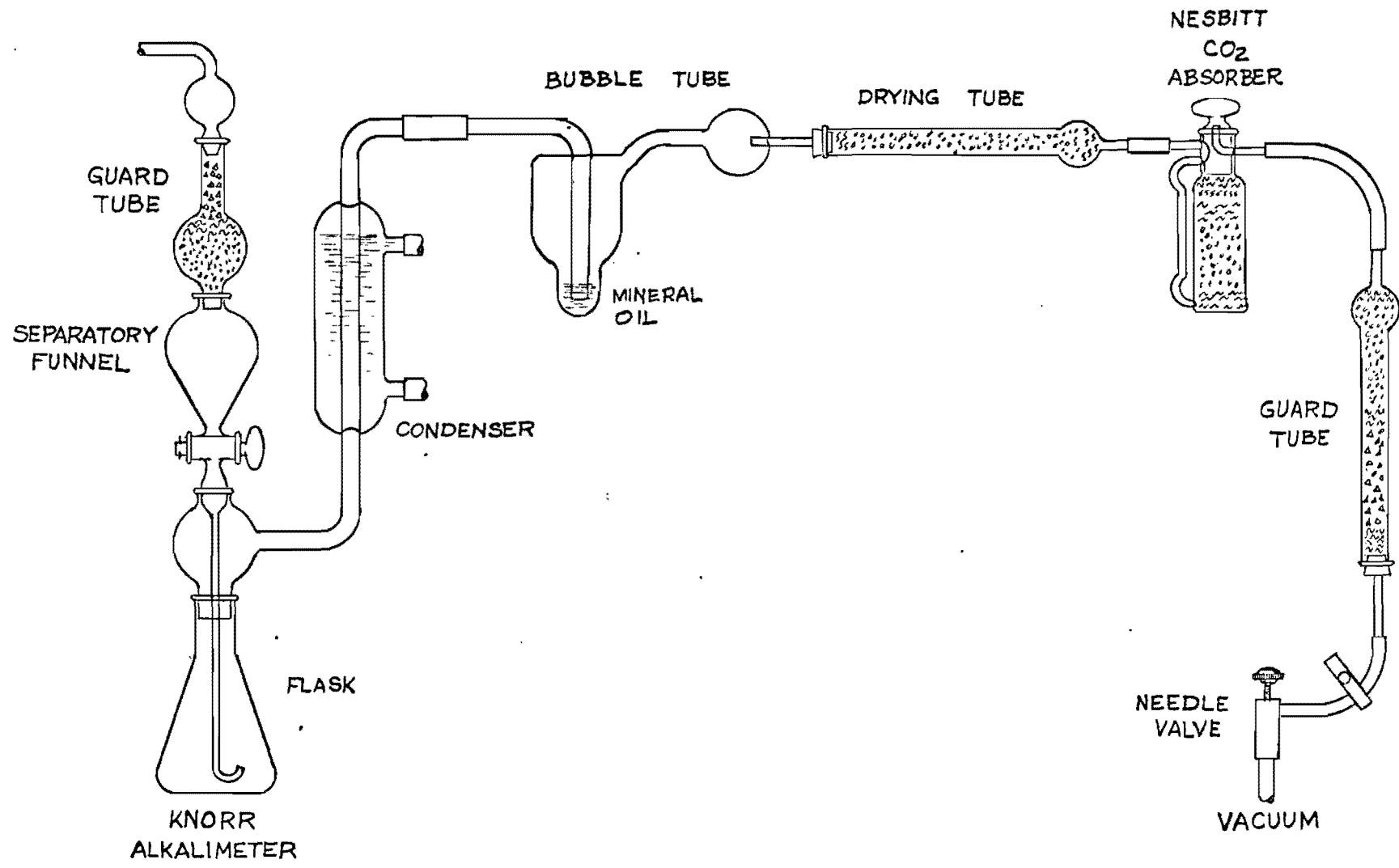


FIGURE 1

APPARATUS FOR THE DETERMINATION OF MINERAL CO<sub>2</sub>

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

Scope

This method is used to determine the ash content of raw and spent shale. The ash content is usually in the 65 to 90% range; however, the method is applicable to any ash level of oil shale.

Outline of Method

The ground sample is ignited in a muffle furnace 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.

Apparatus

- a. Muffle Furnace - Hevi-Duty, 230 volts, safe working temperature - 1750 F, maximum temperature 1850 F, with chromel-alumel thermocouple and Wheelco 0-2000 F controller.
- b. Compressed air line with needle valve leading into the rear of the furnace chamber.
- c. Crucible - Wide Form, Coors Porcelain, Size No. 1.

Procedure

Use the portion of the shale sample ground to -48 mesh. Weigh about 2 grams (to the nearest 0.0001 g) of the sample into a weighed, ignited crucible. Carefully heat the crucible and the sample on the front part of the open muffle furnace until most of the organic matter is burned off. Then place the crucible inside the furnace and ignite at  $950 \pm 25$  C ( $1750 \pm 45$  F) for two hours. Adjust the needle valve on the air line so that about 500 ml per minute of air enters the furnace. (This will ensure sufficient oxygen for burning during the two hour period.)

Remove the crucible from the furnace, allow to cool on the hard asbestos surface by the furnace for a minute, and then in the desiccator for at least one hour. Weigh the crucible and ignited sample to the nearest 0.0001 g. (Be sure no particulate matter is adhering to the outside of the crucible.)

Calculation and Report

$$\text{Wt \% Ash} = \frac{R}{S} \times 100$$

Where

R = the weight of the residue, in grams  
S = the weight of the sample, in grams

Report results to the nearest 0.1% Ash.

Discussion

This procedure is used for normal shale samples with negligible moisture. The moisture content of typical raw and spent shales is about 0.3% and 0.05% respectively. Moist shales are first dried at 105 C (221 F) before ignition.

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

Scope

This method is used to determine moisture content of raw and spent shale.

Outline of Method

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

Apparatus

- a. Oven - 230 v., maximum temperature 140 C, with thermometer and regulator.
- b. Evaporating dish - Pyrex, size E

Procedure

Use the portion of the shale sample ground to -48 mesh. Weigh about 10 grams (to the nearest 0.0001 g) of the sample into a weighed, dry, evaporating dish. Heat the sample in the oven at 105 C (221 F) for two hours. Transfer the sample to the desiccator and allow it to cool for at least one hour. Weigh the dish and dried sample to the nearest 0.0001 g.

Calculation and Report

$$\text{Wt \% Moisture} = \frac{L}{S} \times 100$$

Where,

L = the loss in weight of the sample, in grams

S = the weight of the sample in grams

Report results to the nearest 0.01% Moisture

Discussion

The two-hour drying time in the oven has been found adequate for normal shale samples whose moisture content is less than 0.50%. Where shale samples, whose moisture content is significantly above this level, are encountered, an additional one hour heating period should be used as a check on complete moisture removal.

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

Scope

This method is used to determine the total carbon and hydrogen contents of oil shale, shale oil, and recycle gas. The concentrations usually determined are from 5 to 20 percent in shales and 80 to 85 percent in shale oils. Recycle gas contains approximately 12 pounds of carbon and 1 pound of hydrogen per thousand standard cubic feet.

Outline of Method

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 Ascarite 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.

Apparatus

The apparatus (shown in Figures 1 and 2) consists of the following:

- a. Organic Combustion Furnace - Multiple Unit, Type 123-T, manufactured by Hevi-Duty Heating Equipment Company, Watertown, Wisconsin. For automatic operation, the furnace is modified as shown in Drawing RB 265 (not attached).
- b. Oxygen - USP, cylinder, with 2-stage regulator, valves, and flowmeter (approximately 35 ml. of air per minute maximum rate).
- c. Nesbitt Absorbers - (2 needed).
- d. Combustion Tube - Vycor, 19 mm OD, 3 feet long.
- e. Combustion Boat - Porcelain, Size 6.
- f. Stoppers - Silicone Rubber, Amber, Size No. 1 (2 needed).

- g. Chromel-Alumel Thermocouples - No. 14 B & S Gauge, placed in the center of each furnace section.
- h. Pyrometer - West Instrument Corporation, Model I, 0-1,000 C. with a 6-position switch.
- i. Gas Adapter - Pyrex, Custom-made, illustrated in Figure 2.
- j. Bottle - Aspirator, Tubing Outlet, Polyethylene, 2-gallon.
- k. Rubber Tubing - Amber Latex, 5/32" O.D., 1/32" wall.
- l. Gas Sample Tube - Cylindrical, with straight stop-cocks on both ends, 1,000 ml.
- m. Rotameter - Brooks Instrument Company, Inc., Hatfield, Pennsylvania. Tube Size 1-15-6, Glass Ball.
- n. Timer - Gra Lab Universal, Model No. 171, 125 V, 0-1 hr. Dimco-Gray Company, Dayton, Ohio.

Reagents and Materials

- a. Asbestos Fiber - Acid-washed and ignited.
- b. Asbestos - Platinized, 5%.
- c. Ascarite - 8 to 20 mesh.
- d. Magnesium Perchlorate - Anhydrous.
- e. Silver Wool - For micro analysis.
- f. Silver Wire - 34 B & S Gauge, pure grade.
- g. Copper Gauze - 20 mesh.
- h. Lead Dioxide-Asbestos Mixture - Prepare by thoroughly mixing four parts-by-weight of lead dioxide (brown powder, ACS grade, suitable for micro-analysis) with 1 part-by-weight of asbestos fiber.
- i. Lead Chromate-Copper Oxide Mixture - Prepare by thoroughly mixing one part-by-weight of lead chromate (Special Micro 12 to 20 mesh) with 2 parts-by-weight of copper oxide (black wire, ACS grade, suitable for micro analysis).
- j. Brine, 25% - Prepare by using 2.5 pounds of rock salt for each gallon of solution.

General Instructions

Set the furnace controls to maintain the following temperatures:

1. Sample Furnace (4-inch)
  - a. Shale Oil and Organic Standards . 700± 10 C.
  - b. Raw and Spent Shale, and Inorganic Standards . . . . . 950± 10 C.
2. Middle Furnace (12-inch) . . . . . 680± 10 C.
3. End Furnace (8-inch) . . . . . 190± 10 C.

Adjust and maintain the flow of oxygen through the combustion tube at 20 to 25 ml. per minute.

Keep the middle and end furnaces, and the oxygen flow, on continuously.

Packing the Combustion Tube

Start packing the combustion tube at the outlet end. First insert a No. 1 Silicone rubber stopper containing a 50-mm length of 8-mm O.D., 1-mm I.D. capillary tubing. Thread about 10 strands of the silver wire, 60-mm long, through the capillary (This serves to conduct heat along the capillary so that no moisture will remain in it.) Pack the rest of the combustion tube loosely with the following, in the order given:

1. 10 mm of silver wool
2. 5 to 7 mm of asbestos
3. 200 mm of 4:1 PbO<sub>2</sub>-asbestos mixture
4. 5 to 7 mm of asbestos
5. 35 mm of crumpled silver wire
6. 5 to 7 mm of asbestos
7. 250 mm of 1:2 PbCrO<sub>4</sub>-CuO mixture
8. 5 to 7 mm of asbestos
9. 20 mm of platinized asbestos
10. 20 mm of crumpled silver wire
11. 30 mm roll of copper gauze

Care should be taken to pack the materials loosely, but to avoid leaving spaces that would allow channeling of the gases.

