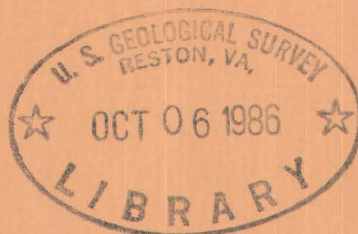


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# A Photometric Method for the Estimation of the Oil Yield of Oil Shale

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*Trace Elements Investigations Report 152*

*Open Filed 10/19/51. GS-B-992.*

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

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A PHOTOMETRIC METHOD FOR THE ESTIMATION  
OF THE OIL YIELD OF OIL SHALE

by

Frank Cuttitta

May 1951

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A PHOTOMETRIC METHOD FOR THE ESTIMATION  
OF THE OIL YIELD OF OIL SHALE

by

Frank Cuttitta

ABSTRACT

A method is presented for the distillation and photometric estimation of the oil yield of oil-bearing shales. The oil shale is distilled in a closed test tube and the oil extracted with toluene. The optical density of the toluene extract is used in the estimation of oil content and is converted to percentage of oil by reference to a standard curve. This curve is obtained by relating the oil yields determined by the Fischer assay method to the optical density of the toluene extract of the oil evolved by the new procedure. The new method gives results similar to those obtained by the Fischer assay method in a much shorter time. The applicability of the new method to oil-bearing shale and phosphatic shale has been tested.

INTRODUCTION

As thousands of oil shale samples have been assayed in the Trace Elements laboratory, Geochemistry and Petrology Branch, the purpose of the investigation was to study the applicability of photometric procedures to the estimation of oil yield of oil-bearing shales in

an effort to develop a simple and rapid method for the determination of oil content of shales and phosphatic shales.

The results of the determination should have a direct correlation with the results obtained by the Fischer assay method so that Fischer determinations could still be used.

The analysis of oil shales is usually made by the Modified Fischer Retort Method 1,2,3/ (hereinafter referred to as the Fischer method or Fischer assay). In this method the shale is retorted in a special cast-aluminum retort, and the oil yield is determined by condensing and measuring the volatilized oil. Using one still, an assay by the Fischer method requires approximately two hours for completion. The Fischer method also requires rather elaborate apparatus and is not a convenient method for fast routine work where, in many cases, the primary object is to screen large numbers of samples.

For qualitative determinations closed-tube distillation of oil has been used by Trask 4/ and Takahashi.5/ When a rock rich in bitumens

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1/ Stanfield, K. E., and Frost, C. I., Method of assaying oil shale by a Modified Fischer Retort: U. S. Bur. Mines Rept. Inv. 3977, 1946; 4477, 1949.

2/ Karrick, L. C., Manual of testing methods for oil shale and shale oil: U. S. Bur. Mines Bull. 249, 1926.

3/ Guthrie, B., Studies of certain properties of oil shale and shale oil: U. S. Bur. Mines Bull. 415, 1938.

4/ Trask, Parker D., Origin and environment of source sediments of petroleum, Houston, Texas, Am. Petroleum Inst., 1932.

5/ Takahashi, Junichi, The marine kerogen shales from the oil fields of Japan: Tohoku Imp. Univ. Sci. Repts., 3d ser., vol. 1, pp. 63-156, 1923.

is subjected to destructive distillation, the oil formed by the distillation accumulates in the horizontal test tube just behind the water. Generally, the lightest constituents of the oil are partly mixed with the water, and the heavier and darker fractions are found toward the hot end of the tube. By looking down the tube during the heating, droplets of oil can be seen issuing as a fine mist from the sample and condensing on the sides. The volume of oil produced by distillation varies greatly and may be so slight that no distillate is visible and only the odor of oil can be detected.

In attempting to estimate the oil content of oil-bearing shale, no correlation could be established between the Fischer assay and a gravimetric determination of the oil evolved in the closed-tube distillation. However, volumetric determination of the oil evolved in the closed-tube distillation was about twice as rapid as the Fischer assay method and gave results comparable to those obtained by the Fischer method. Details of the volumetric determination will be published in a forthcoming Trace Elements report, now in preparation, and entitled "A volumetric method for the estimation of the oil yield of oil shale," by Frank Cuttitta and F. S. Grimaldi.

The following report shows the feasibility of using the optical density of a toluene solution of the oil evolved in a closed-tube distillation as a rapid and quantitative method for the estimation of the oil yield. The method consists of destructively distilling a 0.5-g sample of oil shale in a closed test tube, extracting the oil evolved with toluene, and measuring the optical density of the



solution with a filter photometer. The amount of oil is read from a curve (fig. 1) relating the oil yields by Fischer assay to the optical density of the toluene extract of the oil distilled by the new procedure. To obtain this curve the optical densities ( $\times 10$ ) of the oil obtained by the new procedure were plotted against the percentage of oil as given by the Fischer method. A scatter diagram was obtained and a mean straight curve was fitted visually through the points. The estimated oil yields as obtained by using the standard curve (fig. 1) differed from the Fischer oil yields by an average of 0.37 percent absolute. The maximum difference between the determined (Fischer assay) and the estimated oil yields was 0.94 percent. Figure 2 is the same curve expressed in terms of the relationship of optical density ( $\times 10$ ) to Fischer oil yield in gallons per ton of shale.

This linear relationship (fig. 1) was established from a study of 75 samples of Chattanooga shale from Tennessee chosen to represent the different grades of shale likely to be encountered in that area. The recommended procedure is to establish similar optical density - oil yield relationships for other specific areas, such as Idaho and Montana, from representative samples. However, a study of 10 samples from the Phosphoria formation in Montana and Idaho showed that figure 1 (established for samples of Chattanooga shale) was applicable also for assay of these samples. This similarity in relationship of optical density to oil yield for the two areas gives some hope that the same curve can be applied to the use of this method for oil shales from other areas.

