Extraction of organic materials from Green River, Wyoming oil shale
by Raymond Clayton Suiter

A THESIS Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering
Montana State University

Abstract:
A study was made of the possibility of recovering worthwhile organic material from Westvaco's Green. River, Wyoming oil shale.

Alkaline extractions of oil shale In the presence of potassium permanganate and of previously air oxidized oil shale were both studied.

A sealed Parr reaction apparatus was used to make the extractions. The aim was to extract the organic material from the shale with alkaline solutions. In the alkaline-permanganate extractions, the organic material in the shale was. oxidized with potassium permanganate during the extractions. In the air oxidation studies, the shale was oxidized with air previous to the alkaline extractions. Air oxidation would be used in a commercial operation.

An investigation was made to determine how much of the organic, material in the shale could be recovered by the alkaline-permanganate extraction and subsequent treatment of the resulting extraction liquors. The recovery of the organic material was done in two steps. The first step recovered the acid insoluble material merely by acidifying the extract liquors. The second step recovered the acid soluble material by extracting it from the liquors with acetone. Approximately 6.7 per cent of the shale was recovered as organic material. This recovery corresponded to 70-80 per pent of the organic material available in the shale. A series of statistically designed runs was made to determine the best conditions for obtaining optimum yields of organic material from the shale.

Air oxidation studies were made using a heated glass air oxidation column, The oxidized shale was extracted with alkaline solutions and the liquors were treated for recovery of the organic materials they, contained.

In these air oxidation runs, about 10 to 20 percent of the available organic, material was recovered. Considerable work was done on identifying the extraction products obtained. Most of the identification work was done with the aid. of a Beckman IR-4 infrared spectrophotometer. The products were found to be essentially,complex organic acids with possible lactone or anhydride structures attached. However, some crystals which were recovered in the second- step of the analytical procedure were found to be of an entirely different nature. No definite identification of the crystals could be made with the available comparison charts. The extraction products were essentially short-chain or. cyclic compounds with very little aromatics present.

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ABSTRACT

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INTRODUCTION

In recent years the Westvaco division of Food Machinery and Chemical Corporation has been producing a very high-grade soda ash from trona-sodium sesquicarbonate - a mineral composed of hydrous sodium carbonate and sodium bicarbonate. Although this soda ash which is produced in Green River, Wyoming is almost 100 per cent sodium carbonate, it contains varying amounts of organic impurities. The trona lies in large mineral deposits several hundred feet under the ground. The trona deposits are in a bed which is encased above and below by two beds or layers of oil-bearing shale. It is believed that the organic impurities in the soda ash are derived from these two beds of shale. Water draining through the upper layer of shale has probably leached and washed out a certain amount of organic matter which was then deposited in the bed of trona. In view of this, Westvaco recently decided that it might be worthwhile to find out if there are any organic materials in the shale or in the soda ash impurities which are worth recovering. This investigation includes a study of recovering the organic material from only the shale itself.

One portion of the work done on identifying the various organic materials found in the Green River trona and as impurities in the various stages of the Westvaco Soda Ash production was reviewed (2). This work, done by the Cancer Research Laboratory at the University of Utah, indicated that the organic materials in the trona and the organic materials which are impurities in the soda ash production contain:

a. Monobasic acids
b. Dibasic acids
c. Rosin acids
d. Steroids

In addition to the above compounds, the organic matter studied was also found to contain small amounts of unsaturated fatty acids, and indicated a possibility of containing some sphingomyelins. The amount of organic impurities present varied somewhat at different stages of the soda ash production. The work done by the Cancer Research Laboratory was aimed at identifying any materials in the trona organic material or the soda ash impurities which might be of value to Westvaco. Quantitative determinations have been developed only on the steroid fraction of the organic material. The Cancer Research Laboratory found these steroids to be present in the trona, shale, soda ash, etc., only to the extent of a few parts per million.

As for the other organic compounds, the rosin acids might also be considered for their economic value. These acids have been found to be very similar in nature to rosin acids found in the alkaline liquors derived in pulp and paper manufacture. The monobasic and dibasic acids might also be of some economic value.

As a result of the identification work done by the Cancer Research Laboratory and similar work done on other oil-shales, the Green River shale was suspected to contain organics quite different from the organic material in most other oil-bearing shales. Any differences probably result from the type of strata which surrounds the shale beds.

Since considerable work had already been done on the identification of the organic material present in the natural shale, it was decided that this investigation should include a study aimed at discovering what quantity and what type of organics could be recovered by performing different extractions of the oil-shale. It was also decided that more valuable compounds than those already present might be obtained by changing the nature of the compounds in the shale during the extractions. It was felt that this change might be brought about by oxidizing the shale either before or during the extractions.

A survey of previous work done on the extraction of oil-shale showed that the Bureau of Mines had extracted Colorado oil-shale with solutions of potassium permanganate and caustic soda (3). In this work the investigators found that the alkaline permanganate extractions could convert about 80 per cent of the kerogen* to organic acids. Approximately half of these acids were found to be of high molecular weight and insoluble in the acidified extraction solution, while an equal amount were found to be lower molecular weight acids and soluble in the acidified extraction solution. The Bureau of Mines found that the lower molecular weight acids were mainly a mixture of oxalic, succinic, glutaric, adipic, pimelic, and suberic acids and a few other unidentified acids. In earlier work done by the Bureau of Mines (4), acids very similar to the higher molecular weight insoluble

*In this article, kerogen was defined as the organics recoverable by shale retorting.

acids were studied. These acids (regenerated "humic" acids) were found to be very complex acid mixtures. No positive identification could be made concerning the "humic" acids.

Other work has also been done on alkaline permanganate extractions of oil-shale by Stefanovic and Dragomir (5). In this work the investigators used alkaline-permanganate solutions in acetone for the extractions. These investigators suggested that the extraction products consisted mainly of long aliphatic chains which were partly unsaturated. The products were acidic and had little or no aromatic structures present.

Since the Green River shale was suspected to contain different organic material than the shale used in the Bureau of Mines studies and other studies, it was decided that possibly the alkaline-permanganate extractions of the Green River shale would likewise yield different products. Therefore, this report is an investigation of alkaline extractions of oxidized Green River oil-shale. In this investigation, however, soda ash was used as the alkaline ingredient instead of caustic soda. Soda ash was used because it is cheap and available to Westvaco. Some work was also done on air-oxidation of the oil-shale followed by alkaline extractions. Potassium permanganate would be an impractical oxidizing agent in a commercial extraction. A study was made on obtaining maximum yields and determining the best extraction conditions for obtaining these maximum yields of organic material. Also, included in this report is an identification study of the organic product obtained.

EQUIPMENT USED

A. Extraction Apparatus

In order to extract the Green River, Wyoming oil-shale with alkaline solutions, a Parr sealed reaction apparatus was used. This reaction apparatus is shown in Figure 1. A block flow diagram of the actual extraction procedure (Figure 3) shows where the reaction apparatus fits into the procedure.

Figure 1A illustrates the sealed reaction bomb which was used. The extraction starting materials were mixed directly in the bomb. The bomb was then closed by placing the stainless steel fitted head on top of the bomb. This head was held in place and sealed by the threaded bomb cap containing socket-head sealing screws. The sealed bomb was then ready to be heated and agitated.

Figure 1B shows where the sealed bomb was placed in the reaction apparatus. The bomb was placed inside the insulated heating jacket. The heat input to this jacket was supplied by two wire heating elements. One element was for maximum temperature and was controlled by a switch on the metal switch box on the base plate. The other heating element was for smaller heating input and was controlled by the Variac on the base plate. In this investigation, the maximum heater was used to achieve the desired extraction temperature. This heater was then turned off and the temperature was maintained by using the smaller heating element to balance the heat losses from the bomb. The temperature was measured by inserting an iron-constantan thermocouple in the thermowell in the bomb. The thermowell may also be seen in Figure 1. The thermocouple leads were connected to a Minneapolis-Honeywell Brown "Electronik" temperature indicator. The temperature indicator used was a single-point precision indicator.

The sealed bomb was agitated throughout the heating period by the use of a motor-run drive mechanism. In this way, the extractions could be carried out for a considerable length of time to make sure the extraction was complete.

The specifications and a description of the vital parts in the Parr reaction apparatus are as follows:

Bomb cylinder: The bomb cylinder has a nominal size of 500 milliliters and an effective charging capacity of about 275 milliliters. The cylinder was made from a solid forging of stainless steel and is capable of withstanding very high pressures.