### Packing Absorbers

a. Nesbitt CO<sub>2</sub> Absorber

Pack the absorber as follows: Place a 1/2-inch thick pad of moderately packed glass wool at the bottom. Follow this with a 2 1/2-inch layer of loosely-packed Ascarite, 1/4-inch of glass wool, 1/2-inch of magnesium perchlorate, and finally 1/2-inch of glass wool. This absorber should be replaced when it is 1/2 exhausted as indicated by the Ascarite changing from brown to white. Discard the white spent Ascarite; retain the brown.

b. Nesbitt H<sub>2</sub>O Absorber

Pack the absorber as follows: Place a 1/2-inch thick layer of moderately-packed glass wool on the bottom. On top of this, add a 3/4-inch layer of magnesium perchlorate, a 1/4-inch of glass wool, 1 1/2-inches of magnesium perchlorate, and 1/2-inch of glass wool. Replace the packing (retaining the dry magnesium perchlorate) when the 3/4-inch layer of magnesium perchlorate appears wet.

### Procedure for Raw and Spent Shale

Use the portion of the shale sample ground to minus 48-mesh. Weigh 0.9± 0.1 g. of shale (to the nearest 0.001 g.) into an ignited combustion boat. (Put as much of the shale as possible into the center of the boat.) Have the sample furnace heated to 950± 10 C and in the pulled-back position.

Place the two absorbers (which have been purged with oxygen and weighed to the nearest 0.0001 g.) in position with their ports open. Attach the magnesium perchlorate H<sub>2</sub>O absorber next to the combustion tube, and connect the Ascarite CO<sub>2</sub> absorber to the water absorber with a short length of latex tubing.

Remove the inlet stopper from the combustion tube and carefully, but rapidly, insert the sample boat into the tube, past the sample furnace, and up to within one inch of the middle furnace. Replace the stopper and bring the sample furnace just up to the sample boat. Set the timer to 45 minutes, with the "Alarm" switch on. Turn the motor traverse switch on. The sample furnace traverses three inches in about one hour, at which time it should be close up to the middle furnace. At that time, it activates the timer which sounds an alarm at the end of a

45-minute "soak" time. Remove and close the absorbers, turn off the motor traverse switch, and move the sample furnace back to its start position.

Cool the absorbers near the balance for 45 minutes, vent them momentarily, and reweigh them to the nearest 0.0001 g.

Note: Take extra care to keep the absorbers clean and dry at all times. Do not wipe them before weighing because static charges on the glass will cause errors.

### Procedure for Shale Oil

Use the water-and-sediment-free liquid product (crude shale oil) as obtained by the procedure, "Treatment of Liquid Product Samples". Weigh 0.15± 0.01 g. of sample (to the nearest 0.0001 g.) into an ignited combustion boat. Have the sample furnace heated to 700± 10 C and in the pulled-back position. Continue as in "Procedure for Raw and Spent Shale" above, starting with "Place the two absorbers...".

### Procedure for Recycle Gas

#### a. Calibration of Gas Sample Tube

Clean and dry the gas sample tube and weigh it to the nearest 0.1 g. Fill it, including the stopcock bores, but not the tubules, with distilled water. Reweigh to the nearest 0.1 g. Record the water temperature.

Calculate the volume as follows:

$$V = \frac{W}{D}$$

where,

V = the volume of the tube, in milliliters

W = the difference in weight between the empty and full sample tube, in grams

D = the density of distilled water at the recorded water temperature, in grams per milliliter

#### b. Collecting a Sample

Fill a calibrated 1-liter gas sample tube with a 25% brine solution. With the sample gas, purge a short length of hose attached to the gas sample holder, then while still purging, attach the sample

tube. With the hose at the top, open the top stopcock, and then the bottom; allow the brine to flow into a container. When the sample tube is full of gas, close the bottom stopcock, and then the top one.

c. Procedure

Attach the sample tube to the apparatus as shown in Figure 2, and allow it to equilibrate for at least 15 minutes. Then dip the bottom tubule about 1/8-inch below the surface of water held in a small beaker. Open the bottom stopcock and allow excess gas to escape, then close the stopcock. Record the temperature (T) at the sample tube and the barometric pressure (b).

The middle and end combustion furnaces should be maintained at the temperatures mentioned previously. The sample furnace should be kept at 950 C and close to the middle furnace. A closely wrapped roll of copper gauze, three inches long should be inserted in the combustion tube under the sample furnace.

Position the T-stopcock so that both the oxygen supply and the sample tube will be connected to the furnace. Connect the absorbers which have been purged with oxygen, and weighed to the nearest 0.0001 g. Open both stopcocks on the sample tube, then release the pinch clamp on the tube leading from the 25-percent brine reservoir. Adjust the brine rate so that the sample tube will be full of brine in about 40 minutes. When the brine reaches the top of the upper tubule, close both stopcocks (top one first) and tighten the pinch clamp.

Continue purging with oxygen for an additional 20 minutes. Disconnect and seal the absorbers, and let them equilibrate near the balance for at least 45 minutes. Momentarily vent the absorbers, then weigh them to the nearest 0.0001 g.

Calculations

a. Raw and Spent Shale, and Shale Oil

$$\text{Wt \% Carbon} = \frac{(27.29) (\text{CO}_2)}{S}$$

$$\text{Wt \% Hydrogen} = \frac{(11.19) (\text{H}_2\text{O})}{S}$$

where,

CO<sub>2</sub> = the increase in weight of the CO<sub>2</sub> absorber, in grams.

H<sub>2</sub>O = the increase in weight of the H<sub>2</sub>O absorber, in grams.

S = the weight of the sample, in grams.

Report results to the nearest 0.1%.

b. Recycle Gas

$$\text{lbs. Carbon/MSCF}_{\text{DG}} = \frac{(44.88) (\text{CO}_2) (273 + T)}{(b-a) (V)}$$

$$\text{lbs. Hydrogen/MSCF}_{\text{DG}} = \frac{(18.40) (\text{H}_2\text{O}) (273 + T)}{(b-a) (V)}$$

where,

CO<sub>2</sub> = the increase in weight of the CO<sub>2</sub> absorber, in grams.

H<sub>2</sub>O = the increase in weight of the H<sub>2</sub>O absorber, in grams.

b = barometric pressure, in mm. Hg.

a = vapor pressure of 25% brine solution at the temperature near the sample tube (see attached Table I).

T = temperature near the sample tube, in °C.

V = volume of the sample tube, in liters.

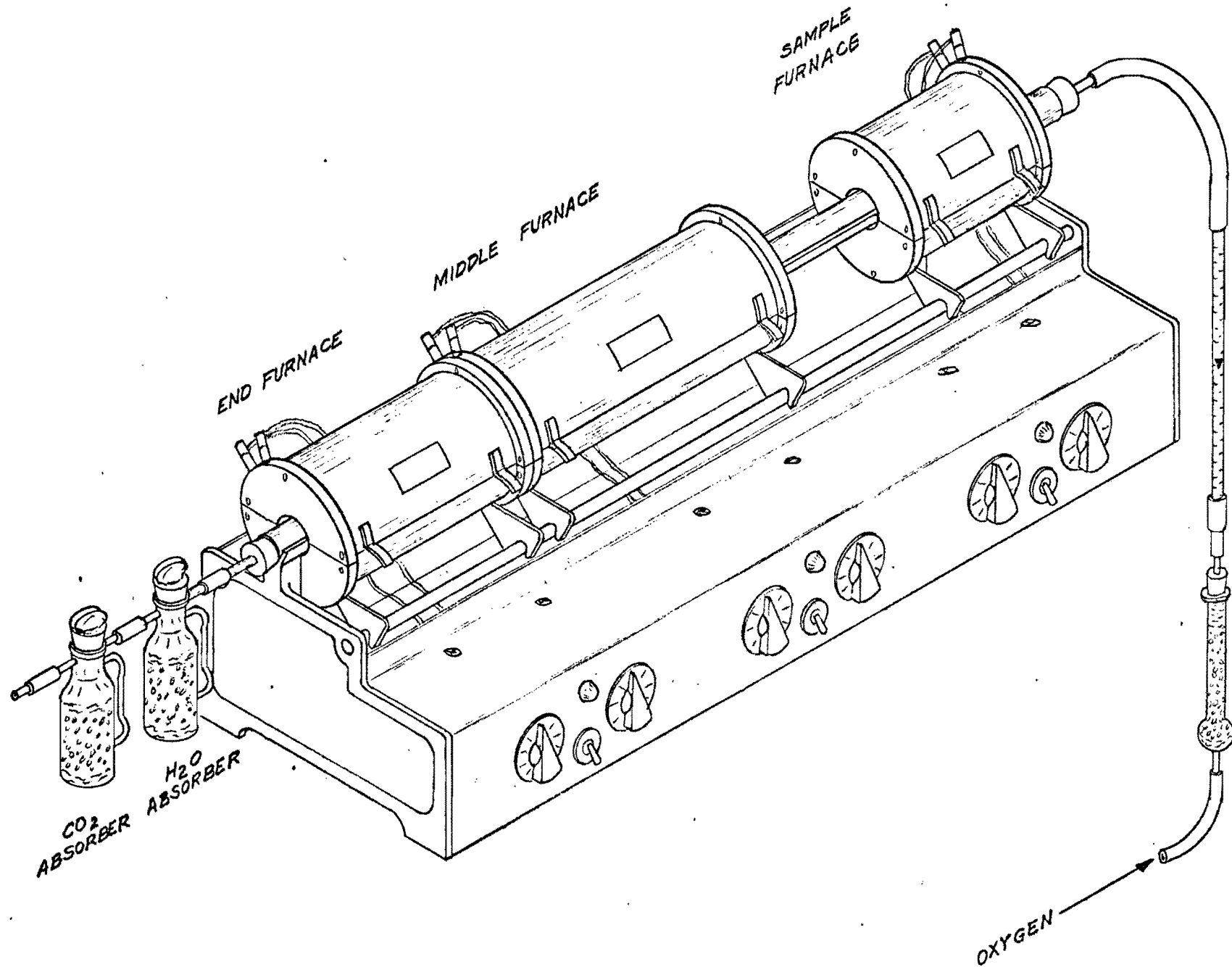
MSCF<sub>DG</sub> = thousand standard cubic feet of dry gas (1 atm. and 60 F)

Report results to the nearest 0.1 pound.

TABLE I

VAPOR PRESSURE OF 25% BRINE AT VARIOUS TEMPERATURES

<u>Temperature, C</u>	<u>Vapor Pressure, mm Hg</u>
20	14.2
21	15.1
22	16.1
23	17.1
24	18.1
25	19.2
26	20.4
27	21.7
28	23.0
28	24.3
30	25.8
31	26.2