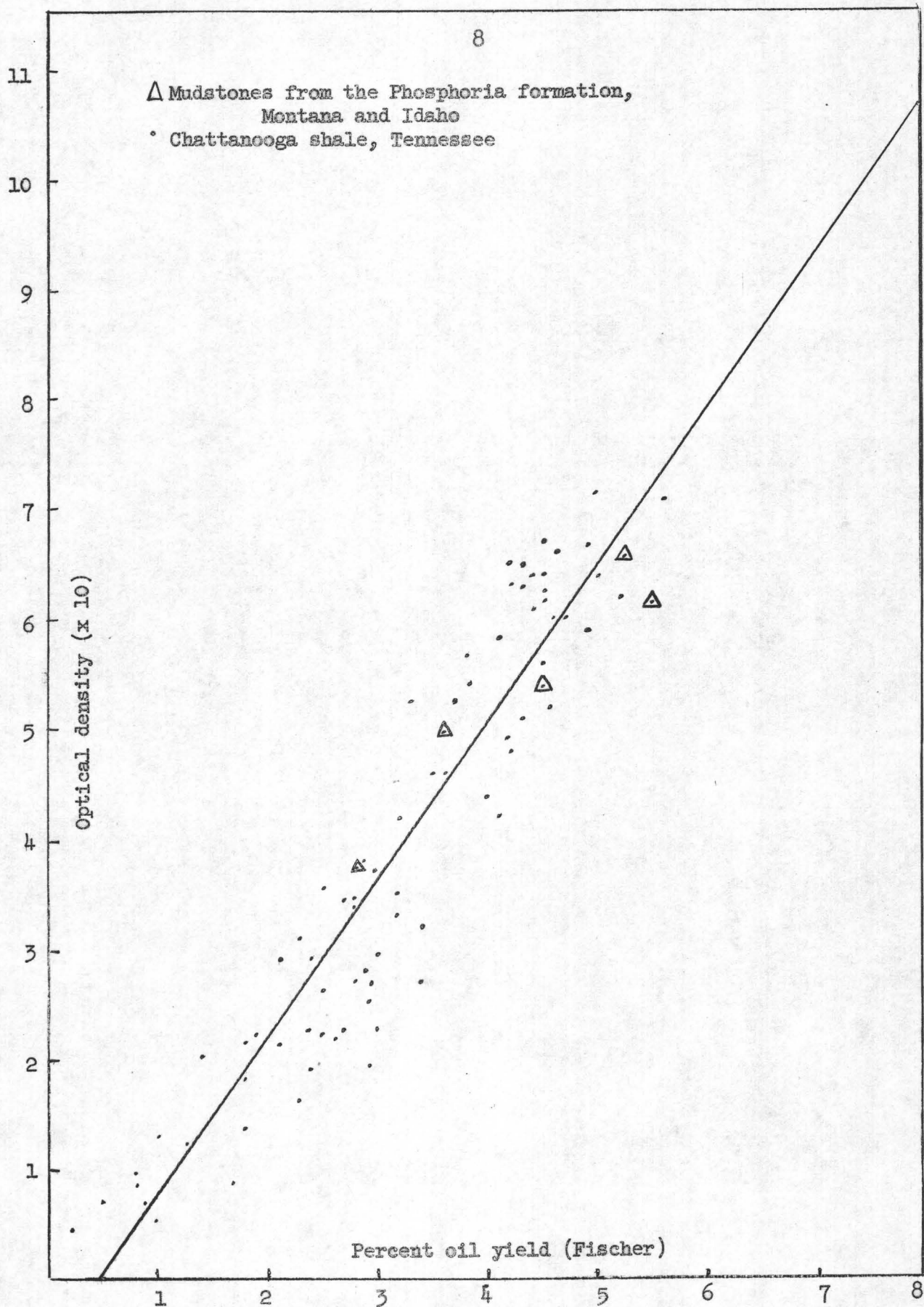


Figure 1.--Relation of optical density (x 10) to percentage oil yield by Fischer assay method

