# A METHOD FOR APPROXIMATING THE ORGANIC CONTENT OF OIL SHALES BY WEIGHT LOSS ON IGNITION ANALYSIS

by

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## ABSTRACT

Although the Fischer Assay is the accepted method of characterizing oil shale grade, the procedure requires relatively expensive equipment and is time consuming. An alternative method is to analyze for total organic carbon which is also time consuming and complicated by the high carbonate mineral content of most oil shales. An alternative method has been developed to estimate, quickly and effectively, oil shale grade by a simple weight loss on ignition analysis at 500°C. This procedure has proven effective for estimating Fischer Assay, total organic carbon and high heat content for samples from Colorado (C-a tract), Utah and Kentucky (Eastern) over a wide range of ore zones and oil shale grades.

## INTRODUCTION

Most laboratories equipped for energy research routinely determine the high heat content (BTU/lb, kJ/kg)or total organic carbon content (% TOC) of energy resources, and those interested in oil shale resources determine the oil content by Fischer Assay. The procedures require special equipment and are often time consuming, and, further, a relatively large sample (∿100g) is required for the Fischer assay. Mineral benefication testing typically involves large numbers of samples, some of which are relatively small (i.e. a few grams), and so a quick, accurate estimate of their organic content attributes (Fischer assay, TOC, high heat content) is highly desirable.

By examining the thermal decomposition of the organic and mineral matter in oil shale (Heady, 1952; Jukkola et al., 1953), it is evident that most minerals present in oil shale do not decompose below a temperature of ∿ 500°C. Accordingly, an alternative method to estimate Fischer Assay, total organic carbon, or high heat content for a wide variety of domestic oil shales by a simple weight loss technique has been developed. This method saves time and money, increases lab productivity, and requires only readily available equipment, little operator training and small samples.

## BACKGROUND

The Modified Fischer Assay technique (Stanfield and Frost, 1946, 1949) has long been the standard method for estimating oil yield for resource evaluation of oil shale. In this method, the oil shale is crushed to minus 8 Mesh and heated from ambient temperature to 500°C in a special cast aluminum retort according to a specific temperature profile. One hundred grams of sample are required per determination. The gaseous vapors evolved from the retort are cooled and the condensed portion, containing both shale oil and water are collected and centrifuged to separate the water from the lighter oil. The oil yield is typically reported in terms of gallons of oil per short ton (GPT) or liters per metric tonne (lpt) of oil shale. This method does not yield quantities that specifically duplicate a commercial retorting process, but rather, is used mainly for resource evaluation and benefication process testing.

Numerous methods have been proposed to predict the oil content of oil shale without the laborious distillation and collection of the oil products by retorting. The most obvious method, relating the organic carbon content with the oil yield, has generated many relationships (Stanfield et al., 1951; Smith, 1966; Cook, 1974). Other methods reported in the literature include specific gravity analysis (Smith, 1956), microwave radiation (Judzis et al., 1977), laser pyrolysis (Hanson et al., 1975), and pulsed nuclear magnetic resonance (Miknis et al., 1974).

## EXPERIMENTAL

### Oil Shales Samples.

Seven different oil shale samples were used in this study; four from Colorado, two from Utah and one from Kentucky. The Colorado samples were from the Mahogany, L-5, R-4, and R-5 Zones, all a part of the Parachute Creek Member of the Green River Formation located in the C-a tract (Rio Blanco Oil Shale Company) of the Piceance Creek Basin. The stratigraphic relationship of these zones is shown in Figure 1 (Desborough, 1978). The lean or L zones alternate with the rich, R zones. The Utah samples, Zones 5 and 7, are a part of the Parachute Creek Member of the Green River Formation located in the Unita Basin. Stratigraphically, Zone 5 is above Zone 7 but both are located below the well-known Mahogany Zone. The Eastern oil shale sample was from the

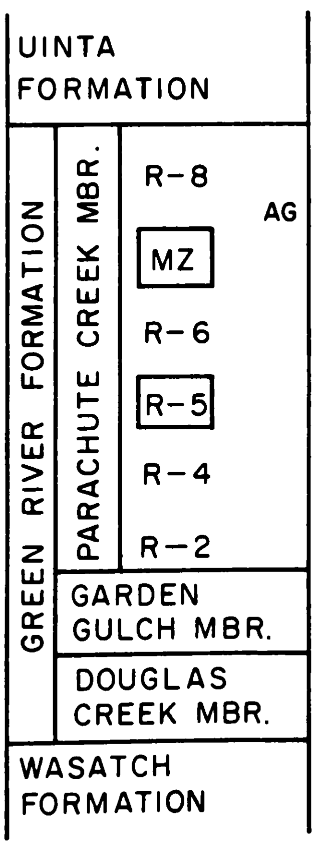


Figure 1. Stratographic relationship between Colorado oil shale zones. AG= A groove (modified after Desborough, 1978).