TOTAL C-H IN SHALE, SHALE OIL, AND RECYCLE GAS  
FIG.1 CARBON-HYDROGEN APPARATUS

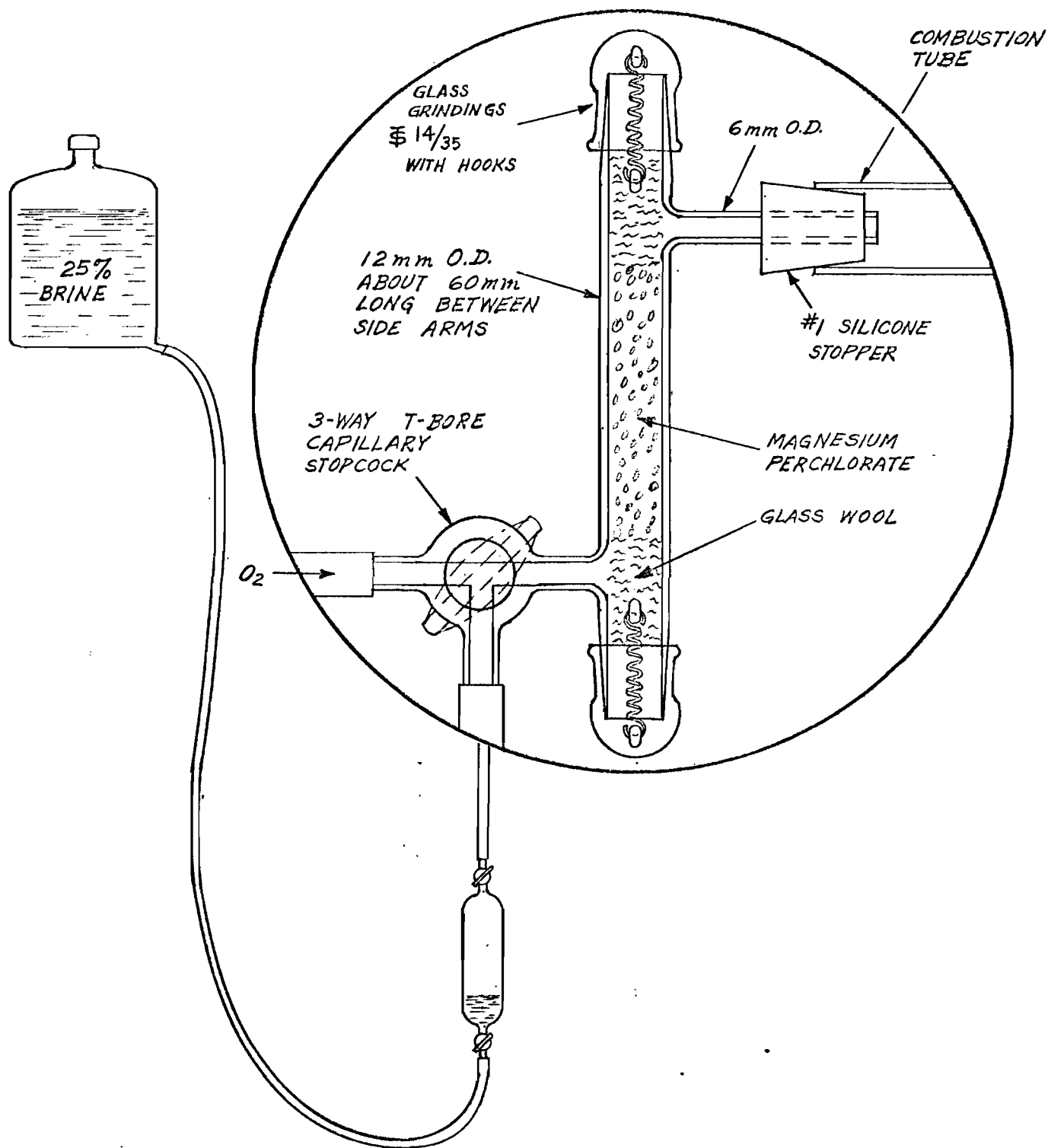


FIG. 2  
RECYCLE GAS ADAPTATION FOR C-H DETERMINATION

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

Scope

This method is used to determine the total nitrogen content of shale and shale oil. The range of concentrations is usually 0.1 to 3%; however, any concentrations between about 100 ppm and 50% can be determined. All types of compounds except those having a nitro or -N=N- group, or nitrogen in a ring, can be determined.

Outline of Method

The sample is decomposed by digestion with concentrated sulfuric acid and a catalyst; 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.

Apparatus and Materials

- a. Digestion and Distillation Apparatus, Kjeldahl - Precision Scientific Company, Cat No. 5482, 6-position.
- b. Flask, Kjeldahl - 800-ml, long neck, Pyrex, with Kool-Grip cork jacket.
- c. Connecting Bulb - Fisher Scientific Company, Cat. No. 13-188, fitted with a No. 7 rubber stopper.
- d. Flask - 500-ml Erlenmeyer, Pyrex.
- e. Hengar Grandules - plain (not selenized).
- f. Buret - 25-ml, graduated in 0.1 ml divisions.

Reagents

- a. Sulfuric Acid - Reagent-grade, conc., sp. gr. 1.84.
- b. Mercury Metal - Redistilled, N. F.
- c. Potassium Pyrosulfate - Fused powder, ACS grade.

- d. Zinc Metal - Dust, low nitrogen.
- e. Boric Acid-Methyl Purple Solution - Prepare by dissolving  $8 \pm 0.1$  g. of reagent-grade boric acid in distilled water, adding 4 ml of methyl purple indicator solution (available from Fisher Scientific Company, Cat. No. SO-I-9) and diluting to 1 liter.
- f. Standard Sulfamic Acid Solution, 0.1000 N - Prepare by weighing exactly 9.7100 g. of reagent grade sulfamic acid ( $\text{NH}_2\text{SO}_3\text{H}$ ) into a 1 liter volumetric flask. Dissolve the salt in distilled water and dilute to 1 liter.
- g. Sodium Hydroxide Solution - 50% W/W, for Kjeldahl Nitrogen Determination.

### Procedure

#### a. Digestion

Use the portion of shale sample ground to minus 48-mesh, or the water-and-sediment-free liquid product (crude shale oil) as obtained by the procedure, "Treatment of Liquid Product Samples".

Weigh  $2.5 \pm 0.2$  g. of shale or  $0.5 \pm 0.1$  g. of crude shale oil into an 800-ml Kjeldahl flask. (Weigh to the nearest 0.001 g.) Add  $30 \pm 1$  g. of potassium pyrosulfate,  $25 \pm 1$  ml of sulfuric acid,  $1.3 \pm 0.1$  g. of mercury, and 2 Hengar granules. Heat, gently at first, then more strongly until the mixture boils. If frothing occurs, reduce the heat until the frothing stops. Swirl the contents periodically. As digestion progresses, the dark charred material will gradually lighten to a transparent straw-colored liquid. In the process, some acid will usually be consumed. Add acid in 1 to 3-ml increments to keep the volume at about  $25 \pm 1$  ml. After the solution has become straw-colored, boil it gently for one hour, then cool to room temperature. Add 250 ml of distilled water slowly, with swirling, to dissolve precipitated salts. Cool the solution to ice temperature.

#### b. Distillation

Rinse the connecting tube and trap with distilled water and turn on the condenser cooling water. To a 500-ml Erlenmeyer flask, add 50 ml of the boric acid-methyl purple solution. Place the receiving flask under the delivery tube so that the end of the tube is about 1/16-inch from the bottom of the flask.

Add 6.0 ± 0.1 g. of powdered zinc to the ice-cold solution in the Kjeldahl digestion flask. Incline the flask and slowly add, down the side, 85 ml of 50% sodium hydroxide solution to form two layers. Do not mix the solutions at this time, since this will cause a loss of ammonia. Quickly connect the digestion flask to the connecting bulb and distillation apparatus. Turn on the heat and immediately mix the contents of the flask by swirling. Distill until the receiving flask contains about 200 ml. Disconnect the receiving tube; remove it and the flask together. Rinse the liquid clinging to the tube into the flask.

c. Titration

Fill a clean 25-ml buret with 0.1000 N sulfamic acid solution. Titrate the distillate to the first permanent gray end point. Record the volume of the sulfamic acid solution used.

Whenever new reagents are used, make a blank determination, in duplicate, exactly as in the above procedure but omitting the sample.

Calculation and Report

$$\text{Wt \% Nitrogen} = \frac{N(V_A - V_B)(14.01)(100)}{(S)(1000)} = \frac{(0.1401)(V_A - V_B)}{(S)}$$

Where:

N = the normality of the sulfamic acid solution (0.1000 N).

V<sub>A</sub> = the volume of 0.1000 N sulfamic acid solution used for the sample titration, in milliliters.

V<sub>B</sub> = the volume of 0.1000 N sulfamic acid solution used for the reagent blank, in milliliters.

S = the weight of the sample, in grams.

Report the nitrogen content as follows:

Less than 0.1%, to the nearest 0.001%

0.1 to 5.0%, to the nearest 0.01%

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

ANALYTICAL LABORATORY

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

Scope

This method is used to determine the API gravity of crude shale oil. The range is normally from 17° to 26° API.

Outline of Method

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

Apparatus

- a. Viscosimeter Bath - Kinematic, High Precision, 0.02 F Termonitor Controlled, Sargent, is suitable. (Fill with mineral oil.)
- b. Test Tubes - Pyrex, 150 mm x 18 mm
- c. Pipets - see attached Drawing No. RE SK 18; available from Scientific Glassblowing Co., Houston, Texas
- d. Horizontal Pipet Support - 5 1/2 inch x 6 1/2 inch; 6 pipet capacity.

Procedure

Use the water-and-sediment-free liquid product (crude shale oil) as obtained by the procedure, "Treatment of Liquid Product Samples".

Pour about 10 ml of the oil sample into a test tube and heat it in the 100 F constant temperature water bath. Insert a standardized pipet into the test tube with the oil. Leave the cover off the bath. Allow the oil, test tube, and pipet to equilibrate for 15 minutes.

With the test tube still in the water bath, apply suction to withdraw a pipetful of oil. The oil should not rise more than 1/8 inch above the calibration mark. Adjust to the mark. Wipe the outside of the pipet dry and lay it on the pipet support next to the balance. After a 10 minute equilibration period, weigh it to the nearest 0.001 gram.

Calculation and Report

Refer to the prepared table to read the API gravity at 60 F for the observed weight of pipet + oil, for the pipet used (note the letter marked on the bulb).

Report results to the nearest 0.1° API.

Discussion

For each pipet, a computer table has been furnished listing weight of pipet + oil, specific gravity at 60 F, and API gravity at 60 F. These tables have been prepared from the weight of the empty pipet, the calibrated volume of the pipet at 60 F, correction factors for temperature, and the relationship between API gravity and specific gravity. The equations used in the computer are the following:

$$T = (0.9990 S - 0.01398) (V) + P$$
$$G = 141.5/S - 131.5$$

Where,

- T = the weight of pipet + oil, in grams (at 100 F)
- S = specific gravity at 60/60 F
- V = the volume of the pipet, in milliliters
- P = the weight of the empty pipet, in grams
- G = API gravity at 60 F

If a computer table is not available, the calculation is made as follows:

$$D = \frac{T - P}{V}$$

$$S = D + C$$

Where,

- D = specific gravity (density) at 100 F
- C = correction found using table below:

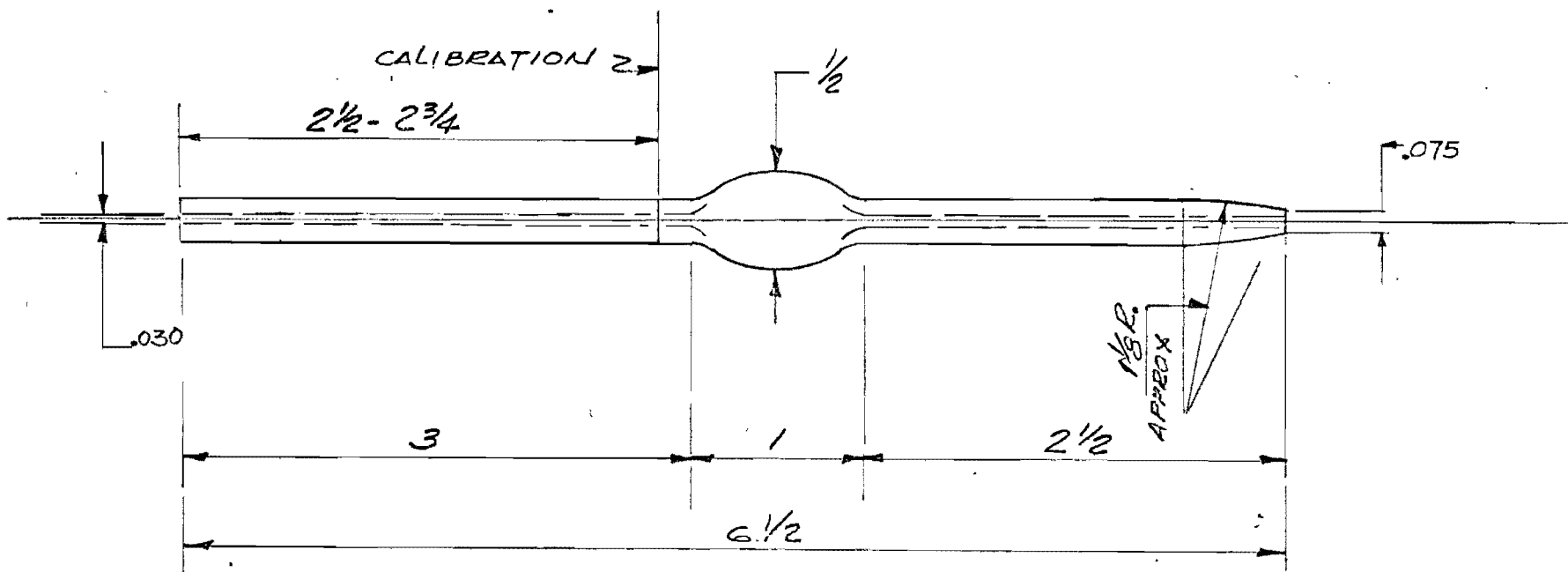
D	C
0.800 - 0.843	0.010
0.844 - 0.916	0.009
0.917 - 1.000	0.008

Note: These corrections were obtained by converting the specific gravities determined at 37.8/37.8 C to 37.8/15.6 C by multiplying by the factor 0.995, (density of water

at 37.8/density of water at 15.6 C) then converting these values to specific gravities at 15.6/15.6 C by the use of standard conversion tables.\*

Use the S.G. at 60 F - API Gravity at 60 F tables to convert S to G.