Bomb head: The bomb head was also made from solid forging of stabilized stainless steel and was machined to fit the cylinder exactly. It contains a small groove for holding the head gasket.

Head gasket: This gasket fits between the head and the cylinder and spreads when the bomb is sealed. It was made of seamless annealed copper and has a diamond-shaped cross-section.

Bomb closure: This piece of the Parr apparatus was made of heat treated chromium-nickel steel and was threaded to screw on to the bomb. It contains eight socket-head screws which bear against steel washers on the bomb head and thus compress the head gasket.

Thermowell: The thermowell is a copper cup sealed in the bottom of the bomb cylinder.

Thermocouple: Thermocouples used were made of iron-constantan and were connected to the Minneapolis-Honeywell temperature indicator.

Heater: The heater tube is inserted within the heating jacket and receives the bomb cylinder. This tube is wound with sheathed wire elements controlled by the base plate Variac and the main heater switch. The tube is supported by a heavy aluminum end-plate and heavy sheet asbestos. The tube is encased by another steel shell and the annular space is packed with thermal insulating material. Lead wires to the heating elements are accessible through the rear aluminum plate.

Drive mechanism: The bomb drive consists of an arm attached to the heater trunnion which rocks the bomb assembly through an arc of 45 degrees. This rocking moves the bomb contents from end to end at 36 cycles per minute. A crank connected to a 1/6 hp. motor drives the connecting rod to the rocker arm. A switch on the metal switchbox controls the motor independently of the heater.

In addition to the above vital parts of the extraction apparatus, various other accessories were available to aid in loading and unloading the bomb.

B. Air-oxidation column.

This investigation includes some studies made on air-oxidizing of the Green River shale instead of using potassium permanganate in the extraction mixture. The air-oxidized shale was then extracted with alkaline solutions. For these preliminary studies a simple glass air-oxidation column was constructed as shown in Figure 2. The column was heated by one continuous Nichrome coil of 22 ohms resistance from top to bottom. Previously ground and dried shale was introduced through the top of the glass column. The shale was supported by a rigid stainless steel screen in the bottom of the column. The column was constructed so that about 200 grams of the ground shale could be oxidized effectively. The air stream for effecting the oxidation was introduced through a 1/4-inch inside diameter tube connected to the bottom of the column. The air stream passed through a section of alundum balls before reaching the shale. Since some of the ground shale particles were very fine, they had to be prevented from leaving the column by using a filter-paper trap as illustrated in Figure 2. The heat input to the column was controlled by a Variac connected to the Nichrome coil and the temperature was measured by the use of a thermocouple inserted into the shale bed. The Minneapolis-Honeywell temperature indicator was again used. No attempt was made to measure the air-flow rates in these preliminary studies. The column was operated continuously for several hours.

PROCEDURE AND MATERIALS

A. Procedure

1. Alkaline-Permanganate Extractions

a. Preliminary Runs

The Green River, Wyoming oil-shale was obtained in fairly large pieces (3- to 4-inch chunks). Therefore, before the shale could be extracted, it had to be broken down to a smaller particle size. The shale, which also contained a considerable amount of trona in a crystalline form, was passed through a small jaw crusher and reduced to pieces approximately 1/4 to 1/2 inch across. It was found that the shale itself could be crushed quite easily; however, the inter-mixed trona crystals were very hard and difficult to break, and remained in larger pieces than the shale. After passing through the jaw crusher, the shale was fed into a Montgomery Ward Model G hammer mill. The shale at this point was reduced to a fine powder. At least 90 per cent of the milled shale was -100 mesh. It was felt that this particle size would give a fairly large surface area for the extractions without being so fine as to form a cake.

In the first alkaline-permanganate extractions of the shale an attempt was made to see if any appreciable amount of organic material could be recovered. It was found that the resulting extraction liquors yielded varying amount of organic material, depending on how the liquors were treated. Ethers, alcohols, ketones, and chloroform were all used to remove organic material from the liquors and from the salts left after the liquors were evaporated to dryness. At first, the liquors were extracted just as they were received from the bomb. The same extractions were then made on liquors that had been acidified and on the dried salts left from the evaporation of these acidified liquors. In all cases, it was possible to obtain extracts, the residues of which were mostly amorphous and water-insoluble.

On the basis of the very small amounts of organic material obtained in these preliminary runs, it was decided to increase extraction time by a factor of ten (i.e., from 2 to 20 hours). This increase in the extraction time made the resulting liquors very black and somewhat viscous. Acidification of these black liquors yielded a black tar-like precipitate which could be removed by filtration of the liquors. When the precipitate was removed, it could be observed that the remaining liquor had lost most of the black color. However, on analysis it was found that the remaining liquor still contained organic matter, most of which could be recovered by an acetone extraction.

From the information gathered in these longer runs, an analytical procedure was set up to find out what total amount of organic material was obtainable from the shale by this extraction method. The analyses were designed to determine the amount of organics recovered from the shale under different extraction conditions. Several runs were made in which the amount of potassium permanganate, the amount of oil-shale, and the temperature were varied. The liquors from these runs were then analyzed for organic material. The analytical procedure is illustrated in the block flow diagram in Figure 3 and was carried out as follows:

1. The extraction mixture obtained from extracting the oil-shale was filtered. The shale residue and excess soda ash remained on the filter paper.
2. The basic filtrate or liquor was then acidified with concentrated HCl to a pH of approximately 2. A black tar-like precipitate was obtained on acidification of the filtrate.
3. The precipitate was separated from the liquor and quantitative measurement of the amount of precipitate per charge of shale was obtained.
4. The remaining liquor was evaporated to near dryness and the resulting residue was extracted with 100, 50, 50, and 25 milliliter portions of acetone.
5. The acetone extract portions were filtered and the filtrate evaporated to dryness, the residue taken up in acetone, and the new filtrate again evaporated to dryness.
6. A quantitative weight measurement of the residue

obtained from the acetone extractions was then made.

7. The total per cent recovery of organic material based on the amounts of extraction precipitate and the acetone extracted residue obtained was then determined by addition.

This analytical procedure does not take into account the weight of oxygen picked up in the oxidation of the shale organics.

b. <u>Total Yield Study</u>

After designing the analytical procedure it was decided that an attempt should be made to see if all of the organic material in the shale could be recovered by several extractions of a single sample of oil-shale. A batch extraction was made with the following ingredients:

1. Potassium permanganate - 20 grams
2. Soda ash - 66 grams
3. Lower shale - 133 grams
4. Water - 240 grams

The potassium permanganate and shale portions were added to a 21.5 per cent solution of sodium carbonate in the bomb cylinder of the reaction apparatus. The reaction mixture was then agitated in the bomb for 20 hours at 200° centigrade.

The liquor obtained from this extraction was analyzed by the procedure previously explained. The shale residue was dried and re-extracted with a duplicate of the solution used for the first extraction. This pattern was followed until the shale residue had been extracted six times. After each extraction, the resulting liquor was analyzed for organic material and the extraction residue was dried and re-extracted. A seventh extraction of the shale residue yielded no appreciable amount of organic material and the extractions were concluded.

c. Statistical Design Runs

Analysis of several preliminary runs indicated that the amount of shale, the amount of potassium permanganate, and the temperature were not the only variables which affected the per cent recovery of organic material from the oil-shale. Runs of 2, 10, 20, and 200 hours were made holding all other extraction conditions constant. Analysis of these runs indicated that after 20 hours of extracting the per cent recovery of organic material was practically unaffected by extraction time. Therefore, a series of runs was made holding time constant and varying the following extraction conditions:

1. Oxidation level (amount of $KMnO_4$)
2. Extraction temperature
3. Soda ash concentration
4. Ratio of oil-shale to extraction liquor

These runs were made using a statistical approach and the concept of steepest ascent (1). With the help of the Montana State College Mathematics Department and a research partner, the runs were set up to follow a statistical pattern as shown in Table II. The extraction variables are denoted by X_n as indicated in Table I.

By analyzing the extraction liquors from the statistical runs quantitatively, an expression was determined where the per cent recovery of organic material was defined in terms of the four coded extraction variables. This expression has the form

$$Y = B_0 + B_1Z_1 + B_2Z_2 + B_3Z_3 + B_4Z_4$$

where

$$Z_1 = \frac{X_1 - 100}{33}, \quad Z_2 = \frac{X_2 - 20}{10}, \quad Z_3 = \frac{X_3 - 200}{70},$$

$$Z_4 = \frac{X_4 - 34}{33}$$

The sign of the coefficients (B_n) of the coded extraction variables indicates in what direction the extraction variables must be altered from the mean value used in order to obtain the highest per cent recovery of organic material from the oil-shale. The results of this statistical design are shown later in the report.