Cleveland Member of the Ohio Devonian Shale, located in Lewis County, Kentucky.

The mineralogical variations of these oil shales and the average oil content of the samples used here are shown in Table 1. The C-a tract shales (Colorado) show a wide variation in oil content as seen from a difference in their average grade from 12 to 25 GPT (50 to 104 lpt). The zones have similar mineralogy as they all contain substantial amounts of both siliceous and calcareous minerals, though the silicate/carbonate ratio increases as the depth of the zone increases (Meddaugh and Salotti, 1983). The saline carbonate minerals (dawsonite, nahcolite) appear in the lower oil shale zones. Although the specific mineralogy of the two Utah samples is not known, the Parachute Creek Member in this basin is mostly of the dolomitic marlstone type containing kerogen, marlstone, sandstone, siltstone and tuffs (Baughman, 1978). It is assumed that these zones are as laterally persistent as the Mahogany Zone. The Utah shales are

Table 1. Oil Shale Mineralogy*

| Oil Shale | Typical Grade (GPT/lpt) | Major Minerals (>15 wt.%) | Minor Minerals (5-15 wt.%) | Trace Minerals (<5% wt.%) |
|---|---|---|---|---|
| COLORADO | | | | |
| Mahogany Zone | 25(104) | Dolomite<br>Quartz | Analcite<br>Calcite<br>Illite<br>Albite<br>Orthoclase<br>Ankerite | Pyrite |
| L-5 | 12(50) | Dolomite<br>Albite<br>Orthoclase | Quartz<br>Analcite<br>Orthoclase<br>Illite | Pyrite<br>Dawsonite<br>Analcite<br>Calcite<br>Ferroan magnesite |
| R-5<br>R-4 | 24(104)<br>20(83) | Quartz<br>Dolomite | Albite<br>Orthoclase<br>Dawsonite | Pyrite<br>Ferroan<br>Magnesite<br>Nahcolite |
| UTAH | | | | |
| Zone 5<br>Zone 7 | 17(71)<br>32(134) | | see text for mineralogy | |
| EASTERN | 10(42) | Illite | Quartz | Chlorite<br>Kaolinite<br>Pyrite<br>Feldspar |

* Mineralogical Data from Datta and Salotti (1982) Meddaugh and Salotti (1983)

also known to contain saline carbonate minerals (nahcolite, eitelite, and shortite) (Baughman, 1978). The Eastern shale used here assays 10 GPT (42 lpt) and is a black shale largely consisting of illite and quartz. As evident from Table 1, the Eastern shale is more of a true shale as compared to the marlstone-like Western deposits.

Analytical Techniques.

All samples to be assayed were ground to a nominal 400 Mesh top size, and a representative portion of selected samples were analyzed for the various organic content attributes: total organic carbon percent (% TOC), Fischer Assay oil content (GPT, lpt), high heat content (BTU/lb, kJ/kg) and weight loss on ignition analysis (%).

Total Organic Carbon Percent. Samples were analyzed for total carbon and carbonate carbon by the procedure described by Huffman (1977) using a Coulometric Model 5010 coulometer connected with total carbon (Model 5020) and carbonate carbon (Model 5030) determining devices. The percentage of total organic carbon was reported as the difference between total carbon and carbonate carbon. The coulometer titration accuracy is ± 0.1%. These analyses were made by the Mineral Constitution Laboratory of the Pennsylvania State University and by the analytical department of Gulf Research and Development Company.

Fischer Assay Oil Content. Fisher Assay was determined from the standard test method for Oil from Oil Shale, ASTM designation D-3904. The accuracy of this method (by the same operator) is considered to be ± 1 GPT (±∿4 lpt). Commercial Testing and Engineering performed these analyses.

High Heat Content. The heat content (BTU/lb or kJ/kg) was determined from the standard test method for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter, ASTM designation D-2015. All assays were reported on a dry basis. The repeatability of this analysis is considered to be ± 50 BTU/lb (208 kJ/kg dry basis), if performed by the same operator. Warner Laboratories, Cresson, PA, performed these analyses.

