COMPOSITIONAL DIAGRAMS: A METHOD FOR INTERPRETATION OF FISCHER ASSAY DATA

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BACKGROUND

Oil shale can be broadly classified as a mixture of two major components, that is organic and inorganic derived matter. In the Green River oil shales the organic portion is usually the minor constituent, but may be present in quantities varying from about zero to as great as 50 weight percent within very small vertical intravals, i.e., the varves which define the bedding planes in the deposit. Obviously because of such variations, sampling and sample preparation are extremely important if representative assay data are obtained. However, a major point to be made in connection with this paper is that <u>within any given assay sample the organic concentration probably varies quite widely for the individual shale particles</u>. Statistically this probably accounts for the observation that as a broad general rule, the pyrolytic decomposition seems to take place to form volatile products and organic residue on the pyrolyzed shale in constant proportions and independent of the inorganic matter concentration.

The commonly accepted technique for characterizing oil shale in the U. S. is the Modified Fischer Assay (MFA)(1). Assay data from this technique are usually reported in terms of the volatile components as: oil yield, water yield, and gas plus loss. The retorted shale (often called spent shale) is often omitted. However, it can be accurately reestablished since it is the difference between 100 weight percent and the volatiles. Interestingly the weight fraction of retorted shale is possibly the most accurately determined assay quantity since it is done gravimetrically and does not involve condensation, separation, and density determinations as do the liquid products. For this reason the retorted shale (or its analog, the total volatiles) should be of great value in making correlations with MFA data. In this paper these types of data are used to establish relationships between the oil yield, the total organic matter, and the organic residue remaining on the retorted shale.

COMPOSITIONAL DIAGRAMS

The "compositional diagram" (CD) is a useful tool for visually evaluating oil shale assay data -- particularly the relationship of oil yield to the total organic matter and the organic residue left on retorted shales. The basic concepts used in the development of the CD plot involves only simple material balances, and straight forward assumptions that inorganic decomposition is small and the ratio of the products to total organic matter is not concentration dependent and remains constant for a given assay procedure as follows:

1. Material Balances:

   a. Raw shale:

   organic (x_t) + inorganic (y_i) = 100 wt %   1)

   b. Retorted shale:

   volatiles (x_v) + retorted shale (y_s) = 100 wt %   2)

2. Pyrolysis Mechanism:

   a. Organic matter

$$\text{Organic } (X_t) \overset{\Delta}{\rightarrow} \text{Volatiles } (X_v) + \text{Organic Residue } (X_r) \qquad 3)$$

b. Volatile matter:

$$\text{volatiles } (X_v) \rightarrow \text{gas } (X_g) + \text{water } (X_w) + \text{oil } (X_o) \qquad 4)$$

3. Assumptions:

a. Inorganic decomposition negligible.

$$\text{Inorganic} \overset{\Delta}{\rightarrow} \text{Inorganic} + H_2O + CO_2$$

b. Pyrolysis product distribution constant:

$$\frac{X_o}{X_t} = K_1, \frac{X_w}{X_t} = K_2, \frac{X_g}{X_t} = K_3, \frac{X_w}{X_t} = K_4 \qquad 5)$$

Obviously, neither the organic residue on the retorted shale, nor the total organic are obtained directly from the MFA. However, if one of these quantities is known then the other is easily calculated by equation 3 and these values can be rather uniquely determined from the MFA data if the assumption of constant product ratios holds. The development of a coordinate system showing these relationships is given as figure 1. In this figure line $\overline{AB}$ is representative of equation 1 and gives the relationship between the total organic and the inorganic matter in the raw shale. A line $\overline{AD}$ can also be drawn which represents the weight percent of the organic matter which will pyrolyze to oil during assay. Another line $\overline{AE}$ can also be drawn which represents the total volatiles evolved during the pyrolysis. Obviously the difference between line $\overline{AB}$ (total organic) and line $\overline{AE}$ (total volatiles) must be the organic residue ($\overline{BE}$) which will be found with the retorted shale.

Line $\overline{AE}$ also has a unique relationship to the retorted shale value (Y_s) since the volatile organic must always simultaneously be represented by a point 'G' on the line $\overline{AB}$ in order to fill the requirement of equation 2. By simple geometry it follows that the line $\overline{JG}$ can be established with a point 'H' on the line $\overline{AE}$, giving the following relationships:

1. for the organic residue,

$$\overline{GE} = \overline{HD} = \overline{EB} \qquad 6)$$

2. the gas and water (plus loss):

$$\overline{HG} = \overline{DE} \qquad 7)$$

3. and the oil:

$$\overline{CD} = \overline{JH} \qquad 8)$$

Figure 1 therefore becomes a diagram on which the relationship of the known values (oil, volatiles, or residual shale) from a MFA can be plotted and the value of the other unknowns (inorganic, total organic, and organic residue) can be determined directly, provided the position of the lines $\overline{AE}$ and $\overline{AD}$ can be reliably established. The position of these lines can be determined from literature data by noting that --- the line $\overline{AH}$ in figure 1 bears the same relationship between the oil and the retorted shale as the line $\overline{AG}$ does to the total volatiles and the retorted shale. Therefore a plot of oil yield data (in weight percent)* versus the retorted shale (or its analog the total volatiles) should give a straight line which will be line $\overline{AH}$. Such a plot for a wide range of organic content is given in figure 2. A least square evaluation of these data using the constraint that the 'y' intercept equals 100 weight percent leads to an equation:

$$y_s = -1.282x_o + 100 \qquad 9)$$

The intercept with the x axis gives a value of 78.0 weight percent for the volatiles, a value of 22.0 weight percent for the organic residue, and a value of 60.8 weight percent for the oil as a percent of the total organic.