2. Air-oxidation Runs

Using the air-oxidation column shown in Figure 2, runs were made wherein the Green River shale was air-oxidized and later extracted with alkaline solutions. The oil-shale was finely ground (-100 mesh) and dried for several hours in a forced-air cabinet drier. Approximately 150 grams of the dried shale were used per run. The shale was added to the column through the open top. The column was then pre-heated to approximately 75° centigrade and the air was introduced. The air entered the bottom of the column at a rate such that the bed of shale was thoroughly fluidized. The temperature of the column was then raised until approximately 200° centigrade was reached, and the shale was air-oxidized steadily for several hours.

After the oil-shale had been oxidized, a desired amount was added to an alkaline solution in the bomb. The previously oxidized shale was then extracted for several hours at the desired temperature. The resulting liquors from these runs were analyzed the same as the liquors from the alkaline-permanganate extractions.

B. Materials

In the air-oxidations and extractions of the Green River oil-shale, the following materials were used:

Oil-shale: Shale from the lower Green River bed was used in the extractions since it was known to contain more organic material than the shale in the upper bed. The shale used in the alkaline-permanganate extractions was ground so that it would all pass a 40-mesh screen. The shale used in the air-oxidation studies was ground to -100 mesh.

Potassium permanganate: Baker and Adamson reagent grade $KMnO_4$ was used as an oxidizing agent in the extractions.

Soda ash: Westvaco Soda Ash was used as the alkaline ingredient in the extractions. This soda ash was 99.88 per cent sodium carbonate.

Water: Tap water was used as the extracting solvent.

Air: In the air-oxidation studies, the air was obtained from a Gardner-Denver compressor.

Hydrochloric Acid: Fisher reagent grade concentrated HCl was used for acidifying the extraction liquors.

Acetone: Redistilled commercial acetone was used for extracting the liquors.

QUALITATIVE ANALYSIS OF PRODUCTS

The extraction products from the Green River oil-shale were handled in several ways. It was suspected that some of the products would be acidic in nature because the rigorous oxidation of the organic material would very likely result in acid structures. Also, previous work done on oil-shale oxidation (3, 5) had shown that most of the oxidation products were acids. In view of this, the resinous products obtained were refluxed with alcohols to try and esterify any acids present. In most cases, a small amount of liquids with pleasant odors were obtained. However, most of the resinous substances were only slightly affected by this treatment. Therefore, a selective solvent breakdown of the extraction products was proposed to try to separate the different organic components.

Several runs were made to collect a large amount of extraction liquor. This large batch of liquor was acidified with concentrated HCl to a pH of approximately 2. A large mass of the tar-like precipitate resulted. The precipitate was washed and then dried for several hours. The precipitate was then placed in a 600-milliliter Soxhlet extractor and washed with the various selected solvents. The order of the solvent extractions was as follows:

1. Benzene
2. Chloroform
3. Acetone
4. Methyl Alcohol

Also, a separate portion of the precipitate was washed several times with carbon disulfide. The amount of precipitate which dissolved varied directly with the order in which the solvents were used. It was hoped that this procedure would separate the lower molecular weight portions of the precipitate from the higher ones. The carbon disulfide was used separately in an added effort to extract any low molecular weight portions.

Each of the above extract samples was evaporated to dryness and the residues remaining were analyzed by the use of a Beckman IR-4 infrared spectrophotometer (see Figure 4 through Figure 7). The infrared analysis was used to find out what structural groups were present in solvent extracted portions of the precipitate. Some tests were made toward confirming the infrared analyses.

The liquors remaining after the tar-like precipitates were removed were also analyzed to a certain extent. The organic materials in these liquors were collected as previously explained. In most cases, the organic materials were in a resinous form. However, several of the extractions yielded long needle-like organic crystals along with the resinous product. It was first suspected that the crystals were inorganic. Tests were made to see if the crystals were organic. First of all, melting point determinations made on the crystals showed them to melt at approximately 130° centigrade. It is very unlikely that any inorganic crystals would be present which would melt at this temperature. Also, when placed in a hot flame, the crystals charred and appeared to be carbonaceous. The crystals were very soluble in several organic solvents. After these tests it was concluded that the crystals were organic. Both the crystals and the resinous product were then subjected to infrared analysis.

DISCUSSION OF RESULTS

A. Quantitative Yields

1. Total Yield Study

As mentioned before, a study was made to see what total per cent of the organic material in a single shale sample could be recovered by several extractions. This study yielded some very encouraging results. The first extraction of the 133-gram sample yielded organic material corresponding to 1.54 per cent of the shale weight. In the following five extractions of the original sample a considerable amount of additional organic materials were recovered (see Table III). In all six extractions of the shale sample, approximately 6.7 per cent of the original shale weight was recovered as organic material (Runs 31, 50, 51, 52, 56, 58, 59). Run 52 was made without adding any $KMnO_4$ to determine what part solubility was playing in this study. In this run an additional 0.379 per cent was recovered as organic material. This indicated that solubility was a factor but that most of the additional recovery in each successive run was being made possible by the additional oxidation taking place. Since the Green River shale is known to contain about 8-10 per cent total organic material, the 6.7 per cent recovery corresponded to about

70-80 per cent of the total organic material available in the shale. However, these yields do not take into account the weight of oxygen picked up in the process.

The results obtained in this total yield study showed that alkaline extractions of the oxidized shale could be used to produce organic material from the shale. At this point, no consideration was given to the specific organic material desired.

Of considerable interest during this study was the fact that with the initial extract, only 5.7 per cent of the recovered organic material was obtained by precipitation upon acidification of the extraction liquor. On the second extraction, 55.5 per cent of the recovered organic material was obtained by the acidification step, and on the third extraction, 65 per cent was obtained. After a fourth extraction made in the absence of $KMnO_4$, the amount of acid soluble material recovered was again greater than the acid insoluble material. This remained true for each of the runs thereafter and the ratio of soluble to insoluble material remained quite constant. It is possible that in the first three extractions some of the oxidized organic materials were left in the shale residue because of the solubility limitations of the alkaline liquor and as they were oxidized to a higher level in subsequent runs, they were recovered as acid insoluble materials. In the fifth extraction after the excess oxidized organic material had been removed and in the sixth and seventh extractions where solubility was not a factor because of low yields, this was not the case, and again more of the organic material appeared as acid soluble material.

2. Air-Oxidation Runs

Runs were made in which the oil-shale was air-oxidized and then later extracted with alkaline solutions. Analysis of these runs (Runs 55 and 57) showed that it was also possible to obtain considerable amounts of the organic material from the oil-shale by this method. In Run 55, a high alkaline concentration was used in the extraction and in Run 57, a low alkaline concentration was used (see Table III). In both cases, a considerable amount of the available organic material was extracted. In Run 57, the shale was air-oxidized at a higher average temperature than in Run 55; however, in Run 55, the shale was oxidized 1/2 hour longer. The yields in Runs 55 and 57 were 1.55 and 1.13 per cent of the shale sample, respectively. This corresponds to about 15-20 per cent and 10-15 per cent of the available organic material in the shale.

More air-oxidation studies are now being made by another investigator in a more efficient oxidation unit. It is hoped that very high yields will eventually be obtained by this method.

3. Statistical Design Runs

In an attempt to optimize the extraction conditions for the highest per cent recovery of organic material per single extraction, a series of runs was made following a statistical design. The runs were set up with the help of a fellow research partner and the Montana State College Mathematics Department. The runs were designed (see Tables I and II) to determine in what general direction the extraction variables should be changed from a mean value to obtain the highest yield of organic material in a single extraction. An expression in which the per cent recovery is defined in terms of the extraction variables was determined. This expression was found to be

$$Y = 1.669 - 0.453Z_1 + 0.266Z_2 - 0.268Z_3 - 0.104Z_4$$

The per cent recovery of organic material is denoted as Y and the coded extraction variables as follows:

$$Z_1 = \frac{X_1 - 100}{33}, \quad Z_2 = \frac{X_2 - 20}{10}, \quad Z_3 = \frac{X_3 - 200}{70},$$

$$Z_4 = \frac{X_4 - 34}{33}$$

From the calculated values of the coefficients the following general conclusions were drawn:

To approach the highest yield of organic material in a single extraction with 240 grams of solvent, the extraction conditions must be altered as follows:

1. Decrease the amount of shale per charge from 100 grams.
2. Increase the amount of $KMnO_4$ per charge from 20 grams.
3. Decrease oxidation-extraction temperature from 200°C.
4. Decrease the amount of soda ash per charge from 34 grams.

