UNITED STATES GEOLOGICAL SURVEY.

In Trace element investigations report.

TEI-210

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

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March 1952

Prepared by the Geological Survey for the
UNITED STATES ATOMIC ENERGY COMMISSION
Technical Information Service, Oak Ridge, Tennessee

CHEMISTRY

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AEC, Oak Ridge, Tenn.-W23134

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ABSTRACT

A method is presented for the volumetric estimation of the oil yield of oil-bearing shale. The shale is distilled in a closed test tube and the oil extracted with ethyl acetate. The ethyl acetate is volatilized on a steam bath, and the oil residue, while still hot, is centrifuged in a graduated tube at 1500 rpm. The volume of the oil yield is read directly off the calibrated stem of the centrifuge tube. The method yields much the same results as the Fischer assay method in a much shorter time. It is applicable to shale and phosphatic shale.

INTRODUCTION

Oil shales have been assayed by the Bureau of Mines retort method proposed by Karrick (1926), described by Guthrie (1938), and later modified by Stanfield and Frost (1946, 1949). Recently a method relating the specific gravity of the oil shale to its oil yield was developed by the Bureau of Mines (Stanfield and Frost, 1950). In the latter procedure the oil yield is determined using a standard curve

established for the particular oil shale deposit. The standard curve is obtained by plotting the specific gravities of more than 50 oil shale samples picked at random against the percentage of oil given by the Modified Fischer retort method.

A rapid method for the photometric estimation of the oil yield of oil-bearing shale (Cuttitta, 1951) has been reported by the U. S. Geological Survey and is now in preparation for publication. In this method the oil shale is destructively distilled in a closed test tube, and the oil evolved is extracted with toluene. The optical density of the toluene extract is converted to percentage of oil by reference to a standard curve. This curve is obtained by relating the oil yields by the Fischer assay method (Stanfield and Frost, 1946, 1949) to the optical density of the toluene extract.

All of these methods are empirical, and the following study is another empirical measure that can be directly correlated with the Fischer method. Although the proposed method does not supersede the photometric method, it can be used to advantage in the estimation of the oil yield of comparatively small samples (as small as 1 g) where a standard curve is not available for a particular oil shale deposit. In addition the method is rapid, so that four or five determinations can be made in the same length of time required for the completion of one Fischer assay determination.

In this proposed method the shale is distilled in a closed test tube, and the oil extracted with ethyl acetate. The ethyl acetate is volatilized on a steam bath, and the oil residue, while still hot, is centrifuged in a graduated tube at 1500 rpm. The volume of the oil

yield is read directly from the calibrated stem of the centrifuge tube.

This work was completed as part of a program undertaken by the Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

PROCEDURE FOR ESTIMATING THE OIL YIELD

Preparation of the sample

A representative portion of the sample, ground to -80 mesh, is dried in an oven at 110 C for 1 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 is the size generally used in the U. S. Geological Survey for chemical analysis. No attempt was made to determine the effect of particle size upon oil yield.

Apparatus

The test tube used in the closed-tube distillation of the shale is a pyrex glass-stoppered tube, 15 x 50 mm, no. J-2345, manufactured by the Scientific Glass Apparatus Co., Bloomfield, N. J., with a no. 16 standard taper glass stopper.

The centrifuge tube used to measure the oil yield of oil shale is the Goetz Phosphorus tube (like Fisher 5-624), and the centrifuge is the International Reinforced, size 2.

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 had 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 1. The embedding of the nichrome element in asbestos 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 C, are obtainable from various manufacturers. The indicating pyrometer used is the Temco, Emil Greiner no. G 9751 which is calibrated in both Fahrenheit and centigrade scales in 50-degree increments up to 2000 F and 1100 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 good temperature control. It will stand nearly continuous use at temperatures up to 600 C and may be used for short intermittent periods up to a maximum of 900 C.