Weight Loss on Ignition Analysis. In this new analytical procedure, oil shale was heated to 500°C (Fischer Assay retort temperature) under a nitrogen atmosphere (1000 $cm^3$/min) in a muffle furnace (Thermolyne Model 10500, i.d. 17x14x9 cm). (Note: the oil shale is not ignited under these conditions, but volatilization of the organic matter occurs near this temperature). The temperature profile used with this furnace was 25 minutes for the chamber to heat from room temperature to 500°C, and the sample was held at 500°C for two hours (a predetermined time based on thermogravimetric analysis). The following procedure was used:

(1) Weigh crucibles (porcelain type, 25 ml capacity) to obtain the tare weight.
(2) Place ∿ 0.5 gm of sample pulverized to a nominal -400 mesh, in crucible. Weigh accurately.
(3) Determine moisture content (105-107°C) according to ASTM designation D-2961, 3302, 3173.
(4) Heat for 2 hours at 500°C in a muffle furnace under a low flow of nitrogen.
(5) Allow crucibles to cool and then place in a dessicator for 20-30 minutes.
(6) Weigh crucible with ash residue and calculate the percent ash and percent volatile matter on a dry basis.

The authors have found the weight loss on ignition analysis to be reproducible with a standard deviation of 0.35% or less.

RESULTS AND DISCUSSION

General Discussion.

The weight loss on ignition is used as a base for estimating the desired organic material content attribute. For example, a predetermined weight loss (volatile percent) versus Fischer Assay, % TOC, or high heat content is determined over a wide range of assay conditions for each shale. Subsequently, the desired organic material content attribute can be estimated for an unknown sample of this shale from the volatile percent and a knowledge of the linear relationship between them.

It is important to point out several features of the weight loss on ignition analysis. Firstly, the 500°C temperature chosen for the volatile percent analysis is of some signifigance. As mentioned previously, this is the same temperature used in the Fischer Assay retort, and, at this temperature mineral matter decomposition, with the exception of the saline carbonate minerals, is not significant. Secondly, the same heating rate and holding time must be used throughout. Thirdly, multiple determinations are possible, depending on the size of the muffle furnace.

Prior to the development of this analytical

Table 2. Typical Linear Regression Equations and Coefficient of Determination Values ($r^2$) for Organic Attribute vs. Volatile % for each Oil Shale. X = volatile % at 500°C.

| | %TOC | $r^2$ | Fisher Assay GPT | $r^2$ | Heat Content BTU/lb | $r^2$ |
|---|---|---|---|---|---|---|
| COLORADO | | | | | | |
| Rich Zones | | | | | | |
| MZ | 0.82 X -2.19 | 0.9982 | 1.73 X - 4.92 | 0.9982 | 166.72 X - 571.47 | 0.9984 |
| R-5 | 0.84 X -4.25 | 0.9843 | 1.86 X - 8.09 | 0.9978 | 165.14 X - 365.40 | 0.9998 |
| R-4 | 0.88 X -7.96 | 0.9940 | 1.89 X -18.78 | 0.9936 | 184.95 X -1682.05 | 0.9956 |
| Lean Zone | | | | | | |
| L-5 | 0.74 X -2.45 | 0.9675 | 1.60 X - 8.90 | 0.9641 | 153.02 X - 408.33 | 0.9756 |
| UTAH | | | | | | |
| Rich Zone | | | | | | |
| Zone 7 | 0.81 X -0.44 | 0.9914 | ND | ND | 172.58 X - 186.28 | 0.9996 |
| Lean Zone | | | | | | |
| Zone 5 | 0.87 X -1.02 | 0.9966 | ND | ND | 173.15 X - 222.46 | 0.9940 |
| EASTERN | 0.84 X -3.34 | 0.9925 | ND | ND | 170.75 X - 848.45 | 0.9887 |
| OVERALL | 0.83 X -3.09 | 0.9485 | 1.77 X -10.17 | 0.9492 | 169.48 X - 612.06 | 0.9571 |

ND = Not Determined
* = For Colorado Shales Only

method, thermogravimetric analyses (TGA) were performed to insure that no significant, non-moisture weight loss occured below 500°C and to determine the holding time required for essentially complete devolatilization of the organic matter of the shale. For example, TGA analyses on three samples of differing grades (7%, 33% and 52% volatile content) of the R-5 shale were made. The TGA apparatus was programmed to simulate a 25 minute heating period from room temperature to 500°C (the temperature profile used for the muffle furnace) and held at that temperature for a period of three hours. The profile for weight loss over time indicated that after a period of two hours, the weight loss was nearly complete for all samples. Consequently, a holding period of two hours at 500°C was chosen for the weight loss analytical procedure. Inflection points indicated on the TGA curves will be discussed later.

Colorado Oil Shales.

Rich Zones. As shown in Table 1, the Mahogany, R-5 and R-4 zone samples are of similar grade but of different mineralogy. The relationship of the three aforementioned assays versus volatile percent for the Mahogany and R-5 Zones are shown in Figures 2 and 3, respectively. Notice that a linear relationship exists over the wide range of samples (5% to ∿45% volatile content). The least squares line of the data (linear regression) is shown for these shales and is summarized for all shales tested in Table 2.