In order to establish optimum extracting conditions more definitely, other sets of statistically designed runs would have to be made. The above information was established with the hope of having an idea of what type of extraction conditions should be used with later air-oxidation studies. At the present time, the detailed study of the air-oxidation of the oil-shale which is being carried out by another investigator is aimed at optimizing both the air-oxidation conditions and the extraction conditions by the use of statistical designs.

B. Qualitative Results

The products obtained in preliminary extractions were amorphous tar-like materials. These products were suspected to be complex acid mixtures and several attempts were made to esterify them. It was evident that some esterification took place; however, most of the tar-like material remained unchanged. Since high conversions were not obtained, it was decided that possibly the tar-like materials should be left unchanged for identification analysis. Infrared analysis was chosen for trying to obtain a product identification.

Infrared analysis was made on the tar-like precipitate obtained from the acidification of the extraction liquors (see Figure 4-A). The numbers of the absorption contributions listed below refer to the absorption peaks which are likewise numbered on the infrared analysis charts. Interpretation of all of the infrared analysis charts was accomplished with the aid of Dr. C. Baker of the Montana State College Chemistry Department, and the results obtained are as follows:

1. Broad band spectra contribution of the OH in a carboxylic (COOH) structure.
2. Aliphatic carbon-hydrogen stretch or bonding.
3. Contribution of either a lactone or an anhydride structure.

4-7. All broad band spectra contributions of different types of carbonyl structures (i.e., possibilities are 4. - acid; 5. - ketone or cyclic; 6. - aldehyde; 7. - ketone or aldehyde).

8. Broad band characteristic of complex acid structures.
9. The same as 8.
10. Possibly either anhydride or lactone absorption or acid contribution.
11. Possible methylene or ($-CH_2-$) linkage.

From the above analysis, it may be concluded that the precipitate is more than likely a mixture of complex acids with the presence of several types of carbonyl groups. Also, the presence of a lactone or an anhydride is indicated by the peaks at 5.5 and 5.6 microns. Since there is also a possibility of cyclic compounds being present, the precipitate was analyzed for sulfur and nitrogen to see if these elements could be tied up in heterocyclic structures. The analysis showed the precipitate to contain 0.91 per cent nitrogen and 2.15 per cent sulfur.

A second infrared analysis was made on a carbon disulfide solution obtained from washing the precipitate with pure CS_2.

Interpretation of this infrared chart is as follows (see Figure 4-B):

1. Broad band spectra contributions of the OH in a carboxylic (COOH) structure.
2. Aliphatic carbon-hydrogen stretch or bonding.
3. Contribution of either a lactone or an anhydride structure.
4. One type of carbonyl structure contribution (possibly aldehyde but probably acid carbonyl).
5. Broad band contribution of CS_2 solvent.
6. Possibly either lactone, anhydride or acid contribution.

It may be noticed that in both Figure 4-A and Figure 4-B there is a considerable amount of carbon-hydrogen bonding. However, this carbon-hydrogen bonding is in cyclic compounds rather than straight-chain as suggested in other work done on oil-shale oxidation (5). This may be assumed because the sharp band of methylene absorption at 14.2 microns shows only slightly or not at all. This is true with all of the extraction products which were analyzed in this investigation.

The third infrared analysis was made on the benzene-extracted portion of the tar-like precipitate (see Figure 5-A). In each of the solvent extracted portions of the precipitate, the solvent was evaporated and the infrared analysis was made on the remaining film. Interpretation of Figure 5-A is as follows:

1. Broad band spectra contributions of the OH in a carboxylic (COOH) structure.
2. Aliphatic carbon-hydrogen bonding.

3-4. Both either a contribution of a lactone or an anhydride structure.

5. Probably contribution of acid carbonyl structure.

6-7. Broad band spectra caused by complex acid structures.

8. Possibly a lactone or an anhydride contribution.

Figure 5-B is the infrared analysis of the chloroform extracted portion of the precipitate and shows a substance very similar to that shown in Figure 5-A. The interpretation of Figure 5-B is:

1. Broad band spectra contributions of the OH in a carboxylic (COOH) structure.

2. Aliphatic carbon-hydrogen bonding.

3. Probably contribution of acid carbonyl groups.

4-6. Broad band spectra caused by complex acid structures.

7. Probably a small amount of methylene ($-CH_2-$) bonding.

The main difference between Figure 5-A and Figure 5-B is the absence of the lactone or anhydride absorption in Figure 5-B.

Infrared analysis charts Figure 6-A and Figure 6-B again show two substances of practically identical nature except for the presence of the lactone or anhydride structural absorption band in Figure 6-A. Figure 6-A shows the acetone extracted portion of the precipitate, while Figure 6-B is an analysis of the methyl alcohol extracted portion. Both portions are essentially very complex acid mixtures.

Figure 7-A and Figure 7-B are charts from the analysis of the products obtained from the acetone extractions of the oil-shale extract liquor after the tar-like precipitate was removed. Figure 7-A is the analysis of the long needle-like crystals obtained in several of the extractions. This chart could only be partially

interpreted with the present information. Interpretation of Figure 7-A is as follows:

1. Very sharp but unidentified absorption band.
2. Shows the lack of any carbon-hydrogen stretch or bonding.
3. Possibility of a small amount of carboxylic (COOH) structure.
4. Unknown broad band spectra contribution.
5-6. Possibly different carbonyl structures.
7. Contribution characteristic of complex acid structures.
8. Possibly an acid structure but unlikely because of its position.
9. Could be methylene absorption but this is unlikely because of the lack of carbon-hydrogen bonding in 2.

It may be concluded from the weak identification data obtained in 7-A, that a great deal more identification work must be done on the crystals with more complete facilities. At first, it was suspected that the crystals were amido acid structures (i.e., compounds with a -NH-CO- or -N=C(OH)- linkage and containing the acid -COOH group); however, the absorption regions for such structures are too low in Figure 7-A. Also, analysis of the crystals by the Ninhydrin Test (6) showed no evidence of $-NH_2$ or -NH- groups being present. Analysis of the crystals for elemental nitrogen and sulfur showed them to be 0.201 per cent nitrogen and 0.228 per cent sulfur. Melting point determinations were made and found to be quite sharp in the range 129°-133° centigrade. Assuming that an organic compound melting in this range has a molecular weight of approximately 180, the nitrogen and sulfur determinations were calculated on a mole per cent basis. This made the crystals a compound which was approximately 1.3 mole per cent nitrogen and 1.3 mole per cent sulfur. This indicates that probably these two elements were not present as part of the crystalline structure.

Figure 7-B is the infrared analysis of the resinous gum obtained from the acetone extractions of acidified extract liquors. This analysis shows the gum to be quite similar to some of the extract portions of the heavier precipitate. This again seems to indicate that the only difference between some of the extraction products is some degree of polymerization. Interpretation of Figure 7-B shows:

1. Broad band spectra contribution of the OH in a carboxylic (COOH) structure.
2. Aliphatic carbon-hydrogen stretch or bonding.
3. Lactone or anhydride contribution.
4. Probably acid carbonyl structure contributions.
5-6. Broad band spectra characteristic of complex acid structures.
7. Either lactone, anhydride or acid contribution.

Once again, Figure 7-B is another product which is essentially a complex acid mixture.

Esterification could be used to determine whether the extraction products contain anhydride or lactone structural groups. If any anhydride groups were present, esterification would eliminate the anhydride absorption. However, if lactone structural groups were present, their absorption region would remain unchanged on esterification.

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APPENDIX

TABLE I.

Level of Extraction Variables for Statistical Runs

X - Variable	Code and Level		
	-1	0	+1
X_1 -- Grams Shale	67	100	133
X_2 -- Grams Permanganate	10	20	30
X_3 -- Temperature °C	130	200	270
X_4 -- Grams Soda Ash	1	34	67

TABLE II.