\*"Analytical Methods for Use on Oil Shale and Shale Oil"  
A-1-15, Intra-Bureau Report, OSD 32, Petroleum & Oil-  
Shale Experiment Station, Bureau of Mines, Laramie,  
Wyoming, August 1949.



PYREX GLASS  
ALL DIMENSIONS IN INCHES

NOTE: VOLUME - 1.5 to 2.0 ml.

NO.	DATE	PRINT ISSUED TO	ANVIL POINTS OIL SHALE RESEARCH CENTER RIFLE, COLO.				SCALE FULL SIZE	GRAVITY PIPET
			PROJECT MANAGER-SOCONY MOBIL OIL CO., INC.				DRAWN BY S. J. JONES	
			JOB NO.	CHARGE			STARTED 3-12-65	
			APPROVED	PROCESS	DESIGN S. J. JONES	SAFETY	COMPLETED 3-12-65	
							DIMENS. CHECK	
							LOCATION	
							DRAWING NO. RE SK 18	

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

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Scope

This method is used to determine the amounts of water and sediment in liquid product samples. Liquid product consists of crude shale oil, water, and sediment. The method is most accurate when the total water and sediment content of the sample is less than about 3 weight percent. A more accurate (and the recommended) method for water only, is AP-O-21, Water in Liquid Product by Distillation.

Outline of Method

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 Wt % water and Vol/Wt % sediment calculated.

Apparatus

- a. Centrifuge - International Size 2, Model EXD with 8-place head, aluminum cups, and neoprene cushions.
- b. Centrifuge tubes - 100-ml, oil, pear shape, Kimax; stem graduated up, from 0 to 3 ml by 0.1 ml; body graduated from 3 to 10 ml by 0.5 ml; from 10 to 25 ml by 5 ml; and at 50 and 100 ml.
- c. Water bath - 80 C, with holder for six centrifuge tubes.
- d. Corks - Size 4.
- e. Weighing sling.
- f. Malt Mixer - such as the Hamilton Beach No. 18.

Procedure

The liquid product sample is submitted in a one pint wide-mouthed jar.

The liquid product sample is well mixed on the malt mixer, and about 50 g is immediately transferred to a preweighed centrifuge tube. The sample and tube are weighed to the nearest 0.01 g and then transferred to the water bath.

After 10 minutes, the tube is wiped and placed in the centrifuge. After 10 minutes at 2000 RPM, the tube is removed. If the interface is not sharp, it may be necessary to reheat the oil and centrifuge a second time. The interface may also be sharpened by use of a small diameter wire, or by drawing off some of the supernatant oil and diluting the remainder with an organic water-immiscible solvent such as toluene or xylene.

Read the volume of sediment and of water to the nearest 0.05 ml (or as close as practical).

#### Calculation and Report

The density of the water is assumed to be 1.00 gm/ml

$$\text{Wt \% Water} = \frac{W}{S} \times 100$$

$$\text{Vol/Wt \% Sediment} = \frac{T}{S} \times 100$$

Where,

W = the volume of the water, in milliliters

T = the volume of the sediment, in milliliters

S = the weight of the liquid product sample, in grams

Report results to the nearest 0.05%.

#### Discussion

If there is little or no water present, the amount of sediment may be difficult to read. In this case, record the volume of the water, then add about 1 ml of distilled water to the sample. shake well, warm if necessary, and centrifuge for 10 minutes. Read the volume of the sediment.

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

The method used is "Ramsbottom Carbon Residue of Petroleum Products", ASTM D 524-62. Below is a condensed version of the "Procedure" and "Calculation and Report" sections of this method as used in this laboratory.

Outline of Method

Clean crude shale oil is charged to a preweighed 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.

Procedure

Use the water-and-sediment-free liquid product (crude shale oil) as obtained by the procedure, "Treatment of Liquid Samples." If necessary, warm the oil slightly to reduce its viscosity. Strain the sample through a 100-mesh wire strainer.

Weigh a new glass coking bulb, that is clean and dry, to the nearest 0.0001 gram. By means of the hypodermic syringe, introduce approximately 1.5 grams of sample into the weighed bulb, and reweigh to 0.0001 gram. Make sure that no oil remains on the exterior surface or on the inside of the neck of the bulb.

Place the bulb in the selected well in the furnace, and allow it to remain for 20 ± 2 minutes. (Be sure the furnace is at the correct temperature.) Remove the bulb with metal tongs, the tips of which have just been heated. Allow the bulb to cool on the rack for a few minutes and then in the desiccator for one hour. Brush any particles off the bulb, and weigh it to the nearest 0.0001 gram. After the calculation below is made, and the weight of the ignited sample is checked (if necessary), discard the used bulb.

Calculation and Report

$$\text{Wt \% Ramsbottom Carbon Residue} = \frac{R}{S} \times 100$$

Where,

R = the weight of the residue, grams  
S = the weight of the sample, grams

Report results to the nearest 0.1%.

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Rifle, Colorado

Analytical Laboratory

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

The method used is "Ash from Petroleum Oils", ASTM D 482-63, with slight modifications. Below is the version of this method used in this laboratory.

Outline of Method

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.

Apparatus

- a. Muffle Furnace - Hevi-Duty Type 62, 230 volts, safe working temperature 1750 F, maximum temperature 1850 F, with chromel-alumel thermocouple, and West 0-2000 F temperature indicator.
- b. Heat Lamps - "Infra-Radiator".
- c. Evaporating Dish - Coors procelain, Size 3.
- d. Isopropanol - reagent grade.
- e. Filter paper - Whatman No. 42, 9 cm circle.

Procedure

Place the quart bottle sample in the oven (~140 F) for about one hour to allow any water and heavy sediment to separate. Withdraw approximately 50 grams of the oil, transfer to a previously ignited and weighed evaporating dish, and weigh to the nearest 0.0001 gram. Since the sample may still contain some water, it should be dried before burning. This is done by adding about 10 ml of isopropanol to the weighed oil sample, mixing as much as possible, and heating the oil under the infra-red heat lamps for about one hour. If the oil tends to spatter, add more isopropanol.

Then place a circle of filter paper on top of the oil, and heat the dish and sample with a gas burner until the oil can be ignited with a flame. Maintain at such a temperature that the sample continues to burn at a uniform and moderate rate, leaving only ash and carbon when the burning ceases.

Place the crucible with the residue in the muffle furnace, leaving the door partially open (for oxygen supply) until the carbon has burned off. Then close the door, and heat at 1750 ± 45 F for two hours.

Handling of the dish with the light ash during the remainder of the analysis should be done with great care to avoid losing any ash. Turn off the hood in the furnace room. Carefully remove the crucible from the furnace, allow it to cool for a few minutes, and then place it in a desiccator until cool enough for weighing. Weigh the crucible and ash to the nearest 0.0001 gram.

Calculation and Report

$$\text{wt \% Ash} = \frac{R}{S} \times 100$$

Where,

R = the weight of the residue in grams  
S = the weight of the sample, in grams

Report results to the nearest 0.01%.

AP-O-13  
Revised October 2, 1967

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

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The method used is "Saybolt Viscosity", ASTM D 88-56. Two viscosity measurements are made - one at 130 F, the other at 210 F.

Use the water-and-sediment-free liquid product (crude shale oil) as obtained by the procedure, "Treatment of Liquid Product Samples. Determine the viscosity at 130 F using the Precision 2-position viscometer, catalog no. 4962 determine the viscosity at 210 F using the Precision 4-position viscometer, catalog no. 74966.

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

The method used is "Cloud and Pour Points", ASTM D 97-57. Below is a condensed version of the "Procedure" of this method as used in this laboratory.

Outline of Method

The crude shale oil is cooled in steps 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.

Procedure

Use the water-and-sediment-free liquid product (crude shale oil) as obtained by the procedure, "Treatment of Liquid Product Samples." Pour the oil into the test jar to the mark; about 50 ml is required. Assemble the cork and thermometer according to paragraph 5 (b) of the ASTM procedure. Heat the oil, without stirring, to 115 F. Place the test jar in the cooling apparatus (filled with ice and water) according to paragraphs 5 (d), (e), and (f) of the ASTM procedure. When the temperature reaches 105 F, remove the jar from the cooling jacket and look for oil movement according to paragraphs 5 (g) and (h) of the ASTM procedure.

Note that the pour point is 5 F above the temperature where no movement is observed. (The pour point of crude shale oil from the Gas Combustion Retort will usually be approximately 85 F.)

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

The method used is 'Distillation at Reduced Pressure of Petroleum Products', ASTM D 1160-61, at 10 mm pressure. Some details of the method as used in this laboratory are given below.

Outline of Method

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

Apparatus

The apparatus used conforms to the specifications of the ASTM method. Some of the particular components used in this laboratory are described below.

- a. Flask (insulated), Column (insulated), Condenser, Receiver, Heater, Cold Traps, and Thermocouple - available from Scientific Glassblowing Company, Houston, Texas.
- b. Potentiometer - Honeywell Model 2720.
- c. Pressure Measuring System - Vacuum gauge, Model 68, available from Fischer Scientific Company, Catalog No. 11-250.
- d. Pressure Regulating System - RGI Absolute Pressure Control, C2200, available from Cole-Parmer Instrument and Equipment Company, Catalog No. 911, with bleed needle valve.
- e. Vacuum System - Single stage vacuum pump, Welch No. 1404 B (33.4 liters/minute) - 15 gallon surge tank.
- f. Coolant Circulating System - 12-quart round bottom jar Automerse Heater, 850 watts, available from Fischer Scientific Company, Catalog No. 11-463-10V3 Circulating Pump, Eastern Centrifugal Pump, Model D-6, Type 100, 1550 rpm.
- g. Filter Funnel - 100-mesh, as described in ASTM D 88.

Reagents

- a. Mercury - Instrument grade.
- b. Calcium Chloride - 8 to 12-mesh.

Procedure

Use the water-and-sediment-free liquid product (crude shale oil), as obtained by the procedure, "Treatment of Liquid Product Samples". Dehydrate the sample as described in section A5 of the appendix of the ASTM method. Filter the dried oil through the 100-mesh filter funnel.