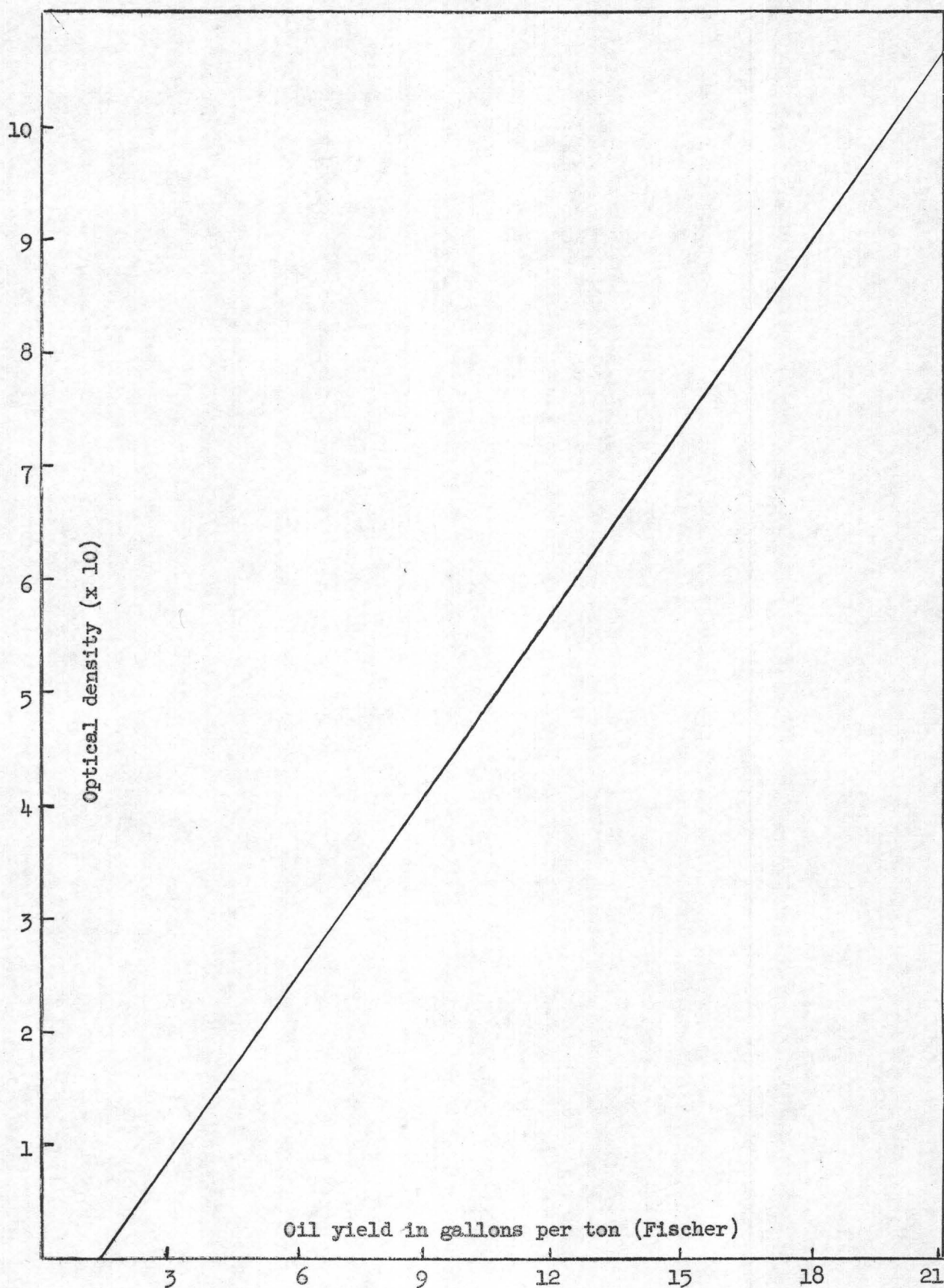


Figure 2.--Relation of optical density (x 10) to Fischer oil yield in gallons per ton



The method is simple, rapid, and accurate, and 8 to 10 determinations can be made in the same length of time required for the completion of one Fischer assay.

#### PROCEDURE FOR ESTIMATING THE OIL YIELD

##### Preparation of the sample

A representative -80 mesh portion of the sample is dried in an oven at 110°C for one hour. Oven drying may be omitted for samples to be assayed on the "as received" basis. A -80 mesh sample size was selected because this size is used generally in the Geological Survey for chemical analysis. No attempt was made to determine the effect of particle size upon oil yield.

##### Apparatus

The test tube employed in the closed-tube distillation of the shale is a pyrex, glass-stoppered test tube; 16 x 150 mm; no. J-2345; manufactured by the Scientific Glass Apparatus Co., Bloomfield, N. J.; with a no. 16 standard taper glass stopper.

The tube furnace used was made by winding a coil of nichrome (no. 26 B and S), the coils spaced about 1/8-inch apart, on an iron tube that has been covered with a piece of asbestos (or mica) to avoid short circuiting the winding. The inner tube and its resistance wire are covered with several layers of asbestos and finally coated with alundum (alumina with clay binder). The details of this furnace are shown in figure 3. The embedding of the nichrome element in asbestos

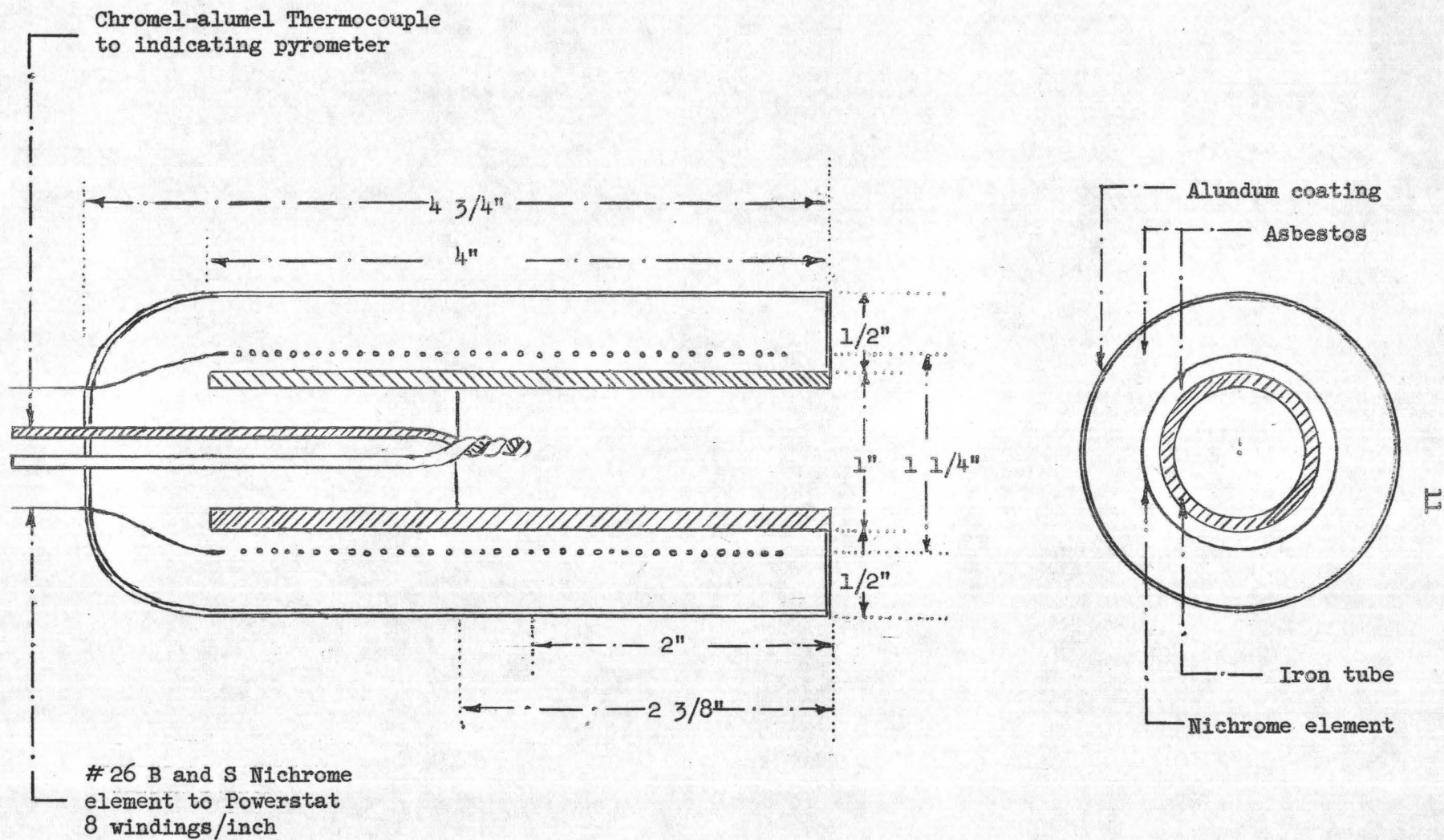


Figure 3.--Details of tubular electric furnace

and alundum offers protection from physical damage, minimizes oxidation, and assures a uniform distribution of heat.