Series of Statistical Runs Made

Code	Run No.	X_1	X_2	X_3	X_4	% Recovery
-1-1-1-1	61	67	10	130	1	2.06
1-1-1 1	62	133	10	130	67	1.13
-1 1-1 1	63	67	30	130	67	2.57
1 1-1-1	64	133	30	130	1	1.99
-1-1 1 1	39	67	10	270	67	1.62
1-1 1-1	65	133	10	270	1	0.81
-1 1 1-1	66	67	30	270	1	2.24
1 1 1 1	67	133	30	270	67	0.94
0 0 0 0	68	100	100	200	34	1.59
0 0 0 0	69	100	100	200	34	1.78

TABLE III. ANALYSIS OF EXTRACTION PRODUCTS FROM OIL-SHALE EXTRACTIONS

								PRODUCT ANALYSIS				
Run No.	Remarks	Extr. Time (hr)	Extr. Temp. °C	Gm. $KMnO_4$	Gm. Soda-Ash	Gm. Low-Shale	Gm. H_2O	Total Ext. Vol. (ml)	Aliquot Vol. (ml)	Gm. ppt.	Gm. Acetone Res.	Total % Recovery
30	200 hr. Ext.	200	200	20	66	133	240	232	119	0.141	0.542	1.00
31	Run for total % Recovery Det'n.	20	200	20	66	133	240	371	121	0.038	0.630	1.55
50	Residue from 31. (2nd Extr.)	20	200	20	66	133 (orig. wt.)	240	335	150	0.405	0.325	1.22
51	Residue from 50. (3rd Extr.)	20	200	20	66	133	240	346	150	0.543	0.292	1.45
52	Residue from 51. (Check run) (No $KMnO_4$)	20	200	0	66	133	240	300	150	0.124	0.127	0.379
56	Residue from 52. (4th Extr.)	20	200	20	66	133	240	290	150	0.242	0.713	1.38
58	Residue from 56. (5th Extr.)	20	200	20	66	133	240	375	150	0.068	0.206	0.513

TABLE III. ANALYSIS OF EXTRACTION PRODUCTS FROM OIL-SHALE EXTRACTIONS (continued)

								PRODUCT ANALYSIS				
Run No.	Remarks	Extr. Time (hr)	Extr. Temp. °C	Gm. $KMnO_4$	Gm. Soda-Ash	Gm. Low-Shale	Gm. H_2O	Total Ext. Vol. (ml)	Aliquot Vol. (ml)	Gm. ppt.	Gm. Acetone Res.	Total % Recovery
59	Residue from 58. (6th Extr.)	20	200	20	66	133	240	240	120	0.036	0.083	0.179
53A	Low Amount Soda Ash	20	200	20	7	133	240	340	150	0.572	0.644	2.06
53B		20	200	20	7	133	240	340	150	0.490	0.640	1.95
54	High Amount $KMnO_4$	20	200	40	66	133	240	345	150	0.276	0.703	1.70
55*	Air-Oxid. Run	20	200		58	120 (of air oxid.)	217	294	150	0.503	0.443	1.55
57*	Air-Oxid. Run & Low Soda Ash	20	200		5.7	110 (of air oxid.)	209	410	150	0.204	0.248	1.13
60	No Soda Ash	20	200	20	0	133	240	350	150	0.612	0.368	1.72
61	Statistical Des. Run	20	130	10	1	67	240	375	150	0.181	0.371	2.06

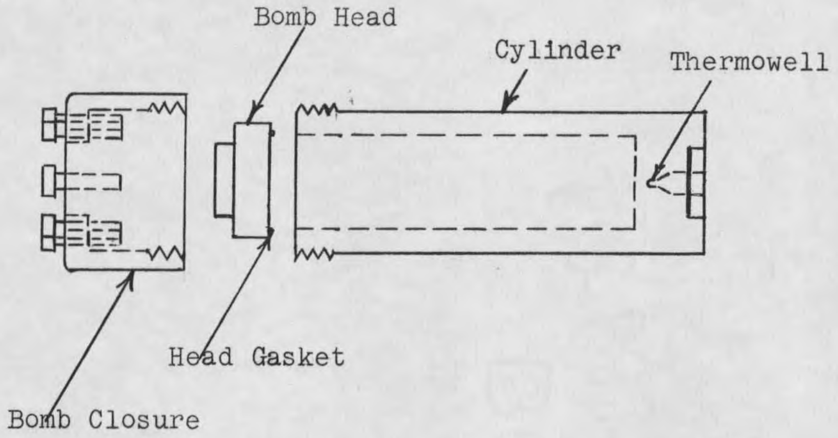
*Air oxidation conditions used in runs 55 and 57 were as follows:

Run No. 55 Air oxidation for 1/2 hour at 110°C
for 3 hours at 115°C

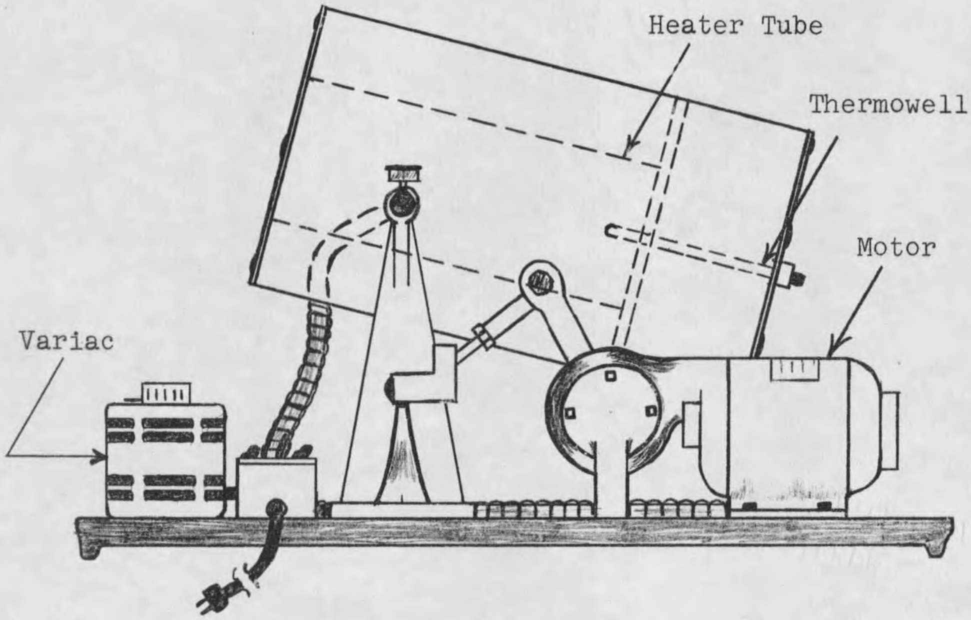
Run No. 57 Air oxidation for 3 hours at 200°C
for 6 hours at 200°C

TABLE III. ANALYSIS OF EXTRACTION PRODUCTS FROM OIL-SHALE EXTRACTIONS (continued)

								PRODUCT ANALYSIS				
Run No.	Remarks	Extr. Time (hr)	Extr. Temp. °C	Gm. $KMnO_4$	Gm. Soda-Ash	Gm. Low-Shale	Gm. H_2O	Total Ext. Vol. (ml)	Aliquot Vol. (ml)	Gm. ppt.	Gm. Acetone Res.	Total % Recovery
62	Statistical Des. Run	20	130	10	67	133	240	365	150	0.426	0.197	1.13
63	Statistical Des. Run	20	130	30	67	67	240	405	150	0.034	0.600	2.57
64	Statistical Des. Run	20	130	30	1	133	240	515	150	0.323	0.448	1.99
65	Statistical Des. Run	20	270	10	1	133	240	445	150	0.244	0.117	0.805
66	Statistical Des. Run	20	270	30	1	67	240	330	150	0.347	0.328	2.24
67	Statistical Des. Run	20	270	30	67	133	240	445	150	0.110	0.303	0.920
68	Statistical Des. Run	20	200	20	34	100	240	400	150	0.172	0.425	1.59
69	Statistical Des. Run	20	200	20	34	100	240	425	150	0.248	0.381	1.78
39	Statistical Des. Run	20	270	10	67	67	240	370	150	0.100	0.340	1.62



A. BOMB CYLINDER



B. EXTRACTION APPARATUS

(not to scale)

FIGURE 1. PARR EXTRACTION APPARATUS.