Follow the Procedure in the ASTM method, using 10 mm pressure. Adjust the temperature of the coolant to  $125 \pm 5$  F.

Use form OSRC-24 to record the required data.

Calculation and Report

Complete form OSRC-24. Use Chart 53-12\* to convert the temperature readings at 100 mm to equivalent temperature at 760 mm.

Discussion

Use the prepared table to determine the weight of sample equivalent to 200 ml at 125 F. The table was prepared from the following relationship:

$$S = 194.88D$$

Where,

S = the weight of the sample, in grams, equivalent to 200 ml at 125 F.

D = the density of the sample, in grams/milliliter at 60 F.

The density is obtained directly from standard API Gravity-Density-S.G. conversion tables.

\*"Vapor Pressure Charts for Petroleum Hydrocarbons", J. B. Maxwell and L. S. Bonnell.

AP-O-16  
Revised October 3, 1967

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

The method used is "API Gravity of Petroleum Products"  
Hydrometer Method, ASTM D 287-55.

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

If there is any water present in the sample, it is separated  
by allowing the sample to stand in a separatory funnel for  
about one hour. The water and some of the oil is drawn off  
the gravity measurement is made at room temperature on the oil  
remaining.

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

Analysis of Recycle Gas  
(AP-G-17)

Scope

This method is used to determine CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO, Ar, and H<sub>2</sub> in gas combustion retort recycle gases.

Outline of Method

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.

Apparatus and Materials

- a. Gas Chromatograph - Fisher Gas Partitioner, Model 25V; column No. 1, 30-in., 30% HMPA (hexamethylphosphoramide) on 60/80 mesh Columpak; column No. 2 - 6 1/2 ft., 42/60 mesh activated Molecular Sieve 13X - 1/2-ml sample loop.
- b. Thermal Stabilizer - Model 27 for Fisher Gas Partitioner.
- c. Recorder - Sargent Model SR-25 with 1.0 mv. range plug.
- d. Drying Tube - available from Fisher Scientific Co., cat. no. 11-134-125 (filled with indicating drierite, 10-20 mesh).
- e. Drying Tube - straight form, single bulb, Pyrex, 100 mm. (filled with anhydrous magnesium perchlorate).
- f. Bubble column assembly - available from Fisher Scientific Co., cat. no. 6-390-65.
- g. Carrier Gases - Helium 99.99%; Nitrogen 99.996%.
- h. Gas Regulator - (for carrier gases) Gas chromatography regulator No. 8G, available from Matheson Co. (2 needed)
- i. Calibration gas mixtures - at the nominal concentrations listed below, analyzed standards.

Nominal Vol %

<u>Gas</u>	<u>A</u>	<u>B</u>
CO <sub>2</sub>	16	30
O <sub>2</sub>	0.1	1
H <sub>2</sub>	6	2
CO	3	6
CH <sub>4</sub>	1	3
N <sub>2</sub>	65	55
He	Bal.	Bal.

- j. Cylinder gauge and valve (for calibration gases) - No. 52 needle valve with tank gauge, available from Matheson Co. (2 needed).
- k. Gas holder - Approximately 5-cubic feet capacity, brine resistant.
- l. Brine solution, 25% - Prepare by using 2.5 pounds of rock salt for each gallon of solution.

Collecting a Sample

The sampling system is shown in Figure 1. Approximately 1 1/2 cubic feet of gas per hour is sent from the retort, through a heat-traced line, to the laboratory. At the laboratory, the proper valves are opened and the flow into the gas holder is regulated to collect about 3 cubic feet of gas during a run. The sample in the gas holder can be conveyed directly to the laboratory chromatograph for gas analysis.

Preparation of Instrument for Analysis

The recorder should be kept on "Standby" and the thermal stabilizer should be kept on, whenever it is expected that the instrument may be used within about 3 days. When the chromatograph is to be used for the gases other than hydrogen, use the helium carrier gas; for hydrogen, use the nitrogen carrier gas. Attach the "quick-connect" couplings from the proper carrier gas supply and the bubble flowmeter. Adjust the flow to 80 ± 0.5 ml per minute. Put the Partitioner on 2 percent sensitivity. After at least a 15-minute warm-up and stabilization period, disconnect one wire at the recorder and short the input terminals. Turn the recorder to "Pen", and zero the recorder at the right side of the chart (zero divisions) for the gases other than

hydrogen, and at about 80 divisions for hydrogen. Reconnect the Partitioner, and use the "Balance" control to adjust the pen at the same zero as the recorder zero. Set the recorder to "Record" whenever sample or standard gases are to be injected into the instrument.

### Calibration

#### (A) For Gases Other Than CO<sub>2</sub> and N<sub>2</sub>

The instrument is calibrated with the calibration gas mixtures. At least two standards, bracketing the concentrations expected in the samples to be analyzed, are needed. Calibrate as follows: Conduct a slow stream (about 50 ml per minute) of one of the standards through the 1/2-ml sample loop for at least 10 seconds (making sure that the sample valve knob is in the "out" position). Stop the flow, then immediately push the sample knob in. When the recorder pen begins to trace the first peak, pull the sample knob out again in preparation for the introduction of another standard or a sample. The peaks, after an initial "Composite" peak, will appear in the order shown on the "Gas Analysis Work Sheet" (OSRC-21). (The O<sub>2</sub> and Ar peaks appear as one.) Use the instrument sensitivities shown next to each gas. A typical set of chromatograms is shown in Figure 2. (The small "pips" after CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> are caused by changing the sensitivity.) Make two chromatograms for each standard before and after each group of samples. If the duplicate peak heights on any sample differ by more than 0.5 division, rerun that sample. Average the peaks (measured from the base line at the same sensitivity as the corresponding peak) for each component of the gas mixture, and enter the data on the work sheet. Record the differences (P) between the average peak heights for the two concentrations of each gas in the standards. Record the differences (C) between the concentrations of each component gas. Calculate a factor C/P for each gas except CO<sub>2</sub> and N<sub>2</sub>.

#### (B) For CO<sub>2</sub> and N<sub>2</sub>

Plot the peak heights along the ordinate (vertical axis) versus the concentrations of the gases along the abscissa (horizontal axis) on linear graph paper. Join the points with a straight line.

If there is doubt about the relationships being linear ones, determine peak heights for concentrations between those given, and plot those also, to determine the true relationships.

Subsequently, when standards are run, the two peak heights obtained for each calibration gas can be plotted and then connected by using a straight edge.

### Sample Analysis

With the instrument and gas flow adjusted, open the valves that will permit the sample to pass from the gas holder through the magnesium perchlorate-filled drying tube into the sample loop. Allow it to flow long enough to purge the system completely, then stop the flow, and immediately push the sample knob in. When the recorder begins to record the composite peak, pull the knob out. Use the sensitivities shown for each gas on the "Gas Analysis Work Sheet."

### Calculation and Report

Estimate, to the closest 0.1 division, the peak heights above baseline of the different gases. Enter these peak heights on the work sheet. Calculate the factors from the peak heights of the standard gases, then use these to compute the concentrations of the gases in the sample. After determining the nitrogen concentration, find the oxygen correction and the Argon content from Table I. Subtract the total percentage from 100 to obtain "Others". Report all results to the nearest 0.1 volume percent.

An example of a calculation is shown on the attached "Gas Analysis Work Sheet."

TABLE I

## DETERMINATION OF ARGON CONTENT AND OXYGEN CORRECTION

<u>% NITROGEN</u>	<u>% ARGON</u>	<u>OXYGEN CORRECTION</u>
54 . . . . .	0.7 . . . . .	0.6
55 . . . . .	0.7 . . . . .	0.6
56 . . . . .	0.7 . . . . .	0.6
57 . . . . .	0.7 . . . . .	0.6
58 . . . . .	0.7 . . . . .	0.7
59 . . . . .	0.7 . . . . .	0.7
60 . . . . .	0.7 . . . . .	0.7
61 . . . . .	0.7 . . . . .	0.7
62 . . . . .	0.8 . . . . .	0.7
63 . . . . .	0.8 . . . . .	0.7
64 . . . . .	0.8 . . . . .	0.7
65 . . . . .	0.8 . . . . .	0.7
66 . . . . .	0.8 . . . . .	0.8
67 . . . . .	0.8 . . . . .	0.8
68 . . . . .	0.8 . . . . .	0.8
69 . . . . .	0.8 . . . . .	0.8
70 . . . . .	0.8 . . . . .	0.8
71 . . . . .	0.9 . . . . .	0.8
72 . . . . .	0.9 . . . . .	0.8
73 . . . . .	0.9 . . . . .	0.8
74 . . . . .	0.9 . . . . .	0.8
75 . . . . .	0.9 . . . . .	0.9
76 . . . . .	0.9 . . . . .	0.9
77 . . . . .	0.9 . . . . .	0.9
78 . . . . .	0.9 . . . . .	0.9
79 . . . . .	1.0 . . . . .	0.9

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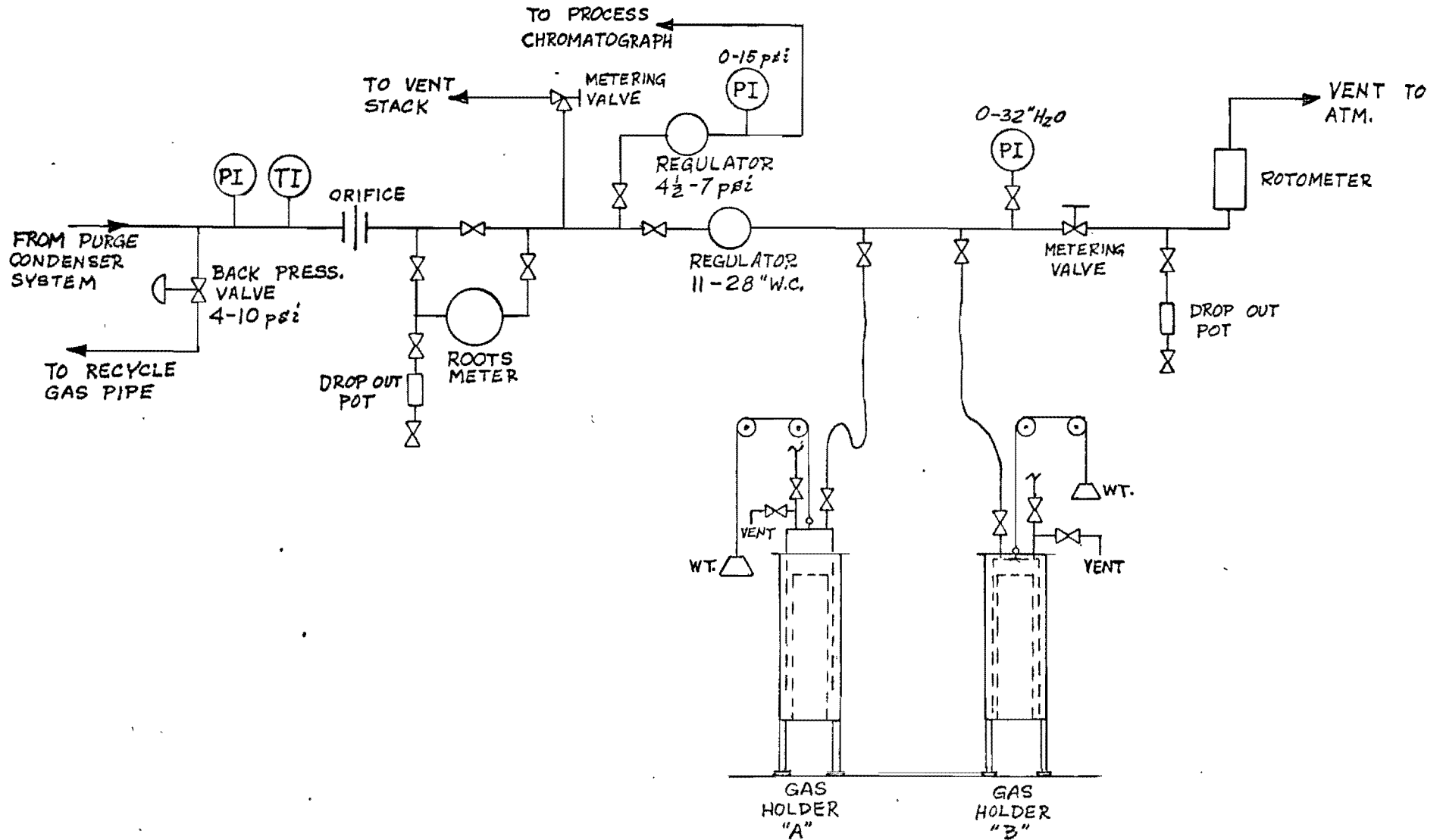