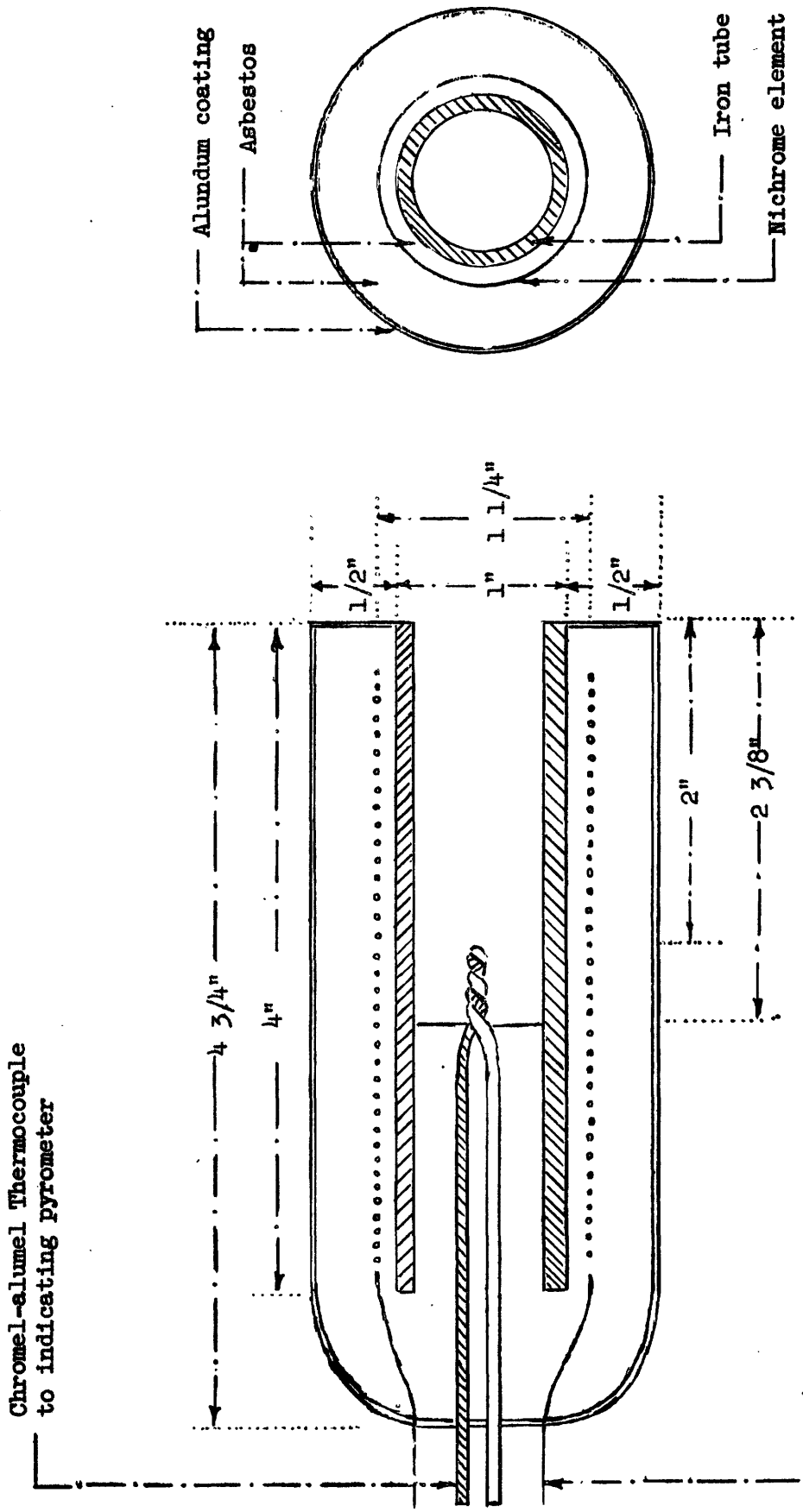

Figure 1.--Details of tubular electric furnace

Recommended procedure

A 1.000-g sample of the dry shale, ground to pass a -80 mesh sieve, is weighed into the test tube. The lower one-third of the glass-stoppered test tube is heated in a horizontal position in the specially constructed small tube furnace at 480 to 500 C for 11 to 14 minutes. It has previously been found (Cuttitta, 1951) that this method of heating give yields of oil that compare with those determined in the Fischer assay method; therefore it is essential that strict adherence to the time and temperature conditions be observed. The exposed upper two-thirds of the stoppered test tube serves as an air condenser. After the distillation period is complete, the closed test tube is removed from the tube furnace and allowed to air cool to room temperature.

Ten milliliters of ethyl acetate is added, the tube is stoppered and shaken vigorously for 20 seconds. The oil extracted by the ethyl acetate is filtered through a dry, 9-cm, no. 589 (white ribbon) S and S filter paper directly into the centrifuge tube. The filter paper and residue are washed with two 3-ml portions of ethyl acetate. The combined extract and washings, now in the centrifuge tube, are placed on a steam bath to volatilize the ethyl acetate.