A chromel-alumel thermocouple (Temco, Emil Greiner no. G 9752) is used for the temperature measurement. Such couples, matched to give the temperature to  $\pm 5^{\circ}\text{C}$ , are obtainable from various manufacturers. The indicating pyrometer (Temco, Emil Greiner no. G 9751) is calibrated in both Fahrenheit and centigrade scales in  $50^{\circ}$  increments up to  $2000^{\circ}\text{F}$  and  $1100^{\circ}\text{C}$ .

Temperatures are regulated by an input control (Powerstat). The powerstat variable transformer used was type 116 (Superior Electric Co., Bristol, Conn.) for 115-volt line, frequency 50/60, output voltage of 0-135, and a maximum output amperage of 7.5. A fixed setting of the powerstat permitted a reasonably constant temperature in spite of the usual line-voltage fluctuations.

The furnace is designed to provide a fast rate of heating with accurate control of temperature. It will stand nearly continuous use at temperatures up to  $600^{\circ}\text{C}$  and may be used for short intermittent periods up to a maximum of  $900^{\circ}\text{C}$ .

#### Recommended procedure

A 0.500-g sample of the dry shale crushed to pass an 80-mesh-per-inch sieve is weighed into a 25-ml. pyrex, glass-stoppered test tube. The lower one-third of the glass-stoppered test tube is heated in the specially constructed small tube furnace at  $480^{\circ}$  to  $500^{\circ}\text{C}$  for 11 to 14 minutes. It is essential that strict adherence to the pre-



determined time and temperature conditions be observed. The exposed upper two-thirds of the stoppered test tube acts as an air condenser. When the distillation period is complete, the closed test tube is removed from the tube furnace and is then allowed to air cool to room temperature.

Then 10 ml of toluene are added, the tube is stoppered, and vigorously shaken for 20 seconds. The oil evolved by the destructive distillation and extracted by the toluene is filtered through a 9-cm, white, no. 589 S and S paper, and the filter paper and residue are washed with two 5-ml portions of toluene. The combined extract and washings are diluted to a final volume of 25 ml with toluene. The optical density ( $\times 10$ ) of the solution of toluene and oil is measured at 420 ~~m $\mu$~~  (blue filter) on a filter photometer with pure toluene set at 100-percent transmission. The instrument used in this investigation was the Lumetron Colorimeter Model 400 A (Photovolt Corp.)

The oil yield of the shale is then determined by reference to the standard curve established for that particular oil-shale deposit. The standard curve was obtained from a study of 80 shale samples assayed in the manner described above. The optical densities ( $\times 10$ ) of oil obtained by the new procedure were plotted against the percentage of oil as given by the Modified Fischer Retort Method (fig. 1). A scatter diagram was obtained and a mean straight line was drawn through the points. (See section on relation of optical density ( $\times 10$ ) to Fischer oil yield under Experimental data for further details.)

To avoid the effect of regional differences in oil yield the recommended procedure is to establish standard curves, as in figure 1, for specific areas. A study of these particular samples from Tennessee, Montana, and Idaho showed the applicability of the same optical density - oil yield relationship (fig. 1) to the two deposits. It is possible that the same standard curve may be applicable to oil shales from other areas.

In order to obtain reproducible results, the following precautions must be observed:

1. The sample must be mixed thoroughly and be representative of the material submitted for assay.
2. The closed-tube system must be gas tight. As a precaution against loosening of the stopper, it is advisable to stopper the test tube after heating has begun and prior to the evolution of vapors from the sample.
3. The proper heating must be maintained within the prescribed limits of time and temperature. To insure correct temperature measurements, the pyrometer must be checked or standardized periodically.

#### Calculations

The graph relating the optical density ( $\times 10$ ) to the percentage of oil yield by the Fischer method is shown in figure 1. The relationship of optical density ( $\times 10$ ) to oil yield in gallons per ton (Fischer) is illustrated in figure 2. Figure 2 was derived from figure 1 by taking an average specific gravity of oil as 0.903. For oil shale samples

from Tennessee, the standard deviation of the specific gravity of the oil (table 1) is 0.013. The following formula is used to convert percentage of oil to gallons per ton:

$$\text{Gallons of oil/ton shale} = 2.65 \times \text{percentage of oil yield.}$$

#### EXPERIMENTAL DATA AND DISCUSSION

The initial work in the development of a new method to determine the oil content of oil shales was to ascertain the effects of different experimental conditions upon the oil yield.

##### Effect of sample weight upon oil yield

Samples of Chattanooga shale having a Fischer assay oil yield of 3 percent ranging from 0.250 g to 2.000 g, in 0.250-g weight intervals, were heated at 480° to 500°C for 11 to 14 minutes. The oil evolved was extracted with toluene, filtered, and diluted to a final volume of 25 ml.

The results of these tests are shown in table 2. Within limits of experimental error, there was no significant difference in the oil yields for the different weights of sample. The oil yield of the shale was determined by using the standard curve (fig. 1) and interpolated to a percent-by-weight yield.

The 0.500-g sample was adopted primarily because this size sample gives favorable density readings for the range of 0.X percent to X.X percent oil.



Table 1.--Specific gravities of oil distillates (60°/60°F)

| Sample no. | Specific gravity | Deviation<br>from mean | Deviation <sup>2</sup> x 10 <sup>6</sup> |
|------------|------------------|------------------------|--|
| LC-15-12   | 0.924            | +0.021                 | 441                                      |
| 15         | 0.920            | +0.017                 | 289                                      |
| 31         | 0.902            | -0.001                 | 1  |
| 33         | 0.910            | +0.007                 | 49                                       |
| LC-15-52   | 0.895            | -0.008                 | 64                                       |
| LC-10-32   | 0.915            | +0.012                 | 144                                      |
| 33         | 0.926            | +0.023                 | 529                                      |
| 34         | 0.915            | +0.012                 | 144                                      |
| LC-10-35   | 0.926            | +0.023                 | 529                                      |
| LC-11-13   | 0.903            | 0.000                  | 0  |
| 15         | 0.918            | +0.015                 | 225                                      |
| 21         | 0.920            | +0.017                 | 289                                      |
| 22         | 0.921            | +0.018                 | 324                                      |
| 31         | 0.923            | +0.020                 | 400                                      |
| LC-11-52   | 0.888            | -0.015                 | 225                                      |
| 17R-6-1    | 0.899            | -0.004                 | 16                                       |
| 2          | 0.906            | +0.003                 | 9  |
| 3          | 0.905            | +0.002                 | 4  |
| 4          | 0.904            | +0.001                 | 1  |
| 5          | 0.903            | 0.000                  | 0  |
| 6          | 0.889            | -0.014                 | 196                                      |
| 7          | 0.896            | -0.007                 | 49                                       |
| 8          | 0.891            | -0.012                 | 144                                      |
| 9          | 0.891            | -0.012                 | 144                                      |
| 10         | 0.886            | -0.017                 | 289                                      |
| 11         | 0.883            | -0.020                 | 400                                      |
| 13         | 0.897            | -0.006                 | 36                                       |
| 14         | 0.899            | -0.004                 | 16                                       |
| 15         | 0.903            | 0.000                  | 0  |
| 16         | 0.914            | +0.011                 | 121                                      |
| 17         | 0.922            | +0.019                 | 361                                      |
| 18         | 0.916            | +0.013                 | 169                                      |
| 17R-6-19   | 0.916            | +0.013                 | 169                                      |