FIGURE 1  
SAMPLING SYSTEM FOR ANALYSIS OF RECYCLE GAS

GAS ANALYSIS WORK SHEET

DATE 4-13-67

ANALYST RJA

GAS	SENS.	AV. PEAK HT.		DIFF. (P)	DIFF. IN CONC. % (C)	FACTOR (C/P)
		STD A-2	STD B-2			
		(15.4%)	(23.7%)			
CO <sub>2</sub>	(2)	<u>11.0</u>	<u>17.1</u>			
O <sub>2</sub>	(10)	<u>0.5</u> (76.6%)	<u>4.0</u> (67.8%)	<u>3.5</u>	<u>0.78</u>	<u>0.223</u>
N <sub>2</sub>	(2)	<u>55.1</u>	<u>48.1</u>			
CH <sub>4</sub>	(25)	<u>3.6</u>	<u>18.4</u>	<u>14.8</u>	<u>2.29</u>	<u>0.155</u>
CO	(25)	<u>3.3</u>	<u>27.6</u>	<u>24.3</u>	<u>3.2</u>	<u>0.132</u>
H <sub>2</sub>	(10)	<u>23.1</u>	<u>3.4</u>	<u>19.7</u>	<u>5.7</u>	<u>0.289</u>

LAB. NO. \_\_\_\_\_ RUN NO. C1028-2

GAS	SENS.	AV. PEAK HT.	FACTOR (C/P)	
CO <sub>2</sub>	(2)	<u>18.6</u>		= <u>25.6</u> %CO <sub>2</sub> (From CO <sub>2</sub> curve)
O <sub>2</sub>	(10)	<u>4.7</u>	X <u>0.233</u> = 0. (Subtract) (0 corr.)	= <u>0.3</u> %O <sub>2</sub>
N <sub>2</sub>	(2)	<u>43.4</u>		= <u>60.2</u> %N <sub>2</sub> (From N <sub>2</sub> curve)
CH <sub>4</sub>	(25)	<u>11.3</u>	X <u>0.155</u>	= <u>1.8</u> %CH <sub>4</sub>
CO	(25)	<u>28.5</u>	X <u>0.132</u>	= <u>3.8</u> %CO
H <sub>2</sub>	(10)	<u>17.1</u>	X <u>0.289</u>	= <u>4.9</u> %H <sub>2</sub>
Argon				= <u>0.7</u> %Ar (From Table 1)
Others				= <u>2.7</u> % (Diff. from 100)

LAB. NO. \_\_\_\_\_ RUN NO. \_\_\_\_\_

GAS	SENS.	AV. PEAK HT.	FACTOR (C/P)	
CO <sub>2</sub>	(2)	_____		= _____ %CO <sub>2</sub> From CO <sub>2</sub> curve)
O <sub>2</sub>	(10)	_____	X _____ = 0. (Subtract) (O <sub>2</sub> corr.)	= _____ %O <sub>2</sub>
N <sub>2</sub>	(2)	_____		= _____ %N <sub>2</sub> (From N <sub>2</sub> curve)
CH <sub>4</sub>	(25)	_____	X _____	= _____ %CH <sub>4</sub>
CO	(25)	_____	X _____	= _____ %CO
H <sub>2</sub>	(10)	_____	X _____	= _____ %H <sub>2</sub>
Argon				= _____ %Ar (From Table 1)
Others				= _____ % (Diff. from 100)

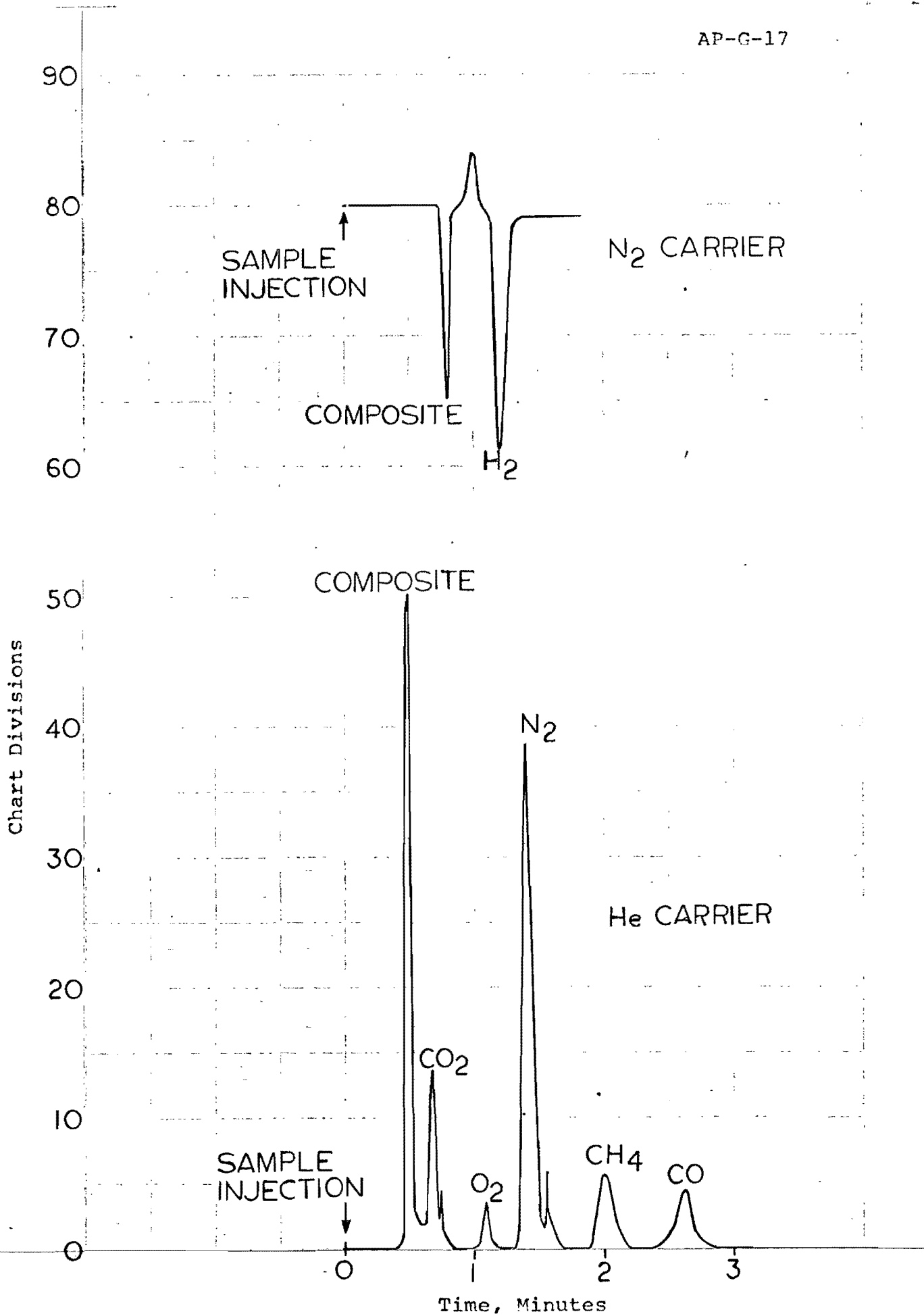


Fig. 2 - APPEARANCE OF TYPICAL CHROMATOGRAM

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, Colorado

Analytical Laboratory

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

Scope

This method is used to determine the amount of material that can be extracted by hot benzene from a sample of shale or shale plus oil.

Outline of Method

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.

Apparatus

- a. Extraction Flask - see ASTM D 473-59
- b. Condenser - see ASTM D 473-59
- c. Extraction Thimble - see ASTM D 473-59
- d. Hot Plate - Precision six hot-plate unit, catalog no. 65500, 115v, 1800 watts; with 25 ampere variable transformer

Reagent

- a. Benzene - Reagent, A.C.S.

Procedure

If possible, grind the sample to minus 48 mesh as described in "Preparation of Raw and Spent Shale Samples"; otherwise use the sample as submitted, taking care to use a representative portion of it.

Weigh a dry extraction thimble, that has been well extracted with benzene, to the nearest 0.001 gram. Place about 10 grams of the sample into the thimble, and reweigh it to the nearest 0.001 gram.

Pour 50 ± 2 ml of benzene into the flask. Hook the thimble containing the sample onto the condenser and lower it into the flask on the hot plate. Seat the condenser firmly on the flask, and turn on the cooling water. (Refer to Figure 1 of ASTM D 473-59)

Adjust the heat so that the level of the benzene in the thimble is about 3/4 to 1 inch below the top. Continue the extraction for fifteen minutes after the benzene dropping from the thimble is colorless. Dry the thimble and extracted sample in air for five minutes, and then in the 105 C (220 F) oven for one hour. Allow the thimble to cool in the desiccator for one hour, and then weigh it to the nearest 0.001 gram.

Calculation and Report

$$\text{Wt \% benzene extractable} = \frac{L}{S} \times 100$$

Where,

L = the loss in weight of the sample (after extraction),  
grams

S = the weight of the sample, grams

Report results to the nearest 0.01%.

Discussion

The ASTM D 473-59 procedure should be consulted as a reference for this method.

After completion of the test, the thimble should be well rinsed with benzene, and dried.

Since benzene is toxic, avoid breathing the vapors and contact with the skin.

Modified Method

Transfer the benzene plus extracted material from the flask into a weighed evaporating dish. Evaporate at 105 C until only a heavy residue remains. Cool, weigh, and then calculate the extractables as given below.

$$\text{Wt \% extractables (modified)} = \frac{W}{S} \times 100$$

Where,

W = weight of extractables, grams

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

Scope

This method is used to determine the distribution of particle sizes (less than 1 inch) of samples of raw and spent shale.

Outline of Method

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

Apparatus

- a. Sieves - with pan and cover, 8-inch, of the following sizes:

<u>Mesh</u>	<u>Inches</u>	<u>Mesh</u>	<u>Inches</u>
--	1.050	8	.093
--	.983	10	.065
--	.742	14	.046
--	.624	20	.0328
--	.441	28	.0232
--	.371	35	.0164
2 1/1	.312	48	.0116
3	.263	65	.0082
4	.185	100	.0058
5	.156	150	.0041
6	.131	200	.0029

- b. Sieve Shaker - Ro-Tap, Electric, 8-inch, is suitable.

Procedure

The shale sample used must be dry. If it is damp, dry with hot air or in the 105 C (220 F) oven; if it is oily, wash well with benzene, then dry with hot air.

Arrange the required sieves on the sieve shaker (largest mesh at top) with a pan at the bottom. Pour the sample (about 1000 g, if available) onto the top sieve and attach the cover. Turn on the shaker, and shake for 30 seconds.

When the segregation is complete, weigh the amounts of sample on each sieve and on the pan to the nearest 0.01 gram.