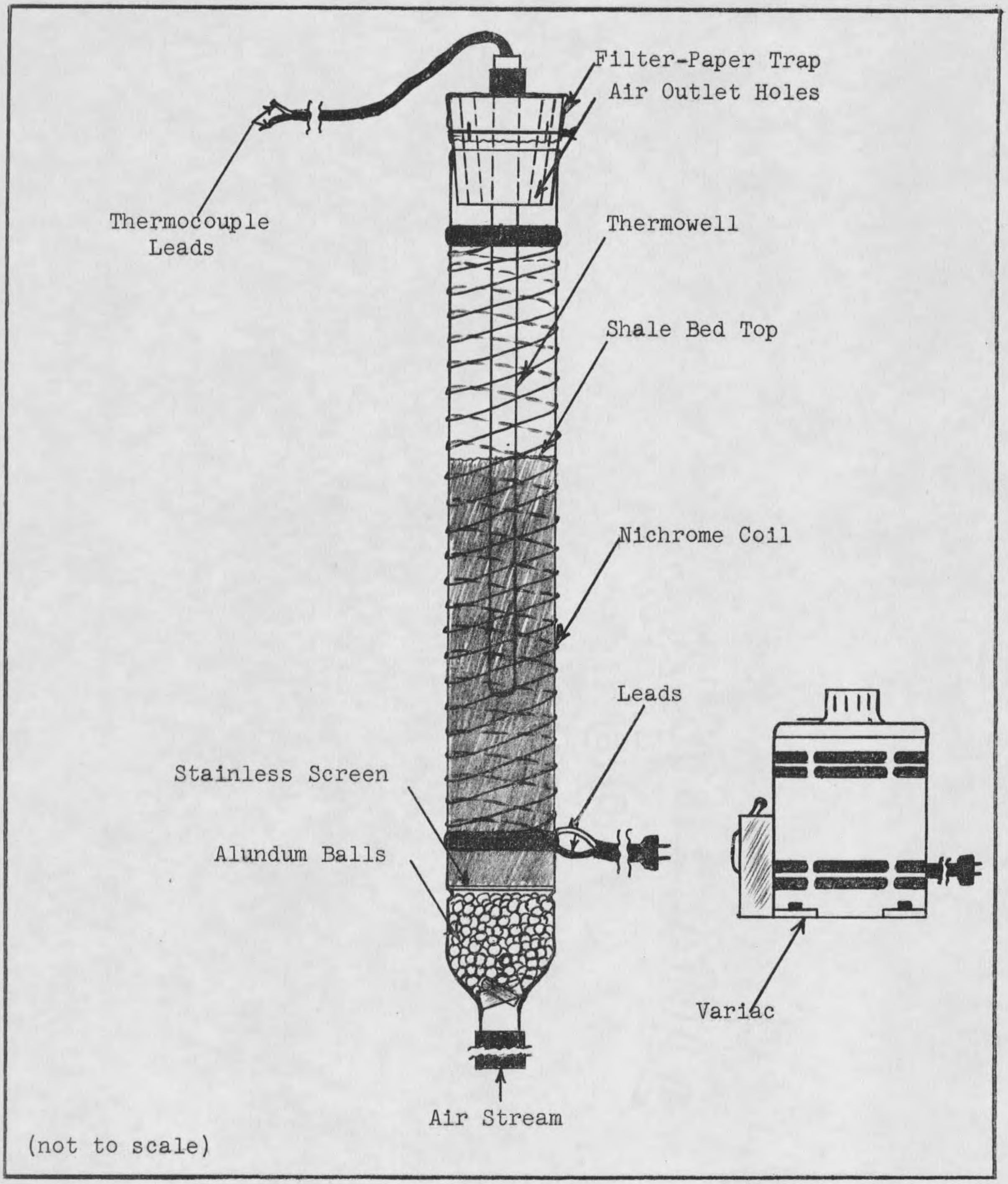


Figure 2. Air-Oxidation Column.

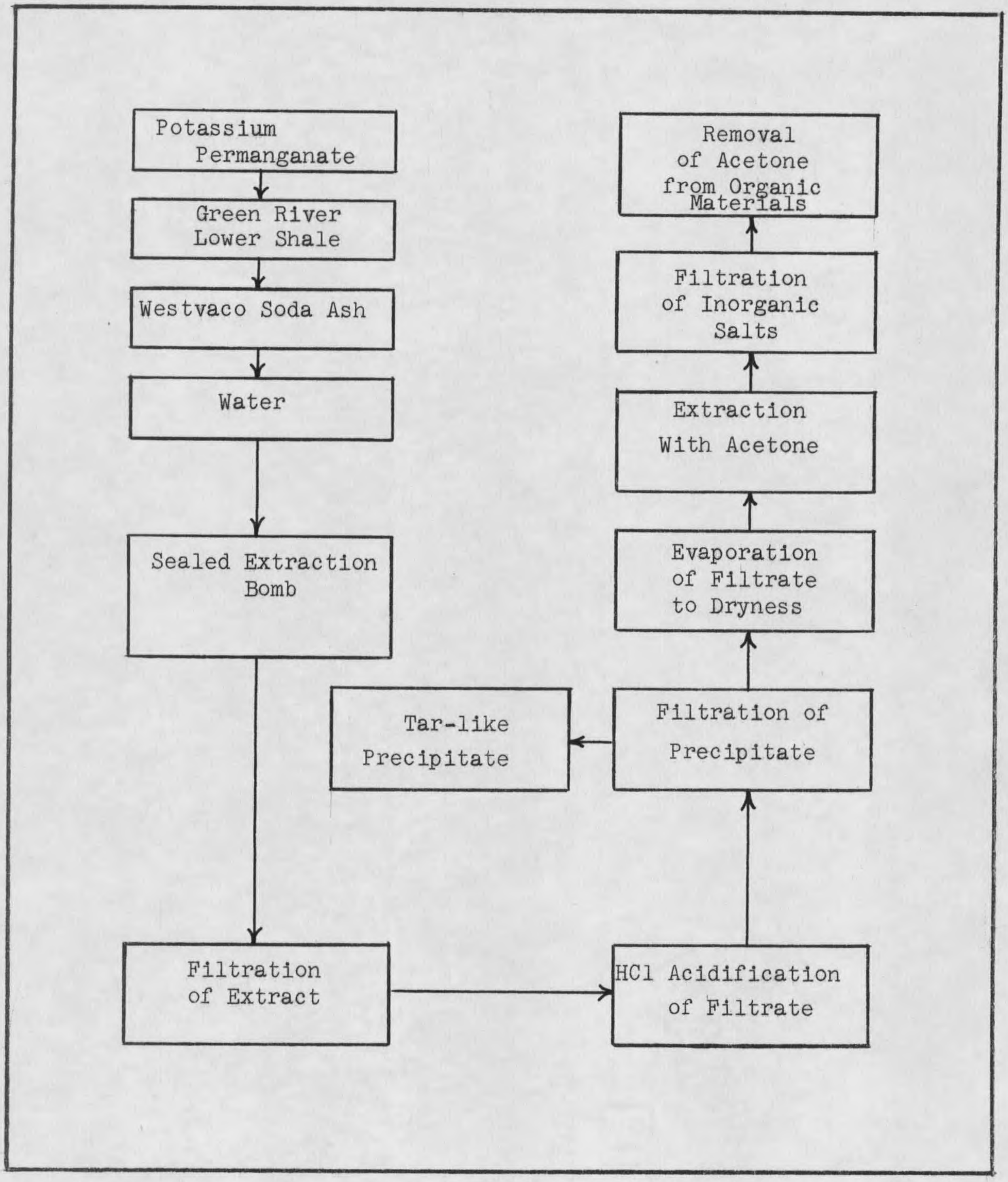
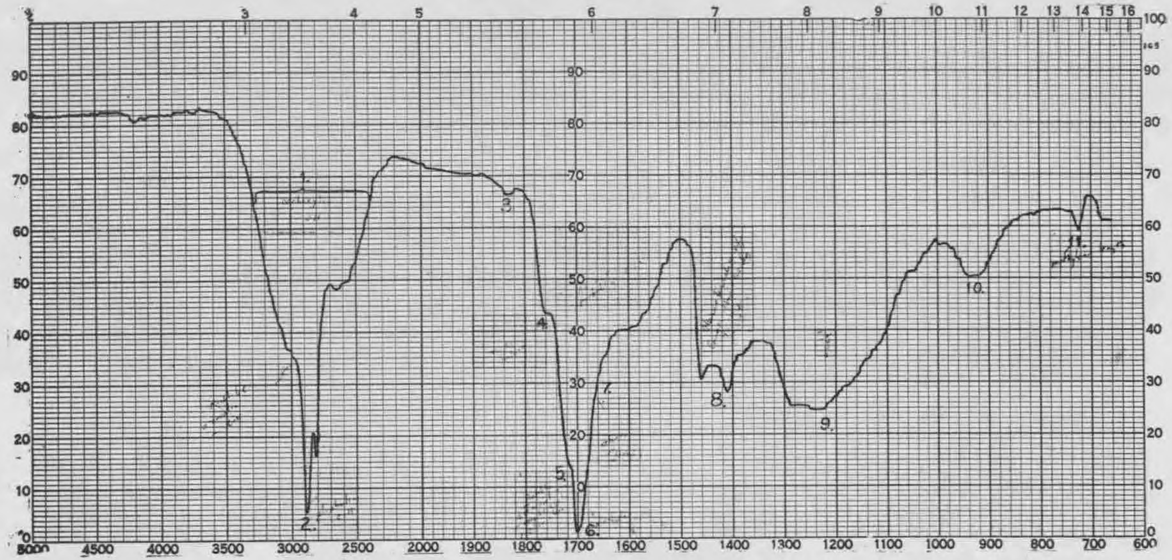


Figure 3. Block Flow Diagram of Alkaline-Permanganate Extractions.