$$n = 33$$

$$\text{mean} = 0.903$$

$$\sum d = 0.367$$

$$\sum d^2 = 0.005777$$

$$\text{Average deviation} = 0.011$$

$$\text{Standard deviation} = 0.013$$

Table 2.--Effect of sample weight upon oil yield

| Sample weight (in grams) | Optical density (x 10) | Percent-by-weight oil yield |
|--------------------------|------------------------|-----------------------------|
| 0.250                    | 1.55                   | 3.10                        |
| 0.500                    | 3.50                   | 2.95                        |
| 0.750                    | 5.55                   | 2.86                        |
| 1.000                    | 7.70                   | 2.90                        |
| 1.250                    | 10.40                  | 3.10                        |
| 1.500                    | 12.00                  | 2.92                        |
| 1.750                    | 14.50                  | 3.00                        |
| 2.000                    | 17.10                  | 3.09                        |

## Effect of heating temperature on oil yield

A study was made of the effect of temperature on the oil yield. A heating time of 13 minutes was chosen arbitrarily. A 0.500-g aliquot of a Chattanooga shale sample containing 4.5 percent oil (determined by the modified Fischer assay) was heated in the manner prescribed under Procedure at the temperatures indicated in table 3. The oil evolved by the distillation was extracted with toluene, filtered, and diluted to a final volume of 25 ml. Measurements of the optical densities (x 10) were made with a Lumetron Colorimeter at 420  $m\mu$  (blue filter).

The results showed that the oil yield is dependent upon the temperature of heating. Table 3 shows that the best temperature range for obtaining reproducible oil yields is from 480° to 500°C. The average optical density (x 10) of the toluene solution of the oil distilled at this temperature range (480° to 500°C) was 5.95. By consulting the standard curve (fig. 1), it was determined that an optical density of 5.95 coincides with a 4.65-percent oil yield, which is very near the oil content of the shale by Fischer assay.

Table 3.--Effect of heating temperature on oil yield

| Temperature (centigrade) | Optical density (x 10) |
|--------------------------|------------------------|
| 260                      | 0.10                   |
| 335                      | 0.40                   |
| 400                      | 2.95                   |
| 420                      | 3.80                   |
| 440                      | 4.90                   |
| 460                      | 5.60                   |
| 480 <sup>1/</sup>        | 5.90                   |
| 480 <sup>1/</sup>        | 6.00                   |
| 480 <sup>1/</sup>        | 5.90                   |
| 500 <sup>1/</sup>        | 6.00                   |
| 520                      | 6.20                   |
| 540                      | 6.90                   |
| 575                      | 7.30                   |
| 600                      | 7.60                   |
| 650                      | 8.10                   |
| 675                      | 8.50                   |
| 705                      | 9.25                   |

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<sup>1/</sup> Average optical density (x 10) in the temperature range 480° - 500°C is 5.95.

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#### Effect of heating time on yield

The effect of heating time on the oil yield was studied. A 0.500-g sample of a Chattanooga shale sample containing 4.5 percent oil was heated at 480° to 500°C for the times indicated in table 4. The oil evolved by destructive distillation was extracted with toluene, filtered, and diluted to a final volume of 25 ml. Measurements of the optical densities (x 10) were made with a Lumetron Colorimeter at 420 mμ (blue filter).

The results of these tests are shown in table 4. It should be noted



that two apparently optimum heating times exist, one from 8 to 10 minutes and the other from 11 to 14 minutes. A series of tests with low-grade oil shales showed that a greater degree of reproducibility was attained when the samples were heated from 11 to 14 minutes than if heated from 8 to 10 minutes. Thus, it was concluded that heating at 480° to 500°C for 11 to 14 minutes gives the most satisfactory and reproducible oil yields. The average optical density ( $\times 10$ ) of the toluene solution of the oil distilled at 480° to 500°C for 11 to 14 minutes was 6.11. Using the standard curve (fig. 1), the oil yield related to an optical density of 6.11 is 4.72 percent. It should be noted that these conditions (heating a 0.500-g sample at 480° to 500°C for 11 to 14 minutes) give results that are in agreement with the Fischer method.

Table 4.--Effect of heating time on oil yield

| Time of heating (minutes) | Optical density ( $\times 10$ ) |
|---------------------------|---------------------------------|
| 2                         | 1.35                            |
| 4                         | 4.80                            |
| 6                         | 5.00                            |
| 7                         | 5.70                            |
| 8                         | 5.85                            |
| 9                         | 5.80                            |
| 10                        | 5.82                            |
| 11                        | 5.90                            |
| 12                        | 6.15                            |
| 13                        | 6.20                            |
| 14                        | 6.28                            |
| 15                        | 6.35                            |
| 16                        | 6.60                            |
| 18                        | 6.70                            |
| 20                        | 6.90                            |
| 22                        | 6.70                            |
| 24                        | 6.80                            |
| 30                        | 6.90                            |
| 35                        | 7.00                            |
| 40                        | 5.38                            |

## Selection of suitable filter

The following tests were made to determine the best filter for density measurements. A composite oil was made by combining 1 ml of each of the oil distillates secured by the Fischer method from 19 samples of Chattanooga shale. Series of 0.50-ml aliquots of the composite oil were diluted to 50 ml with the solvents indicated in table 5 to form stock solutions. A 2-ml aliquot of each of the stock solutions was further diluted to 25 ml with the respective solvents. The optical densities ( $\times 10$ ) were measured with a Lumetron Colorimeter Model 400 A (Photovolt Co., New York, N. Y.). A number of filters were available with the filter photometer used. The one which gave the greatest optical density with the oil solution (referred to pure toluene as a blank) is the blue filter (420  $m\mu$ ). Table 5 shows the variation of the optical density measured with the various filters. The blue filter (420  $m\mu$ ) was found to be best for all the solvents tried and was thus selected for the final procedure.