Values of the coefficient of determination, $r^2$, a measure of the linear correlation between variables X and Y, are also given. For example, 100 times $r^2$ for the R-5 shale TOC relationship indicates that 98% of the variation in the random variable %TOC is accounted for by differences in the variable volatile percent. A perfect linear relationship exists when the correlation coefficient, r, is equal to ± 1 (Walpole and Myers, 1978). Hence, a strong linear relationship is shown for each of the shales tested.

Examination of the regression lines for the Colorado Mahogany, R-5 and R-4 shales (Table 2) generally shows that for each attribute relationship, the value of the Y-intercept decreases with increasing depth in the deposit. A logical explanation for this may be the increasing amounts of saline carbonate minerals present as the zone depth increases in the C-a tract. From the TGA data of Smith (1978) for a mineralogically complex Colorado oil shale, indications are seen of nahcolite (∿200°C) and dawsonite (380°C) decomposition before the 450-475°C conversion of the organic matter (kerogen) to oil. Hence, for a given shale with a significant saline mineral content, such as the R-4 shale, a small change in %TOC (or other attribute) will be represented by a larger change in volatile percent as compared to the other shales, yielding a slightly higher slope and a significantly more negative Y-intercept. TGA data by the authors for the R-5 shale indicate inflection

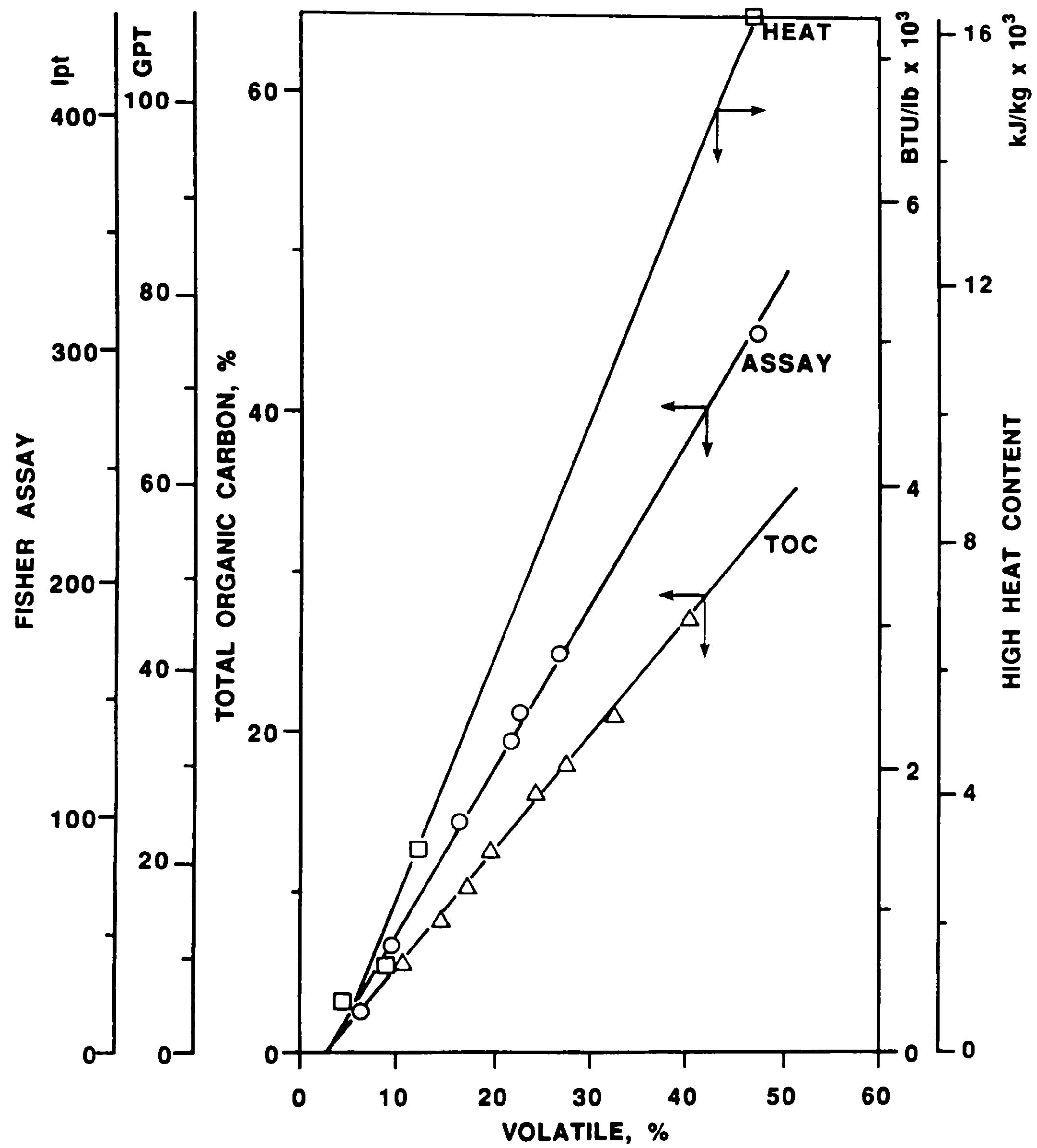


Figure 2. Organic content attribute versus volatile percent for Mahogany zone (MZ).