To aid in the complete volatilization of the ethyl acetate during the final stage of the evaporation, the centrifuge tube is removed from the steam bath and tilted to allow the hot oil residue to flow from the stem into the pear-shaped body of the centrifuge tube. The tube is rotated so that the oil residue coats the lower walls of the tube. The centrifuge tube is now returned to the steam bath for further evaporation. Repeat this removal-and-tilting process until

constant volume is obtained. Repetition of this process three to four times generally effects complete volatilization of the ethyl acetate.

The remaining oil residue is then centrifuged at 1500 rpm for 3 minutes while still hot. The tube is allowed to cool to room temperature, and the volume of oil obtained is read directly from the calibrated stem of the centrifuge tube.

Calculations

The oil yield of the shale is determined by the use of the following formula which converts the measured volume, in milliliters of oil, to percent oil yield:

$$\text{Percent oil yield} = 90.3 \times \text{ml oil yield}$$

The following formula is used to convert the measured volume, in milliliters of oil, to gallons of oil per ton:

$$\text{Gallons of oil per ton shale} = 239.3 \times \text{ml oil yield}$$

Both of the foregoing formulas were derived by taking an average specific gravity of oil as 0.903, which is essentially the density of shale oils (Cuttitta, 1951).

DISCUSSION

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

1. 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.

2. The proper heating must be maintained within the prescribed limits of time and temperature. Although no data are shown in this report, conditions have been established in the preliminary experimental work done on the photometric method (Cuttitta, 1951) which showed that the closed-tube distillation of the sample at 480 to 500 C for 11 to 14 minutes gave the most reproducible results.

3. The ethyl acetate must be completely volatilized or positive errors will result.

4. The centrifuging of the oil residue after volatilization of the ethyl acetate must be done while the oil is still hot. Viscosity of the oil increases with decreasing temperature and negative errors may result from oil coating the interior walls of the centrifuge tube.

This report does not attempt to show the effects upon the oil yield of different experimental conditions, such as, sample size, particle size, heating temperature, heating time, and the stability of the ethyl acetate system. For details and experimental data on the effects of these conditions, the reader is referred to "A photometric method for the estimation of the oil yield of oil shale", by Frank Cuttitta (U. S. Geol. Survey Trace Elements Investigations Report 152, 1951).

To test this method 19 samples of Chattanooga shale from Tennessee were picked at random. The oil content of the shale samples,

having a Fischer assay oil yield ranging from 2.3 to 6.7 percent, was determined by the above method. The results of these tests, shown in table 1, indicate a good correlation with the Fischer assay results.

Advantages of the method

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 an assay by this method. An oil shale assay by the Fischer method requires approximately 2 hours for completion, whereas by the proposed method four or five determinations can be completed in the same length of time.

2. Less sample is required. A 100-g sample is used in the Fischer method, whereas a 1.000-g sample is used in the proposed method. In addition, the same representative sample (-80 mesh) can be used for other analyses.

REFERENCES

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Table 1.--Volumetric estimation of oil yield of Chattanooga shale samples

Sample	Fischer assay (percent)	Oil yield (in ml)	Oil yield (percent)	Difference from Fischer assay
10	2.3	0.03	2.7	+0.4
9	2.5	0.03	2.7	+0.2
8	2.5	0.03	2.7	+0.2
11	2.7	0.03	2.7	0.0
7	2.8	0.03	2.7	-0.1
6	2.9	0.04	3.6	+0.7
12	2.9	0.03	2.7	-0.2
18	2.9	0.04	3.6	+0.7
13	3.0	0.04	3.6	+0.6
14	3.2	0.04	3.6	+0.4
16	3.2	0.04	3.6	+0.4
15	3.9	0.04	3.6	-0.3
4	4.3	0.05	4.5	+0.2
17	4.3	0.05	4.5	+0.2
5	4.5	0.05	4.5	0.0
19	4.6	0.05	4.5	-0.1
3	5.2	0.06	5.4	+0.2
2	6.0	0.07	6.3	+0.3
1	6.7	0.08	7.2	+0.5

$n = 19$
$\Sigma d = 5.7$
Average difference = 0.3 percent absolute
Maximum difference = 0.7 percent

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