Table 5.--Selection of suitable filter

| Filter       |                       | Optical density ( $\times 10$ ) |                           |                  |                     |         |                  |         |
|--------------|-----------------------|---------------------------------|---------------------------|------------------|---------------------|---------|------------------|---------|
| Color        | Wave length<br>$m\mu$ | Chloroform                      | Carbon tetra-<br>chloride | Ethyl<br>acetate | Carbon<br>disulfide | Benzene | Diethyl<br>ether | Toluene |
| Red          | 650                   | 0.40                            | 0.70                      | 0.15             | 0.40                | 0.25    | 0.15             | 0.25    |
| Orange       | 580                   | 0.53                            | 0.95                      | 0.20             | 0.56                | 0.34    | 0.16             | 0.34    |
| Yellow green | 530                   | 1.05                            | 1.54                      | 0.50             | 1.04                | 0.68    | 0.54             | 0.70    |
| Blue green   | 490                   | 1.25                            | 1.75                      | 0.60             | 1.28                | 0.87    | 0.68             | 0.85    |
| Blue         | 420                   | 3.29                            | 3.57                      | 2.59             | 3.62                | 3.02    | 2.58             | 3.00    |
| Violet       | 370                   | 1.14                            | 1.50                      | 0.72             | 1.08                | 0.90    | 0.70             | 0.88    |

## Effect of solvent on color

The effect of solvent on color and the stability with time was studied. A composite oil was made by combining 1 ml of each of the oil distillates secured by the Fischer method from 19 samples of Chattanooga shale. A 0.50-ml aliquot of the composite oil was diluted to 50 ml with the solvents indicated in table 6 to form stock solutions. Two milliliters of this stock solution were further diluted at once to a final volume of 25 ml with each of the different solvents. Optical densities ( $\times 10$ ) were measured at 420  $m\mu$  (blue filter) with a Lumetron Colorimeter after various intervals of time. The results are given in table 6.

Table 6.--Effect of solvent on color

| Solvent                 | Measure of optical density ( $\times 10$ ) |                |                 |                 |                 |
|-------------------------|--|----------------|-----------------|-----------------|-----------------|
|                         | Immediately                                | After<br>1 day | After<br>2 days | After<br>5 days | After<br>7 days |
| Chloroform              | 3.29                                       | 3.70           | 4.25            | 4.75            | 5.80            |
| Carbon<br>tetrachloride | 3.57                                       | 4.25           | 4.80            | 5.00            | 5.90            |
| Ethyl acetate           | 2.59                                       | 2.63           | 2.58            | 2.58            | 2.61            |
| Carbon<br>disulfide     | 3.62                                       | 3.65           | 3.72            | 3.75            | 3.72            |
| Benzene                 | 3.02                                       | 3.08           | 3.02            | 3.04            | 3.03            |
| Diethyl ether           | 2.58                                       | 2.59           | 2.64            | 2.69            | 2.68            |
| Toluene                 | 3.00                                       | 3.00           | 2.99            | 2.99            | 2.99            |

The color of the oil solution was found to be dependent on the solvent used. For the same oil concentration, the colors in chloroform, carbon tetrachloride, ethyl acetate, carbon disulfide, benzene, diethyl ether, and toluene ranged from pale yellow to reddish amber. Some of



the solvents yielded unstable color systems; the color intensities increased with time. Benzene, toluene, and ethyl acetate gave stable reproducible color systems. Toluene was chosen as the solvent because it is chemically more inert than ethyl acetate and is somewhat less of a fire hazard and less toxic than benzene.

#### Color stability of the toluene system

Table 7 shows that the toluene system is exceptionally stable in color. Approximately the same optical density readings were obtained whether the densities were measured within 5 minutes or 3 months. The data in table 7 were obtained on various concentrations of the composite oil in toluene.

Table 7.--Color stability of the toluene system

| Aliquot (ml) | Measure of optical density (x 10) |              |                |
|--------------|-----------------------------------|--------------|----------------|
|              | Immediately                       | After 3 days | After 3 months |
| 1            | 1.07                              | 1.08         | 1.10           |
| 2            | 1.95                              | 1.92         | 1.97           |
| 3            | 2.71                              | 2.73         | 2.75           |
| 4            | 3.50                              | 3.49         | 3.52           |
| 5            | 4.22                              | 4.21         | 4.18           |
| 6            | 4.87                              | 4.90         | 4.75           |
| 7            | 5.55                              | 5.58         | 5.50           |
| 8            | 6.18                              | 6.25         | 6.15           |
| 1            | 1.11                              | 1.10         | 1.10           |
| 2            | 1.96                              | 1.90         | 1.98           |
| 3            | 2.74                              | 2.77         | 2.78           |
| 4            | 3.51                              | 3.53         | 3.52           |
| 5            | 4.20                              | 4.20         | 4.12           |
| 6            | 4.90                              | 4.89         | 4.74           |
| 7            | 5.55                              | 5.60         | 5.55           |
| 8            | 6.18                              | 6.20         | 6.13           |

## Color similarity of various oils

Tests were made to determine if samples from one formation but taken at different locations would yield oil having about the same color characteristics. A limited number of tests were also made to determine if the relationship of figure 1 would hold for oils from different formations and locations.

Fifteen samples of Chattanooga shale from Tennessee picked at random were checked for possible deviations in the color of the oil. Table 8 gives the optical densities ( $\times 10$ ) of solutions of the same concentration of the various oils in toluene. The results indicate that oils from the same formation but different locations would yield essentially the same densities. The range of the optical densities ( $\times 10$ ) is from 9.90 to 10.90.