A



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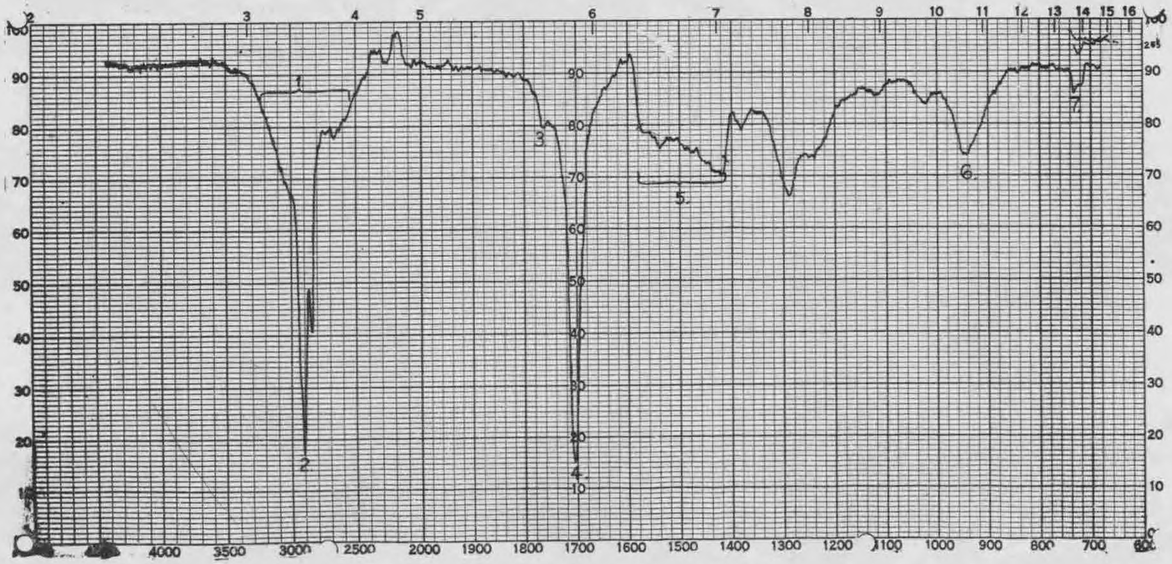
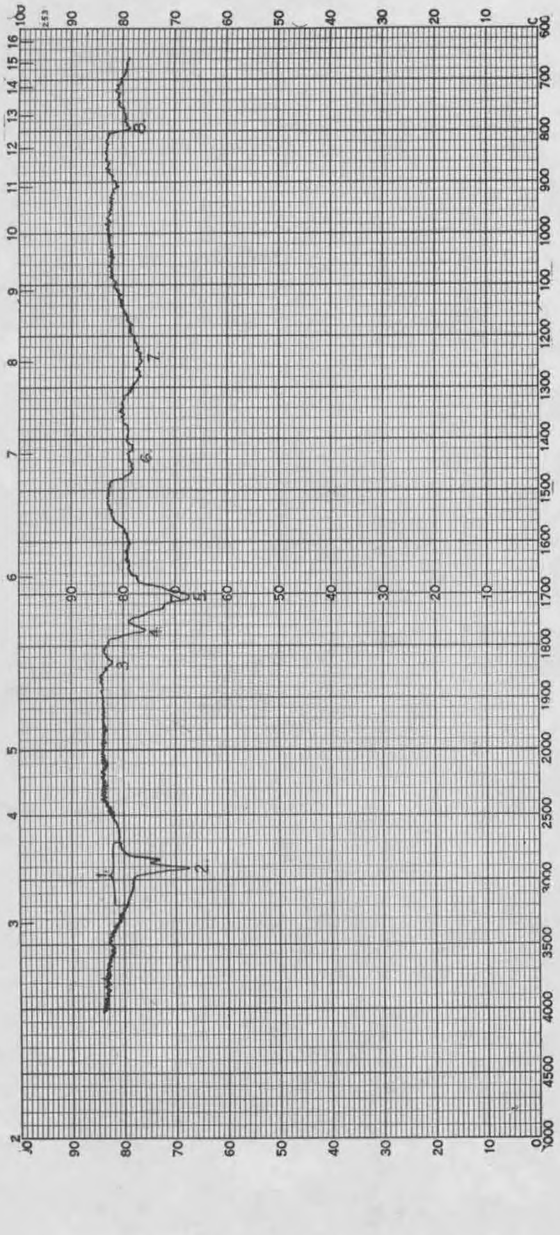


Figure 4-A. Infrared Analysis of Tar-like Precipitate

Figure 4-B. Infrared Analysis of CS_2 Fraction of Precipitate



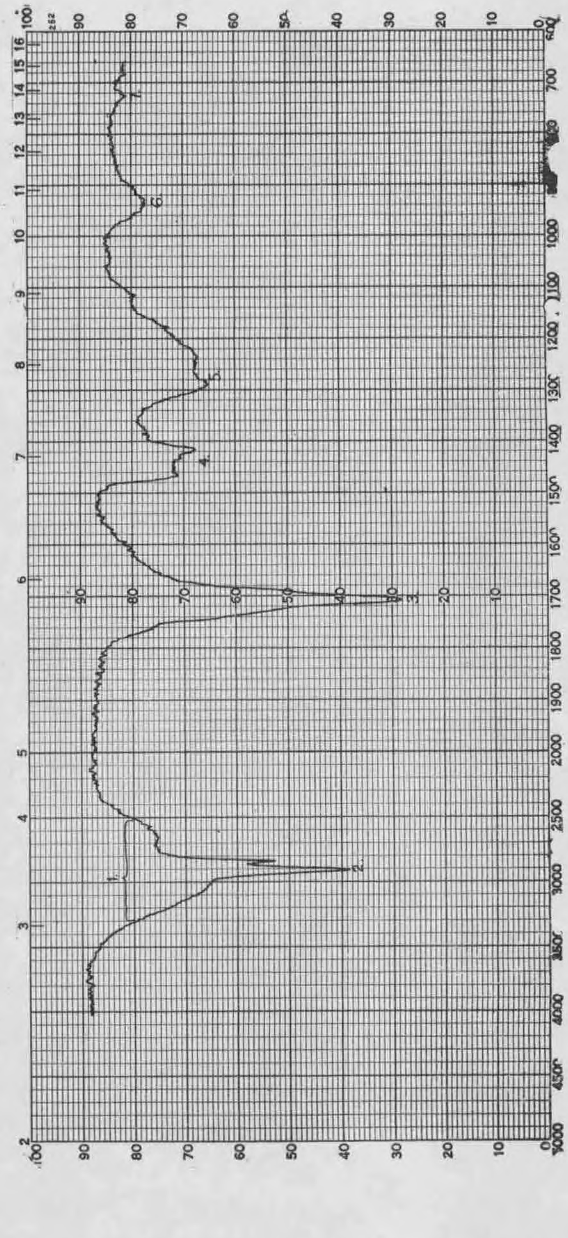
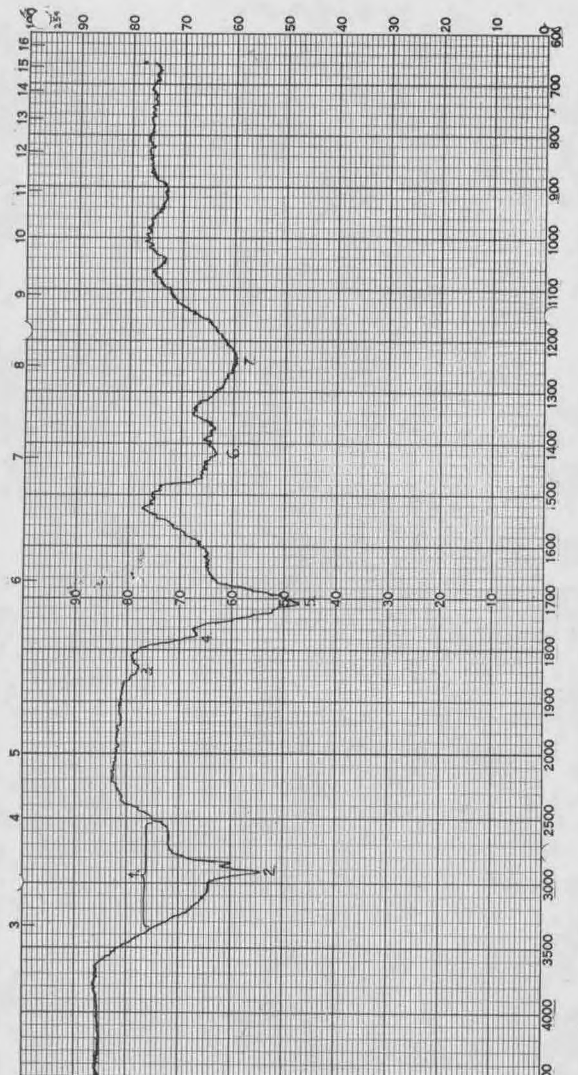