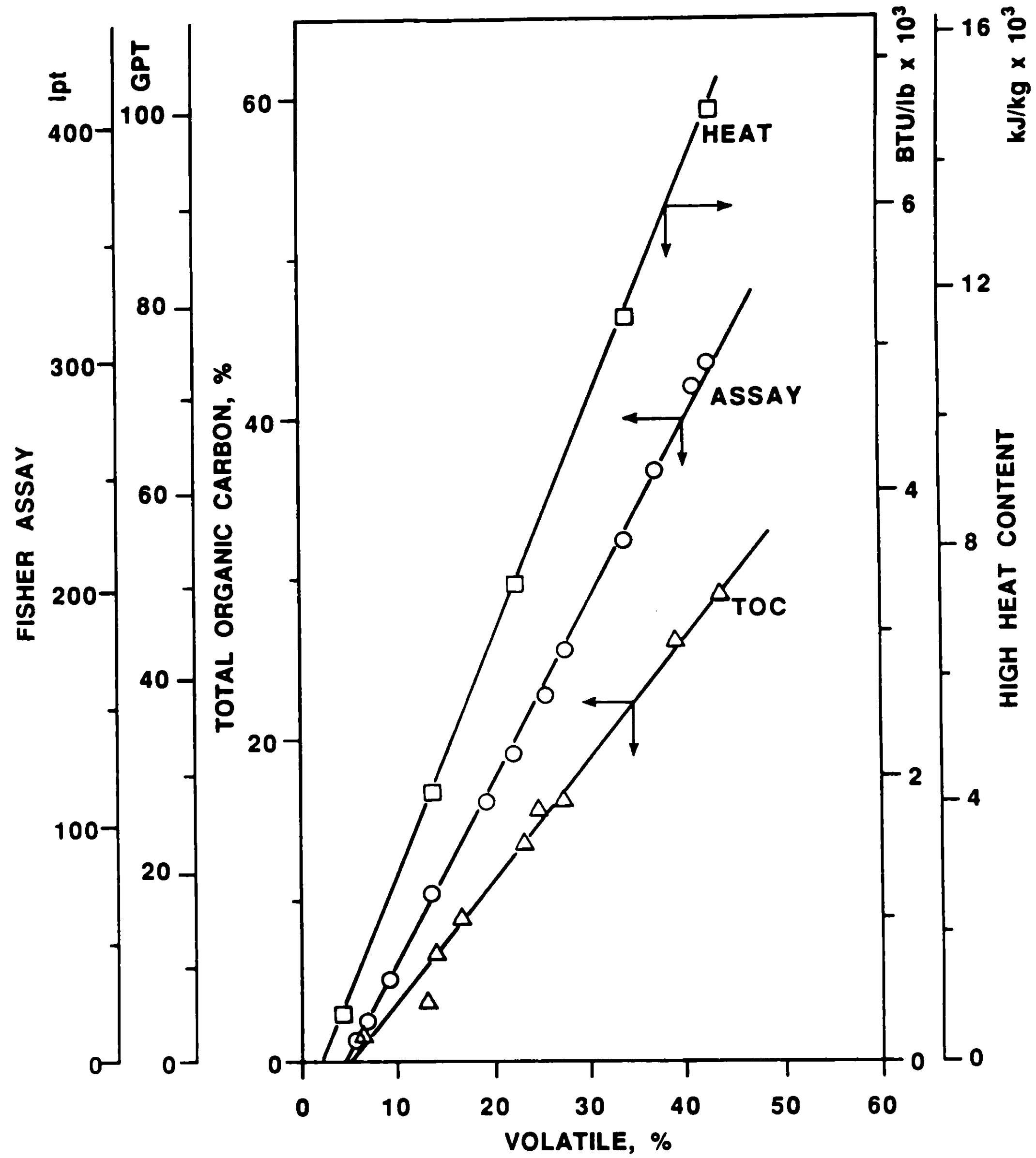


Figure 3. Organic content attribute versus volatile percent for R-5 zone.

points of 370°C and 460°C, which likely represents the decomposition of dawsonite and volatilization of organic matter, respectively.