Calculation and Report

$$T = P + S_1 + S_2 + \dots + S_n$$

$$\text{Wt \% on sieve} = \frac{S}{T} \times 100$$

Where,

- P = the weight of the sample on the pan, in grams
- S = the weight of the sample on each sieve, in grams
- T = the total weight of the sample, in grams

Report the total weight to the nearest 0.1 gram.

Report the weight percent on each sieve and the pan to the nearest 0.1%.

In reporting the amount on each sieve, the identification of particle size is made using the mesh size of the sieve that held the sample and the mesh size of the sieve immediately above, through which that portion of sample passed. A "+" is used to indicate the sieve that retains the sample, and a "-" is used to indicate the sieve passing the sample. An example is given below.

If a portion amounting to 15 Wt % of the total sample was retained on the 20 mesh sieve, and the sieve just above that was 8 mesh, the following notation would be used: "-8 +20 15%."

The total of all weight percentages should equal 100.0.

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Analytical Laboratory

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

Scope

This method is used to determine the (1) loose, (2) packed, and (3) solid densities of raw and spent shale.

Outline of Method

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/milliliter is calculated.

Apparatus

- a. Graduate - volume suitable for amount of sample.

Reagent

- a. Toluene - technical grade.

Procedure

The shale sample used must be dry. If it is damp, dry with hot air or in the 105 C (220 F) oven if it is oily, wash well with benzene then dry with hot air.

Select a graduate of such size that it will be about three-fourths or more filled by the sample.

- a. Loose Density - Weigh the dried shale sample to the nearest 0.01 gram if less than 100 grams, or to the nearest 0.1 grams if more than 100 grams. Pour it into the graduate and read the volume as closely as possible.
- b. Packed Density - Weigh the dried shale sample to the nearest 0.01 gram if less than 100 grams, or to the

nearest 0.1 gram if more than 100 grams. Pour it into the graduate, and jar the sample until a minimum volume is noted. read the volume as closely as possible.

- c. Solid Density - Weigh the dried shale sample to the nearest 0.01 gram if less than 100 grams, or to the nearest 0.1 gram if more than 100 grams. Pour it into the graduate. Use another graduate of the same size to add a known volume of toluene to the shale until it is covered. Dislodge any air bubbles. Read the volume of the sample plus toluene as closely as possible.

Calculation and Report

$$\text{Loose Density} = \frac{S}{V_L}$$

$$\text{Packed Density} = \frac{S}{V_P}$$

$$\text{Solid Density} = \frac{S}{V_T - V_t}$$

Where,

S = the weight of the sample, in grams

V<sub>L</sub> = the volume of the loosely packed sample, in milliliters

V<sub>P</sub> = the volume of the tightly packed sample, in milliliters

V<sub>t</sub> = the volume of the toluene added, in milliliters

V<sub>T</sub> = the total volume of the sample plus toluene, in milliliters

Report densities to the nearest 0.01 gram/milliliter.

Discussion

All of these densities may be determined on the same sample if more than one is requested, the densities should be determined in the order given.

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

Scope

This method is used to determine the water content of liquid products from various portions of the retort product recovery system. The method is a modified version of ASTM Method D 95. It is more accurate than AP-O-10.

Outline of Method

The liquid product is heated with toluene which distills over with water into a trap. The water separates and the excess toluene drains back into the distillation vessel. The volume of water collected in the trap is measured.

Apparatus

The apparatus consists of a variable heater, distilling flask, condenser, and receiving trap.

- a. Heater - Any suitable electric heater to fit the flask in (b) below.
- b. Malt Mixer or Blender
- c. Boiling Stones, such as Hengar granules, are suitable
- d. Distilling Flask - 500-ml, round bottom, short neck,  $\text{\textcircled{R}} 24/40$ .
- e. Condenser - Liebig, Integral, 500 mm jacket,  $\text{\textcircled{R}} 24/40$  on drip tip delivery end.
- f. Receiving Traps - 5, 10, and 25-ml capacity, conforming to ASTM E123 (Calibrate these traps by adding known amounts of water, covering the top surface with toluene, and preparing a table of volumes added versus read).

Solvent

- a. Toluene, Industrial Grade, dry.

Procedure

Weigh 50 to 80 g (to the nearest 0.1g) of well-mixed liquid product into a 500-ml distilling flask. Add 100 ml of toluene, 2 to 3 boiling stones and attach the flask to the condenser-trap system. Bring to a vigorous boil to distill the water-toluene mixture into the receiving trap at a rate of about 2 to 5 drops per second. Distill until successive 15-minute periods show no increase in the water collected in the trap. Allow the trap and contents to come to room temperature, dislodge any droplets with a glass or Teflon rod, and measure the water volume. Interpolate as closely as possible between the scale divisions.

Calculation and Report

$$\text{Water, Wt percent} = \frac{\text{Vol of water in trap}}{\text{Wt of sample}} \times 100$$

Report to the nearest 0.1 percent.

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Rifle, Colorado

Analytical Laboratory

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

Scope

This method is used to determine pH, specific gravity, chloride, carbon dioxide, ammonia, ash, and solids in water produced by the gas combustion retorting of oil shale. These analyses are of interest because of their relationship to corrosion, pollution, disposal, or possible future utilization.

Outline of Method

The sample is divided into several portions which are treated soon after sampling in order to preserve certain transient components. Determinations are made for individual desired components.

Sample for Ammonia and Chloride

As soon as possible after the sample is taken, acidify exactly 1 liter with 1:1 sulfuric acid to pH 2-3, then add 25 ml in excess.\* Filter, then extract with chloroform.

Boil the aqueous solution to eliminate CO<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>S. Boil until the volume is reduced to about 900 ml, keeping the solution at pH 2 to 3 by adding more acid if necessary. Cool the solution and filter it into a 1-liter volumetric flask. Dilute to volume with distilled water.

Ammonia

Take an aliquot for determination of ammonia (approximately 2 ml for an estimated concentration of 1.5% NH<sub>3</sub>) and transfer to a 800-ml Kjeldahl flask. Add 200 ml of distilled water, then make the solution basic with sodium hydroxide and distill the ammonia over as in AP-SO-8. In the calculation, assume the sample weight is equal to the volume of sample taken.

Chloride

Measure a 500-ml portion of the sample into a 600-ml beaker, add 50% sodium hydroxide to pH 10, and evaporate

\*The sample is stabilized at this point, and may be held while the samples for carbonate and pH are taken.

dry under a heat lamp. (Add more NaOH to keep pH at 10 or higher, if necessary.) Ignite at 550 to 600 C to burn off organic matter.

Cool the sample and dissolve the salts in a small amount of distilled water. Filter through a coarse fritted glass crucible. Wash with 3 or 4 10-ml portions of distilled water.

Transfer the filtrate to a 250-ml beaker and adjust to pH3 with nitric acid. Boil to expel sulfides. Cool the solution, then add 20 mg/l silver nitrate solution slowly with stirring. Let the precipitate settle periodically, then add 1 drop of silver nitrate: if no precipitate forms when the drop is added, all the chloride has reacted. At that point, add about a 10% excess.

Heat the solution just to boiling to coagulate the precipitate. Allow it to stand in the dark for about two hours, then vacuum filter through a preweighed filter crucible. Filter the supernatant liquid through first, retaining as much of the precipitate in the beaker as possible. Wash the precipitate in the beaker with three 20-ml portions of 0.01 N nitric acid, pouring the wash solution each time into the filter crucible. Finally rinse the precipitate into the crucible, taking care to transfer all particles.

Dry the filter crucible at about 120 C for two hours. Cool in a desiccator and weigh to the nearest 0.0001 gram. Heat for an additional hour and reweigh. If the weight is constant, calculate the weight % chloride as follows:

$$\text{Wt \% Cl}^- = 0.0495 W$$

Where,

W = weight of silver chloride precipitate, grams.

#### Sample for Carbon Dioxide

As soon as possible after the sample is taken, pipet a 50-ml portion into a flask used for carbonate determination. Immediately seal the flask to the CO<sub>2</sub> evolution apparatus which has been prepared as described in the "Procedure" for "Mineral Carbon Dioxide in Raw and Spent Shale" (AP-S-4). Follow the procedure as given in the method, starting with "Close the stopcock on the separatory funnel....".

Calculate the carbon dioxide (dissolved and as carbonates) as follows:

$$\text{Weight \% CO}_2 = \frac{(W-B)(100)}{S}$$

Where,

W = increase in weight of the Nesbitt absorber for the sample, grams.

B = increase in weight of the Nesbitt absorber for the blank, grams.

S = weight of sample, grams.

Sample for Solids and Ash

Solids

Weigh a 50-ml portion of the original sample into a Pyrex evaporating dish. Evaporate the solution in a hood under a heat lamp. Finally heat in the oven at 105 C for one hour, cool, and reweigh.

Calculate solids as follows:

$$\text{Weight \% Solids} = \frac{100 W_s}{S}$$

Where,

W<sub>s</sub> = weight of solids, grams

S = weight of sample, grams

Ash

Heat the dish, containing the water solids, in a muffle furnace at 500 C for two hours. Weigh the residue.

Calculate ash as follows:

$$\text{Weight \% Ash} = \frac{100 W_a}{S}$$

Where,

W<sub>a</sub> = weight of ash, grams

S = weight of original sample, grams

Determination of pH

As soon as possible after the sample is taken, adjust a small portion (about 50 ml) to room temperature, and determine pH with a pH-meter or short-range pH paper. Report to 0.1 pH-units.

ANVIL POINTS OIL SHALE RESEARCH CENTER  
Rifle, ColoradoAnalytical LaboratoryShale Richness Distribution  
(AP-S-23)Scope

This method is used to determine the range of richness of oil shale.

Outline of Method

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.

Apparatus

- a. Flasks - volumetric, 50-ml capacity.
- b. Graduated cylinders, 50-ml capacity, with ground-glass stoppers.

Reagents

- a. Carbon tetrachloride, Reagent-grade.
- b. Tetrabromoethane, Reagent-grade.

Procedure

1. Prepare a series of solutions of different densities using carbon tetrachloride (CTC) and tetrabromoethane (TBE).

Precaution. Both these solvents are dangerous and toxic - work with them only in a hood and be sure that there is a constant draft from an open window or door. These materials can cause serious bodily injury!

- a. Add 50 ml TBE to 450 ml CTC in a quart bottle and mix thoroughly. (This mixture is 10 volume percent TBE and 90 volume percent CTC.)
- b. Repeat above with 100 ml TBE - 40 ml CTC (20 percent TBE - 80 percent CTC) 150 ml TBE - 350 ml CTC (30 percent TBE - 70 percent CTC), 200 ml TBE - 300 ml CTC (40 percent TBE - 60 percent CTC): 250 ml TBE - 250 ml

CTC (50 percent TBE - 50 percent CTC) - 300 ml TBE -  
200 ml CTC (60 percent TBE - 40 percent CTC). The  
other solution is pure CTC.

Precaution: Keep these bottles tightly stoppered at all times.

If you do not, carbon tetrachloride will preferentially evaporate and increase the density of the mixtures.

2. Determine the specific gravity of each mixture as follows:
  - a. Weigh 50 ml volumetric flask with stopper.
  - b. Add solution to the mark and reweigh.
  - c. Subtract (a) from (b). Multiply this result by 0.0200 to obtain the density of that particular solution.
  - d. Check the room temperature (it should be 23 to 25 C).
3. Place 10.0 g ( $\pm$  0.1 g) of ground shale into each of seven 50-ml graduated cylinders (one graduate for each solution). Add solution to about the 40-ml mark in each graduate and carefully stopper each graduate (use a small amount of silicone grease to seal the joint in order to prevent CTC from evaporating).
4. Shake each graduate for about 30 to 40 seconds, then allow the solid to settle (the settling takes one to three hours as a rule, but it is dependent on the type of shale).
5. Carefully read and record the solid volumes at the top of the graduate. Generally, you can estimate this volume to 1/3 ml.
6. Repeat 4 and 5 twice again.
7. Enter the data on OSRC-29.
8. Average the data from each graduate.
9. Plot the data versus density and richness on probability graph paper. The specific gravity-oil yield relationship given in Applicability of a Specific Gravity-Oil Yield Relationship to Green River Oil Shale J. W. Smith, Ind. Eng. Chem. 3, 306 (1958) is

$$y = 326.624 - 205.998x + 31.563x^2$$

Where,

y = oil yield, gallons per ton  
x = specific gravity 60/60 F

A table is also given in that paper.