Table 8.--Color similarity of various oils

| Lab. number | Optical density ( $\times 10$ ) | Deviation from mean |
|-------------|---------------------------------|---------------------|
| 3215        | 9.90                            | -0.27               |
| 3213        | 10.00                           | -0.17               |
| 2027        | 10.00                           | -0.17               |
| 2029        | 10.00                           | -0.17               |
| 3207        | 10.10                           | -0.07               |
| 3208        | 10.30                           | +0.13               |
| 3216        | 10.30                           | +0.13               |
| 3212        | 10.40                           | +0.23               |
| 2053        | 10.40                           | +0.23               |
| 3209        | 10.60                           | +0.43               |
| 2052        | 10.70                           | +0.53               |
| 2050        | 10.80                           | +0.63               |
| 2051        | 10.80                           | +0.63               |
| 2054        | 10.80                           | +0.63               |
| 2046        | 10.90                           | +0.73               |

$n = 15$

Mean = 10.17

Average deviation = 0.34



In addition, it should be noted that the 80 samples studied in the determination of the optical density - oil yield relationship (fig. 1) showed from the linear nature of the scatter diagram that oils from different formations and localities were similar.

This relationship was used as the basis for correlating the proposed photometric procedure to the Modified Fischer Retort Method.

#### Relation of optical density to Fischer oil yield

Seventy-five samples of Chattanooga oil shale were distilled in the manner described under Procedure. The oil evolved was extracted with toluene, filtered, and diluted to a final volume of 25 ml. Measurements of the optical densities ( $\times 10$ ) were made with a Lumetron Colorimeter at 420 ~~m $\mu$~~  (blue filter). The optical densities ( $\times 10$ ) were plotted against the percentage of oil yield as given by a Fischer assay. A scatter diagram was obtained, and a mean straight line was drawn through the points. The average difference of the Fischer assays from the curve is 0.37 percent absolute. The maximum difference between the determined (Fischer assay) and the curve is 0.94 percent. The percentages of oil yield and the optical densities ( $\times 10$ ) of the toluene-oil solutions are given in table 9.

The choice (visual fitting) of the standard curve is based upon the assumption that positive and negative deviations of the same magnitude are equally probable. This assumption is verified by the fact that a visual inspection shows the pattern of the scatter diagram to be essentially symmetrical with respect to the standard curve. Thus, the standard



Table 9(a).--Relation of optical density to Fischer oil yield  
Chattanooga shale (Tennessee) Lot 1001

| Sample   | Percentage oil<br>(Fischer) | Optical<br>density<br>( $\times 10$ ) | Difference of Fischer assay<br>from standard curve |
|----------|-----------------------------|---------------------------------------|--|
| LC-15-11 | 0.2                         | 0.40                                  | -0.35  |
| 51       | 0.8                         | 0.85                                  | -0.30  |
| 21       | 1.7                         | 0.85                                  | +0.62  |
| 53       | 1.8                         | 1.35                                  | +0.38  |
| 31       | 1.9                         | 2.18                                  | -0.10  |
| 12       | 2.4                         | 1.90                                  | +0.60  |
| 52       | 2.4                         | 2.25                                  | +0.36  |
| 13       | 2.7                         | 2.25                                  | +0.44  |
| 15       | 2.8                         | 2.70                                  | +0.44  |
| 14       | 3.4                         | 3.20                                  | +0.70  |
| LC-15-33 | 4.1                         | 4.80                                  | +0.30  |

$$n = 11$$

$$\sum d = 4.59$$

Table 9(b).--Relation of optical density to Fischer oil yield  
Chattanooga shale (Tennessee) Lot 1002

| Sample   | Percentage oil<br>(Fischer) | Optical<br>density<br>( $\times 10$ ) | Difference of Fischer assay<br>from standard curve |
|----------|-----------------------------|---------------------------------------|--|
| LC-10-14 | 0.8                         | 0.95                                  | -0.36  |
| 15       | 1.0                         | 1.28                                  | -0.38  |
| 31       | 1.4                         | 2.00                                  | -0.48  |
| LC-11-14 | 1.8                         | 1.80                                  | +0.06  |
| LC-10-13 | 1.8                         | 2.15                                  | -0.16  |
| LC-11-13 | 2.1                         | 2.15                                  | +0.12  |
| LC-10-32 | 2.7                         | 3.45                                  | -0.18  |
| LC-11-15 | 2.9                         | 2.70                                  | +0.52  |
| 51       | 3.0                         | 2.25                                  | +0.94  |
| LC-10-34 | 3.0                         | 3.70                                  | -0.06  |
| 33       | 3.5                         | 4.60                                  | -0.16  |
| LC-11-52 | 4.2                         | 4.90                                  | +0.32  |
| 31       | 4.3                         | 6.60                                  | -0.74  |
| LC-10-35 | 4.5                         | 6.25                                  | -0.32  |
| LC-11-32 | 4.9                         | 6.70                                  | -0.22  |
| LC-11-22 | 5.0                         | 6.40                                  | +0.08  |

$$n = 16$$

$$\sum d = 5.10$$

Table 9(c).--Relation of optical density to Fischer oil yield  
Chattanooga shale (Tennessee) Lot 1005 (sample LC-105A-x)

| Sample | Percentage oil<br>(Fischer) | Optical<br>density<br>(x 10) | Difference of Fischer assay<br>from standard curve |
|--------|-----------------------------|------------------------------|--|
| 43     | 0.9                         | 0.65                         | -0.04  |
| 42     | 1.0                         | 0.00                         | +0.50  |
| 45     | 1.0                         | 0.50                         | +0.18  |
| 41     | 1.3                         | 0.10                         | +0.74  |
| 15     | 2.1                         | 2.90                         | -0.40  |
| 21     | 2.4                         | 2.90                         | -0.10  |
| 12     | 3.8                         | 5.40                         | -0.40  |
| 31     | 4.0                         | 4.40                         | +0.46  |
| 14     | 4.1                         | 5.80                         | -0.40  |
| 13     | 4.2                         | 4.80                         | +0.40  |
| 33-# 2 | 4.2                         | 6.30                         | -0.64  |
| 33-# 1 | 4.2                         | 6.50                         | -0.78  |
| 34     | 4.4                         | 6.10                         | -0.30  |
| 35 # 1 | 4.5                         | 5.60                         | +0.12  |
| 35-# 2 | 4.5                         | 6.20                         | -0.28  |
| 32     | 4.6                         | 6.60                         | -0.44  |