Besides mineral decomposition below 500°C, other factors may also influence the relationship between volatile percent and organic matter attribute. For example, the Mahogany zone contains essentially no saline minerals (Table 1) but the equation relating Fischer Assay and volatile percent does not go through the origin as it should, theoretically. The volatilization at 500°C will produce (upon condensation) products of oil, gas and water, while the Fischer Assay relationship reports only the quantity of oil collected from the retort. Furthermore, since volatile percent represents a "total" organic conversion, a one to one relationship with %TOC is not possible, and the equations reveal this fact.

For our specific purposes, when a volatile percent equation yields a negative Fischer Assay (or other attribute), a small (say, 1 GPT) value is assumed for the prediction.

Lean Zone. The linear relationship for each attribute versus volatile percent is shown in summary in Table 2 for the L-5 Zone oil shale. Although the coefficient of determination is slightly lower than those found for the previous shales, a very strong linear relationship is still indicated.

## Utah Oil Shales

High grade (Zone 7) and low grade (Zone 5) shales from Utah also show a strong linear relationship between volatile percent and %TOC and high heat content (see Figure 4 and Table 2). The Fischer Assay relationship with volatile percent was not determined but should also be linearly related to the volatile content in view of the strong correlation between the other two organic content attributes and volatile percent.

## Eastern Oil Shale

The Eastern oil shale from Kentucky, a shale with a high clay content, also shows a linear correlation between these organic content attributes and the volatile percent (see Figure 5 and Table 2). High slopes and substantial Y-intercept values are again noticed, and may be attributed largely to water loss from the clay.

## Overall Relationship

As seen in Table 2, the terms in the equation are very similar. This suggests that a crude overall relationship between volatile percent and the various organic attributes may be assigned. The best overall relationship for each organic matter content attribute using the data points available from all seven oil shales is shown in Table 2. These general equations for domestic oil shales still show reasonable linearity as indicated by the relatively high coefficient of determination values. While use of these overall equations would not be nearly as accurate as the individual equations, and would involve some risk in their application to a specific situation, they should be useful in estimating gross values until a more precise determination for the specific oil shale can be established.

## Discussion

It has been shown that a simple weight loss on ignition analysis is an effective method for the prediction of oil shale Fischer Assay, total organic carbon content, or high heat content. While this procedure provides no description of the oily (e.g., oil specific gravity) or gaseous products, it can be used for quantitative estimates of the oil content of raw oil shales or their beneficiated products. The procedure requires no elaborate or expensive equipment and little operator training. Furthermore, multiple analyses can be performed at one time, which saves time and money. The excellent reproducibility of the volatile percent analysis is aided by the small top size (400 mesh) of the sample being analyzed. This reduces sampling error due to oil shale heterogeneity. Only a small amount of sample is required to estimate the three standard organic content attributes of oil shales.

## Conclusions

Several conclusions can be drawn regarding the use of this weight loss analytical procedure for estimating the organic attributes of oil shale:

(1) Weight loss on ignition analysis at 500°C is an effective and efficient way to predict the Fischer Assay (GPT, lpt), %TOC, and high heat content (BTU/lb, kJ/kg) of an unknown sample.

(2) Each shale yields a unique equation for a given organic content attribute. However, general equations for gross estimations for a variety of shales also appear to be applicable for making crude estimates of their oil content.

(3) Before adopting this procedure, the following caveats should be observed:

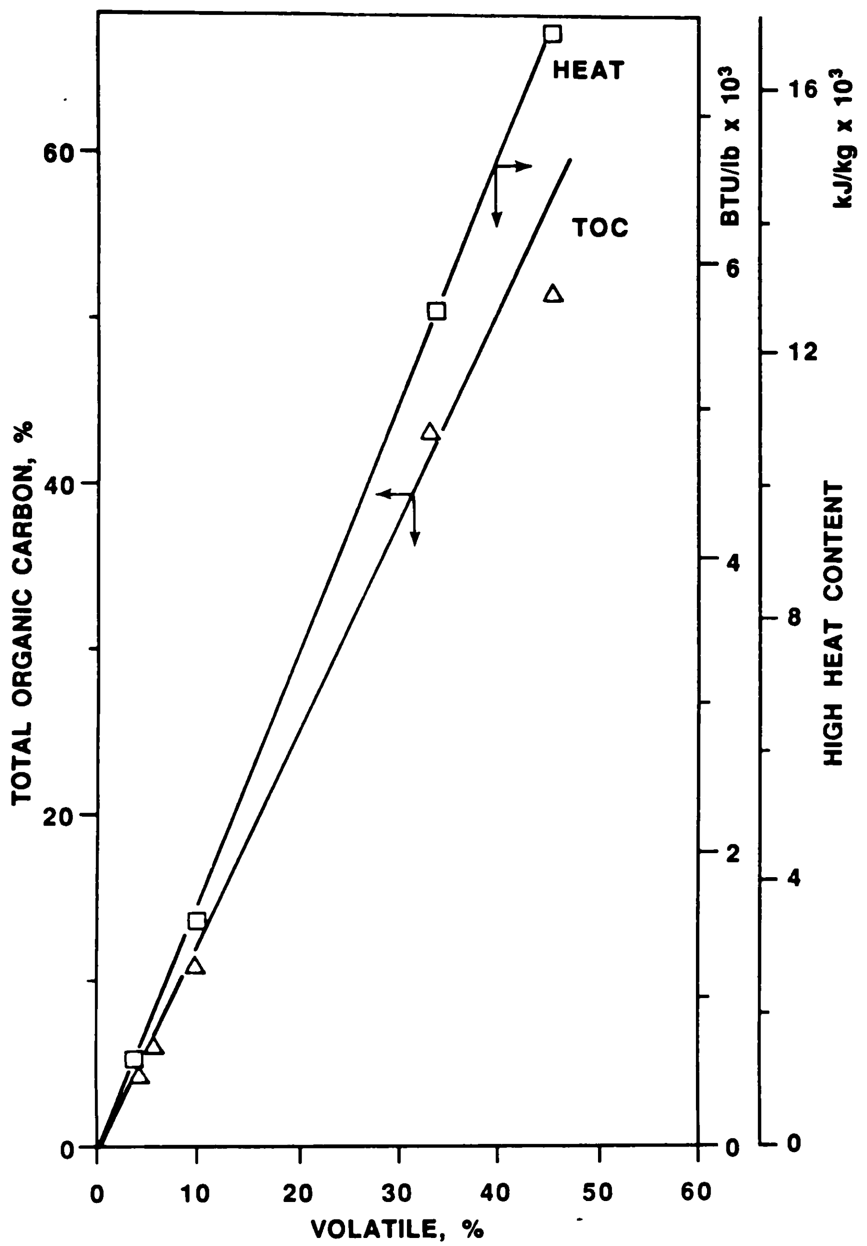


Figure 4. Organic content attribute versus volatile percent for Utah zone 7.