Figure 5-A. Infrared Analysis of Benzene Fraction of Precipitate
Figure 5-B. Infrared Analysis of Chloroform Fraction of Precipitate

A



B

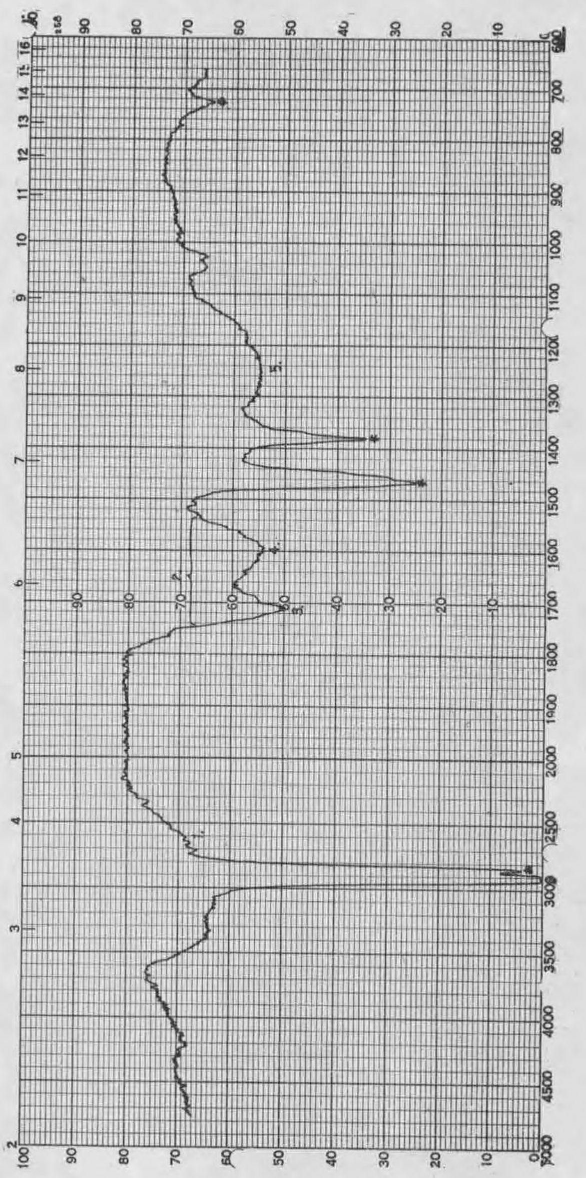
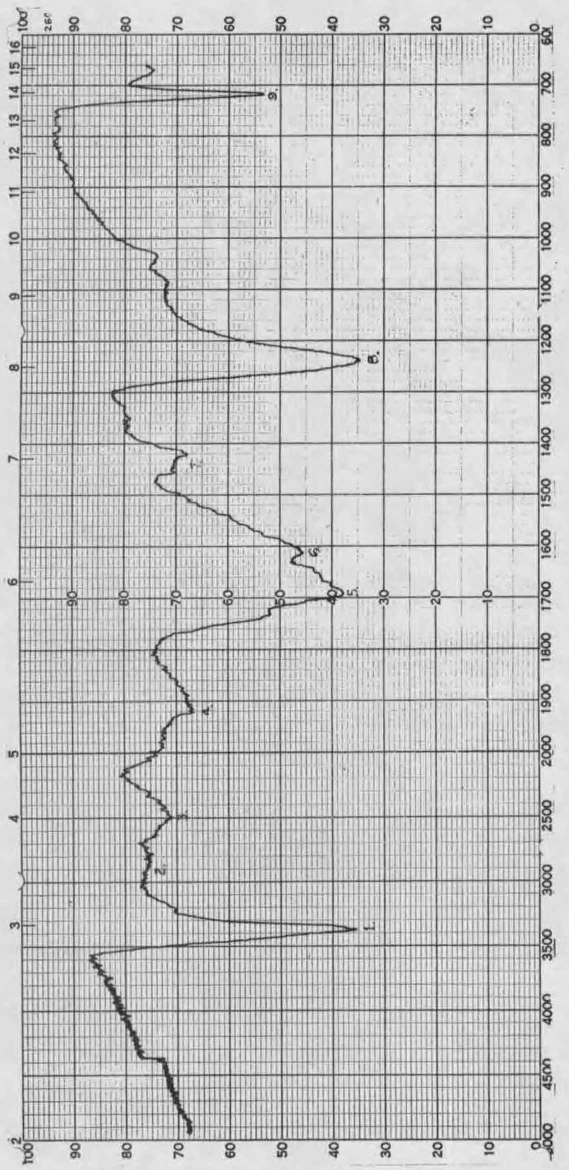
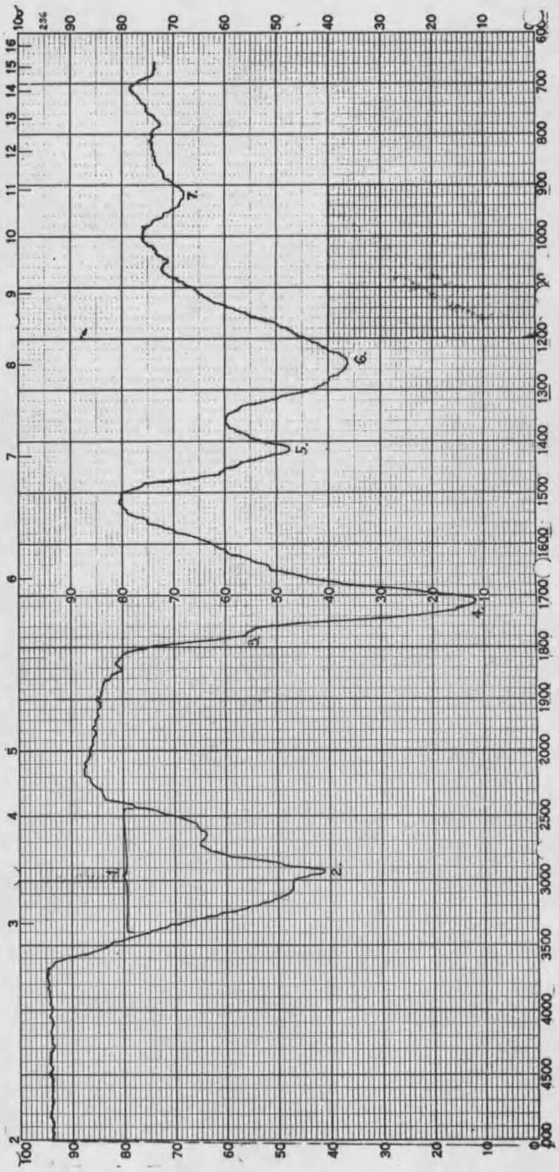


Figure 6-A. Infrared Analysis of Acetone Fraction of Precipitate
Figure 6-B. Infrared Analysis of Methanol Fraction of Precipitate



A



B

Figure 7-A. Infrared Analysis of Acetone Extracted Crystals
Figure 7-B. Infrared Analysis of Acetone Extracted Resinous Material

[redacted]

SuTter, R. C.
Extraction of organic materials from Green River, Wyoming...

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FE 23 '60	Glenn Black
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