$n = 16$   
 $\Sigma d = 6.18$

Table 9(d).--Relation of optical density to Fischer oil yield  
Chattanooga shale (Tennessee) Lot 1012 (sample 13M-7-x)

| Sample | Percentage oil<br>(Fischer) | Optical<br>density<br>(x 10) | Difference of Fischer assay<br>from standard curve |
|--------|-----------------------------|------------------------------|--|
| 22     | 1.3                         | 1.20                         | -0.02  |
| 11     | 2.3                         | 3.10                         | -0.34  |
| 31     | 2.5                         | 3.55                         | -0.44  |
| 52     | 2.8                         | 3.45                         | -0.10  |
| 21     | 3.2                         | 3.30                         | +0.42  |
| 33     | 3.3                         | 5.25                         | -0.80  |
| 16     | 3.6                         | 4.60                         | -0.06  |
| 15     | 3.7                         | 5.25                         | -0.42  |
| 14     | 4.4                         | 6.40                         | -0.50  |
| 32     | 4.5                         | 6.70                         | -0.62  |
| 51     | 4.6                         | 5.20                         | +0.52  |
| 12     | 4.9                         | 5.90                         | +0.32  |
| 13     | 5.6                         | 7.10                         | +0.20  |

$n = 13$   
 $\Sigma d = 4.76$

Table 9(e).--Relation of optical density to Fischer oil yield  
Chattanooga shale (Tennessee) Lot 1052 (sample 17R-6-x)

| Sample | Percentage oil<br>(Fischer) | Optical<br>density<br>( $\times 10$ ) | Difference of Fischer assay<br>from standard curve |
|--------|-----------------------------|---------------------------------------|--|
| 10     | 2.3                         | 1.60                                  | +0.70  |
| 9      | 2.5                         | 2.60                                  | +0.20  |
| 8      | 2.5                         | 2.20                                  | +0.50  |
| 11     | 2.7                         | 2.15                                  | +0.70  |
| 7      | 2.8                         | 3.40                                  | -0.04  |
| 15     | 2.9                         | 2.50                                  | +0.68  |
| 12     | 2.9                         | 2.80                                  | +0.48  |
| 18     | 2.9                         | 3.70                                  | -0.14  |
| 6      | 2.9                         | 3.80                                  | -0.22  |
| 13     | 3.0                         | 2.95                                  | +0.42  |
| 14     | 3.2                         | 3.50                                  | +0.28  |
| 16     | 3.2                         | 4.20                                  | -0.18  |
| 17     | 4.3                         | 5.10                                  | +0.30  |
| 4      | 4.3                         | 6.50                                  | -0.70  |
| 5      | 4.5                         | 6.40                                  | -0.40  |
| 19     | 4.6                         | 6.00                                  | -0.02  |
| 3      | 5.2                         | 6.20                                  | +0.40  |
| 2      | 6.0                         | 6.60                                  | +0.92  |
| 1      | 6.7                         | 9.00                                  | -0.10  |

$$n = 19$$

$$\sum d = 7.38$$

curve can be compared to a distribution function of a random sequence.

$$n = 80$$

$$\sum d = 29.81$$

$$\sum d^2 = 15.1007$$

Average difference of the Fischer assays from the curve:

$$\frac{|d_1| + |d_2| + \dots + |d_n|}{n} = \frac{29.81}{80} = 0.37 \text{ percent absolute}$$

From appearances of the scatter diagram (fig. 1), it is believed that the oil content of shales may be determined by the photometric procedure with essentially the same accuracy as by other methods now in use.



To show whether there are variations in the optical properties of the oil from widely separated areas (Phosphoria formation and Chattanooga shale) a closed-tube distillation was made of 10 samples of mudstone from the Phosphoria formation in Montana and Idaho (indicated on fig. 1 by the symbol  $\Delta$ ). The percentage of oil yield and the optical densities of the toluene-oil solutions are given in table 9(f). Figure 1 shows that the data for the Phosphoria formation fit the curve that was drawn for the Chattanooga shale.

Table 9(f).--Relation of optical density to Fischer oil yield  
Mudstone from the Phosphoria formation  
of Montana and Idaho, Lot 1243

| Sample               | Percentage oil<br>(Fischer) | Optical<br>density<br>( $\times 10$ ) | Difference of Fischer assay<br>from standard curve |
|----------------------|-----------------------------|---------------------------------------|--|
| FCA-150-47           | none                        | 0.00                                  |  |
| FCA-181-47           | none                        | 0.05                                  |  |
| RAG-57-47            | none                        | 0.00                                  |  |
| RAH-250-47           | none                        | 0.00                                  |  |
| RAH-253-47           | none                        | 0.05                                  |  |
| DAB-39               | 2.8                         | 3.75                                  | -0.30  |
| ERC-36               | 3.6                         | 5.00                                  | -0.35  |
| LAT-22 $\frac{1}{2}$ | 4.5                         | 5.40                                  | +0.30  |
| ERC-26 $\frac{1}{2}$ | 5.2                         | 6.60                                  | +0.15  |
| LAT-24               | 5.5                         | 6.20                                  | +0.70  |

$n = 5$  (samples containing no oil  
were not considered)

$\Sigma d = 1.80$

$\frac{1}{2}$  0.250-g samples of ERC-26 and LAT-22 were used.

The recommended procedure in making a standard curve is to base it on those samples under study. For other samples, a new curve should be made.

## SUMMARY

A photometric method for the determination of the oil content of oil shale is presented. The proposed method, which utilizes distillation in a closed test tube followed by measuring the density of a toluene solution of the oil, provides a means of determining arbitrarily the oil content of oil shale by the destructive distillation of its organic matter. This method, like the Fischer method, does not determine the total organic matter in shale that may be converted more completely to oil under more favorable conditions. The proposed method has several immediate advantages over the Modified Fischer Retort Method and is recommended for oil-shale assays. The advantages are:

1. Less time is required for the assay. Oil shale assays by the Fischer method require approximately 2 hours for completion, whereas by the proposed method 8 to 10 determinations can be completed in the same length of time.
2. Less sample is required. A 100-g sample is used in the Fischer assay whereas a 0.500-g sample is used in the proposed method. In addition, the same representative sample (-80 mesh) can be used for other analyses.
3. The operation is less difficult and can be controlled more precisely.

The effects are shown of different experimental conditions upon the oil yield by the proposed method: effect of heating time on yield, effect of heating temperature on yield, effect of solvent on color,

stability of color in toluene, color similarity of oils, and the relation of optical density to the Fischer yield.

The proposed method, like the Modified Fischer Retort Method, is an empirical measure, and it has been directly correlated with the Fischer method. The estimated oil yields are considered as reliable as the values obtained directly by the Fischer assay of the samples. The method is fast enough for certain control purposes in mining and processing oil shale for which rapid and accurate results are desired, such as in the assay of thousands of samples.

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