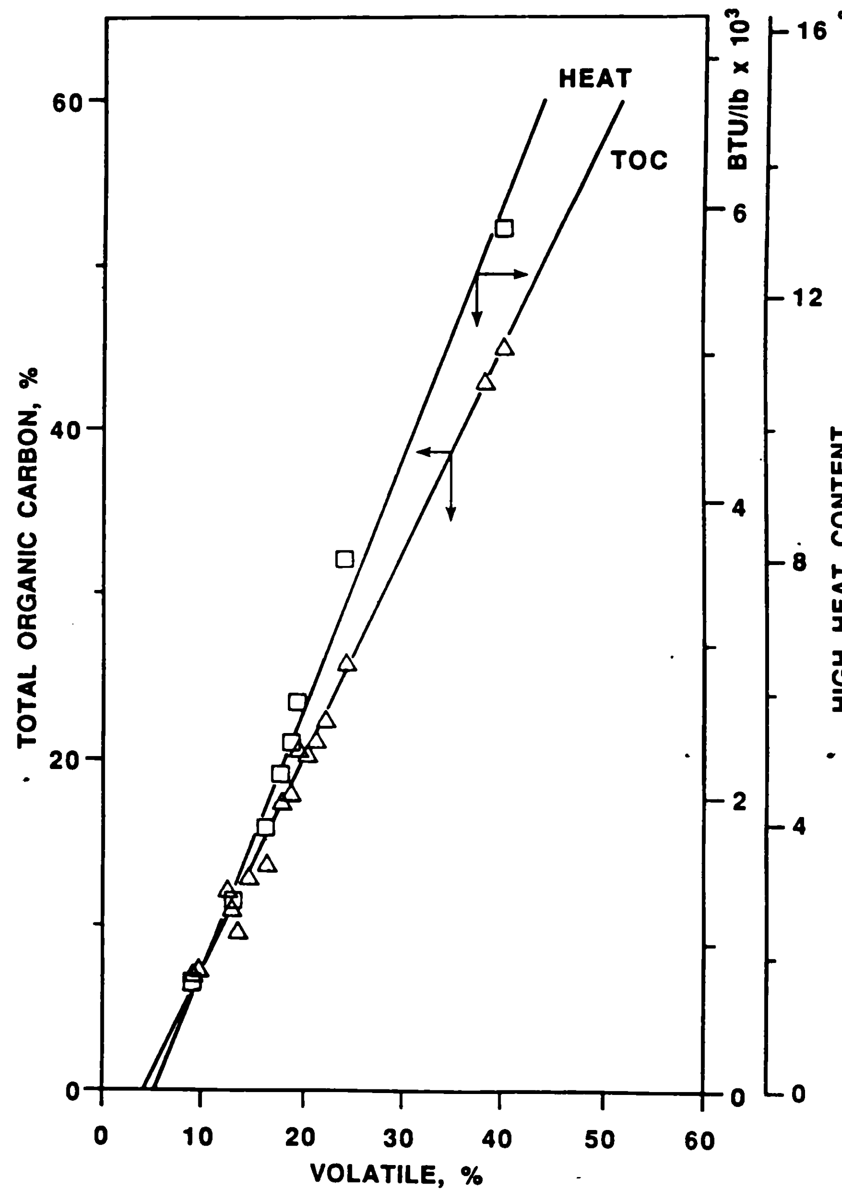


Figure 5. Organic content attribute versus volatile percent for Eastern oil shale.

(a) A mineralogical evaluation should be made of the sample to determine if any minerals with an expected weight loss up to 500°C are present. Saline minerals, such as nahcolite and dawsonite would be important here.

(b) Thermogravimetric Analysis (TGA) should be used to determine if there is a weight loss between the moisture evaluation temperature (105°C) and 500°C, and to evaluate the heating rate and holding time for particular sample types.

(c) For benefication processes, where mineral fractionation during processing is to be expected, regular checks on the validity of the equations for specific samples is indicated.

(4) As with any analytical estimation technique, occasional checks of the relationships are recommended.

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REFERENCES

Baughman, G.L., compiler, 1978, Synthetic Fuels Data Handbook, Second Edition: Denver, Cameron Engineers.

Cook, E. W., 1974, Green River shale-oil yields: correlation with elemental analysis, Fuel, v. 53, p. 16-20.

Datta, R. S., and Salotti, C. A., 1982, Benefication of Eastern oil shale, in 1982 Eastern Oil Shale Symposium, Lexington: Louisville, Kentucky Department of Energy and the University of Kentucky IMMR, p. 227-234.

Desborough, G. A., 1978, A biogenic-chemical stratified model for the origin of oil shale of the Green River Formation: an alternative to the playa-lake model, Geol. Soc. Amer. Bull. v. 89, p. 961-971.

Hanson, R. L., Vanderbough, N. E., and Brookins, D. G., 1975, Characterization of oil shales by laser pyrolsis - gas chromatography, Analytical Chemistry, v. 47, p 335.

Heady, H. H., 1952, Differential thermal study of Colorado oil shale, American Mineralogist, v. 37, n.9 and 10, p. 804-811.

Huffman, E. W. D., 1977, Performance of a new automatic carbon dioxide coulometer, Microchemical Journal, v. 22, p. 567-573.

Judzis, A., Jr., Williams, B., and Hiatt, R. E., 1977, Assaying Green River oil shale with microwave radiation, in J.B. Rubens, ed., Tenth Oil Shale Symposium Proceedings, Golden, Colorado School of Mines, p. 207-212.

Jukkola, E. E., Denilauler, A. J., Jensen, H. B., Barnet, W. I., and Murphy, W. I. R., 1953, Thermal decomposition rates of carbonates in oil shale, Ind. Eng. Chem., v. 45, no. 12, p. 2711-2714.

Meddaugh, W. S., and Salotti, C. A., 1983, Mineralogy and geochemistry of Green River Formation oil shales, C-a Tract, Colorado, in, J.H. Gary, ed., Sixteenth Oil Shale Symposium Proceedings, Golden, Colorado School of Mines, p.113-123.

Miknis, F. p., Decora, A. W., and Cook, G. L., 1974, Pulsed nuclear magnetic resonance studies of oil shales - estimation of potential oil yields, USBM RI 7984.

Smith, J. W., 1956, Specific gravity-oil yield relationships of two Colorado cores, Ind. Eng. Chem., v. 48, no. 3, p. 441-44.

Smith, J. W., 1966, Conversion constants for Mahogany Zone oil shale, Bull. Am. Assn. of Petrol. Geol., v. 50, p. 167-170.

Smith, J. W., 1978 Internal Report, USBM Laramie Energy Research Center, 1973, cited in Synthetic Fuels Data Handbook: Denver, Cameron Engineers.

Stanfield, K. E., and Frost, I. C.,1946, Method of assaying oil shale by a modified Fischer retort, USBM RI 3977.

Stanfield, K. E., and Frost, I. C.,1949, Method of assaying oil shale by a modified Fischer retort, USBM RI 4477.

Stanfield, K. E., Frost, I. C., McAuley, W. S., and Smith, H. N., 1951, Properties of Colorado oil shale, USBM RI 4825.

Walpole, R. E., and Myers, R. H., 1978 Probability and statistics for engineers and scientists, Second Edition, : New York, MacMillan.