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APPENDIX A  
ANALYTICAL LABORATORY FORMS

Several forms have been prepared for use in the laboratory. Each one is a different color so that it may be easily recognized. A summary of the forms is given below and a copy of each is attached.

OSRC-12A	LABORATORY ANALYSIS SHEET	Blue
OSRC-12B	LABORATORY ANALYSIS SHEET	Blue
OSRC-13	FISCHER ASSAY WORK SHEET	Canary
OSRC-15	SUPPLEMENTAL ANALYTICAL LABORATORY REPORT	Pink
OSRC-20	QUALITY CONTROL RESULTS REPORT	Green
OSRC-21	GAS ANALYSIS WORK SHEET	Goldenrod
OSRC-22	ANALYTICAL "QUICK-YIELD" SHEET	Yellow
OSRC-24	DISTILLATION DATA SHEET	Salmon
OSRC-29	SHALE RICHNESS DISTRIBUTION	Blue Mineo- tone

LABORATORY ANALYSIS SHEET

ANVIL POINTS OIL SHALE RESEARCH CENTER

Date Sampled \_\_\_\_\_

Run No. \_\_\_\_\_

Sample Time: RS \_\_\_\_\_; SS \_\_\_\_\_

FISCHER ASSAY

RAW SHALE       SPENT SHALE

_____	_____	Gal/Ton
_____	_____	S.G., g/ml
_____	_____	Oil, wt %
_____	_____	Water, wt %
_____	_____	Sp. Shale, wt %
_____	_____	Gas & Loss, wt %
_____	_____	COKING TENDENCY

RETORT SHALE MOISTURE

\_\_\_\_\_ wt %

RAW SHALE FISCHER ASSAY MOISTURE

\_\_\_\_\_ wt %

MINERAL CO<sub>2</sub>

\_\_\_\_\_  \_\_\_\_\_ wt %

ASH (SHALE)

\_\_\_\_\_  \_\_\_\_\_ wt %

MOISTURE

\_\_\_\_\_  \_\_\_\_\_ wt %

CARBON

\_\_\_\_\_  \_\_\_\_\_ wt %

HYDROGEN

\_\_\_\_\_  \_\_\_\_\_ wt %

BENZENE EXTRACTABLES

\_\_\_\_\_  \_\_\_\_\_ wt %

SHALE RICHNESS DISTRIBUTION  
(See attached graph)

SCREEN ANALYSIS  
(See back of this sheet)

All results are "as received" unless noted. "Moisture" designates the moisture content of the -48 mesh material used for "Ash", "Mineral CO<sub>2</sub>", "Carbon", and "Hydrogen". The "FA Moisture" is for the sample used for the Fischer Assay.

COMMENTS \_\_\_\_\_

DATE COMPLETED \_\_\_\_\_

CHECKED BY \_\_\_\_\_

**LABORATORY ANALYSIS SHEET**

**UNIV. POINTS OIL SHALE RESEARCH CENTER**

Date Sampled \_\_\_\_\_

Run No. \_\_\_\_\_

**LIQUID PRODUCTS**

	<u>D3 PUMPOUT</u>				<u>T3 PUMPOUT</u>	
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>1</u>	<u>2</u>
WATER, wt %	_____	_____	_____	_____	_____	_____
GRAVITY, °API	_____	_____	_____	_____	_____	_____
<input type="radio"/> OIL ASH, wt %	_____	_____	_____	_____	_____	_____

DISTILLATION (See attached sheet - OSRC-24)

**VENT PURGE PRODUCT**

OIL WT, g \_\_\_\_\_  
 WATER VOL, ml \_\_\_\_\_  
 GRAVITY OIL, °API \_\_\_\_\_

**VENT GAS**

MAJOR COMPONENTS

CO <sub>2</sub>	_____	vol %
O <sub>2</sub>	_____	"
N <sub>2</sub>	_____	"
CH <sub>4</sub>	_____	"
CO	_____	"
H <sub>2</sub>	_____	"
Ar	_____	"
Others	_____	"

C<sub>1</sub> thru C<sub>12</sub>, plus n-Pentane

CH <sub>4</sub>	_____	vol %
C <sub>2</sub> H <sub>4</sub> -C <sub>2</sub> H <sub>6</sub>	_____	"
C <sub>3</sub> H <sub>8</sub>	_____	"
C <sub>3</sub> H <sub>6</sub>	_____	"
i C <sub>4</sub> H <sub>10</sub>	_____	"
n C <sub>4</sub> H <sub>10</sub>	_____	"
o C <sub>3</sub> H <sub>6</sub>	_____	"
n C <sub>5</sub> H <sub>12</sub>	_____	"

CARBON, \_\_\_\_\_ lbs/MSCFDG

HYDROGEN, \_\_\_\_\_ lbs/MSCFDG

COMMENTS \_\_\_\_\_

DATE COMPLETED \_\_\_\_\_

CHECKED BY \_\_\_\_\_

FISCHER ASSAY WORK SHEET

Anvil Points Oil Shale Research Center

Sample No. \_\_\_\_\_ Date \_\_\_\_\_  
 Retort No. \_\_\_\_\_ Receiver No. \_\_\_\_\_ Adapter No. \_\_\_\_\_

Retort + Sample	_____ gm	Retort + Sp. Shale	_____ gm
Retort (-)	_____ gm	Retort (-)	_____ gm
Sample Weight	_____ gm	Spent Shale	_____ gm
Dist. + Sp. Shale (-)	_____ gm	Dist. Weight (+)	_____ gm
Gas + Loss	_____ gm	Dist. + Sp. Shale	_____ gm
Rec. + Adp. + Dist.	_____ gm		
Rec. + Adp. (-)	_____ gm		
Distillate Weight	_____ gm		
Water Vol. (wt.) (-)	_____ gm		
Oil Weight	_____ gm		

OIL	_____ gm	Wt. % OIL	_____
WATER	_____ gm	Wt. % WATER	_____
SPENT SHALE	_____ gm	Wt. % SPENT SHALE	_____
GAS + LOSS	_____ gm	Wt. % GAS + LOSS	_____
SAMPLE WEIGHT	_____ gm		100.0%

<u>SPECIFIC GRAVITY OF OIL</u>		(Oil Weight) (239.6)
Pipet No. _____		(S.G. 60°/60°) (Sample Weight)
Weight (Pipet + Oil) _____ gm		( _____ ) (239.6)
S. G. 60°/60°F _____		( _____ ) ( _____ )
		_____ GALLONS/TON

COOKING TENDENCY \_\_\_\_\_  
 COMMENTS \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Analyst \_\_\_\_\_ Checked By \_\_\_\_\_



ARVIL POINTS ANALYTICAL LABORATORY

QUALITY CONTROL RESULTS REPORT

Name \_\_\_\_\_

Week of \_\_\_\_\_

TEST	SAMPLE	RESULT

Comments \_\_\_\_\_

\_\_\_\_\_

OSRC-20

GAS ANALYSIS WORK SHEET

DATE \_\_\_\_\_

ANALYST \_\_\_\_\_

GAS	SENS.	AV. PEAK HT.		DIFF. (P)	DIFF. IN CONC. % (C)	FACTOR (C/P)
		STD A-2	STD B-2			
		(15.4%)	(23.7%)			
CO <sub>2</sub>	(2)	_____	_____			
O <sub>2</sub>	(10)	(76.6%)	(67.8%)	_____	0.78	_____
N <sub>2</sub>	(2)	_____	_____			
CH <sub>4</sub>	(25)	_____	_____	_____	2.29	_____
CO	(25)	_____	_____	_____	3.2	_____
H <sub>2</sub>	(10)	_____	_____	_____	5.7	_____

LAB. NO. \_\_\_\_\_ RUN NO. \_\_\_\_\_

GAS	SENS.	AV. PEAK HT.	FACTOR (C/P)	
CO <sub>2</sub>	(2)	_____		= _____ %CO <sub>2</sub> (From CO <sub>2</sub> curve)
O <sub>2</sub>	(10)	_____	X _____ = 0. _____ (O <sub>2</sub> corr.)	(Subtract) = _____ %O <sub>2</sub>
N <sub>2</sub>	(2)	_____		= _____ %N <sub>2</sub> (From N <sub>2</sub> curve)
CH <sub>4</sub>	(25)	_____	X _____	= _____ %CH <sub>4</sub>
CO	(25)	_____	X _____	= _____ %CO
H <sub>2</sub>	(10)	_____	X _____	= _____ %H <sub>2</sub>
Argon	.....			= _____ %Ar (From Table 1)
Others	.....			= _____ % (Diff. from 100)

LAB. NO. \_\_\_\_\_ RUN NO. \_\_\_\_\_

GAS	SENS.	AV. PEAK HT.	FACTOR (C/P)	
CO <sub>2</sub>	(2)	_____		= _____ %CO <sub>2</sub> (From CO <sub>2</sub> curve)
O <sub>2</sub>	(10)	_____	X _____ = 0. _____ (O <sub>2</sub> corr.)	(Subtract) = _____ %O <sub>2</sub>
N <sub>2</sub>	(2)	_____		= _____ %N <sub>2</sub> (From N <sub>2</sub> curve)
CH <sub>4</sub>	(25)	_____	X _____	= _____ %CH <sub>4</sub>
CO	(25)	_____	X _____	= _____ %CO
H <sub>2</sub>	(10)	_____	X _____	= _____ %H <sub>2</sub>
Argon	.....			= _____ %Ar (From Table 1)
Others	.....			= _____ % (Diff. from 100)

ANALYTICAL "QUICK-YIELD" SHEET

RUN NO. \_\_\_\_\_

RAW SHALE

Lab No. \_\_\_\_\_

FA \_\_\_\_\_ Oil, gal/ton

LIQUID PRODUCT

Lab No.	_____	_____	_____	_____	_____
Description	_____	_____	_____	_____	Composite
API Gravity	_____	_____	_____	_____	_____
Water, wt%	_____	_____	_____	_____	_____

OSRC-22  
Revised 9/24/65

DISTILLATION DATA SHEET

ASTM D-1160 @10 mm.

LABORATORY NO. \_\_\_\_\_

SAMPLE NO. \_\_\_\_\_

API GRAVITY \_\_\_\_\_ °

SAMPLE WT. \_\_\_\_\_ gm.

RECEIVER TEMP. \_\_\_\_\_ °F.

I.B.P. \_\_\_\_\_ mv. \_\_\_\_\_ °F.

ML.	Pressure mm. Hg	Potential mv.	Temp. °F.	Vol. %	Temp. @ 760mm. °F.
10	.	.		5	
20	.	.		10	
40	.	.		20	
60	.	.		30	
80	.	.		40	
100	.	.		50	
120	.	.		60	
140	.	.		70	
160	.	.		80	
180	.	.		90	
190	.	.		95	
End	.	.			

Dry Ice Trap. Oil \_\_\_\_\_ ml. water \_\_\_\_\_ ml.

COMMENTS \_\_\_\_\_

DATE \_\_\_\_\_ ANALYST \_\_\_\_\_ CHECKED BY \_\_\_\_\_