Mathematically the relationships developed in figures 1 and 2 give some interesting correlations where 'M' is the slope of the line $\overline{AE}$ and x_o is the oil yield in weight percent, as follows:

1. Total organic content: $x_t \cong M^2 x_o \cong 1.644x_o$ 10)
2. Organic Residue: $x_r \cong (M^2-M)x_o \cong 0.361x_o$ 11)
3. Gas and water: $(x_g + x_w) \cong -(1+M)x_o \cong 0.282x_o$ 12)
4. Product Distribution: a. Oil: $\frac{x_o}{x_t} = 1/M^2 \cong 0.608$; b. Residue: $\frac{x_r}{x_t} \cong (1-\frac{1}{M}) \cong 0.220$;

   c. Gas, Water, and Loss: $\left(\frac{x_g + x_w}{x_t}\right) \cong \left(\frac{1+M}{M^2}\right) \cong 0.172$ 13)

It is also possible to independently check the assumption that the product ratios to total organic are constant from literature references. Table 1 summarizes these data.

Table 1. Distribution of Organic Matter

Data Source	Shale Assay	Product to Organic Ratios			
	(g/t)	Oil	Gas + Water	Volatiles	Residue
Smith(5)	25.2[a]	0.543	0.243	0.785	0.215
Goodfellow(4)	33.2[b]	0.569	0.212	0.781	0.220
Stanfield(2)	18-52[c]	0.614	0.159	0.773	0.228
Stanfield(2)	27.7[d]	0.607	0.161	0.768	0.233
Hubbard(3)	78[e]	0.67	msg	msg	msg
(Figure 2)	f	0.61	0.17	0.78	0.22

a. Data from 8 replicate samples; b. Data from 42 replicate samples; c. Averaged data from 9 samples; d. Composited sample of above 9 samples; e. Data for kerogen enriched shales (see Table 2 RI4872); f. Data cover multiple samples ranging from 5 to 93 gal/ton.

As can be seen from Table 1, the ratios for total organic to volatiles and the organic residue are essentially constant with values of about 0.78 and 0.22 respectively -- as had been predicted from the data used in obtaining figure 2. The data of Hubbard covers assay data obtained for kerogen enriched shales and covers a wide range of

*Oil yields are commonly reported as (gal/ton). In the absence of density data, they can be converted to an approximate weight percent using the equation (gal/ton) $\cong$ 2.61 (weight percent).

concentration. Although it is not possible to make a material balance from these data they do show that the ratios of oil to kerogen (also for water to kerogen) are constant over a wide concentration range.

DEVIATIONS FROM THE IDEALIZED CASE

In the preceding section it was shown that a plot of assay oil yield from the Green River oil shales as a function of the retorted shale yield statistically defined a line represented by equation 9. Interestingly, figure 3 shows that much of the more recent MFA data do not fit the relationship -- an observation which is particularly true of some of the better statistical data, i.e., that of Goodfellow[4], Smith[5], and Hubbard[6], as well as that from commercial laboratories. (As noted in Table 1 - Goodfellow's analysis involved 42 replicate determinations.)

It is apparent from figure 3 that the deviation from ideal shows a consistently low retorted shale yield (or high volatile content). Therefore, it could be easily argued that the problem is associated with the decomposition of the inorganic portion of the shale and that the assumption of a 'y' axis intercept of 100 wt percent is not valid. Further, decomposition of the inorganic portion is not entirely unexpected since it is known that a small amount of carbonate decomposition takes place during the MFA procedure, e.g., Smith[5] reports 0.6 weight percent for a typical 25 gal/ton oil shale. However, carbonate decomposition will not account for the magnitude of observed deviation, particularly for low assay oil shales.

The latter is shown by examination of the large quantity of assay data from the cores obtained in drilling exploratory core holes which can be readily obtained by request from the Laramie Energy Research Center of ERDA. MFA data from core holes has the advantage of covering the assay of barren or lean shale in addition to the very rich shales -- something that is not normally done in routine investigation of oil shales.

Figures 4, 5, and 6 show characteristic CD plots for selected intervals of typical cores taken from the oil shales in the Green River Formation for Colorado, Utah, and Wyoming, respectively. As might be anticipated these data show that the retorted shale recovery from samples with zero or negligible oil yield are typically only 98-99 weight percent. The interesting observation is that the dominate volatile loss is associated with water -- not gas as would be the case with carbonate decomposition.

This latter observation suggests that sample preparation, particularly drying, needs to be reevaluated in making the MFA, (or at least determining and reporting the 'as received' or total moisture content of the sample). In discussing the drying procedures used by various individuals one finds considerable variation between laboratories and more importantly from the procedure initially set up by Stanfield and Frost(1). Whereas the latter carefully dried their samples and often reported MFA data on a 'moisture corrected' basis -- one now finds that assays are almost universally being done on an 'air dried' or as received basis.

Failure to correct for moisture not only leads to small inaccuracies in the MFA data as is shown in table 2. It also has a considerable effect on the data points of a CD plot, as shown in figure 3, where the data is also plotted on a moisture-free basis and more nearly fits the derived relationship.

Table 2. Effect of Using Moisture-free Basis On Modified Fischer Assay Data

Assay Item (wt %)	Goodfellow[4] A	Goodfellow[4] B	Smith[5] A	Smith[5] B	Hubbard[7] A	Hubbard[7] B
Retorted Shale	82.40	83.36	86.28	87.45	86.12	87.23
Oil	12.60	12.75	9.51	9.63	10.06	10.19
Gas (+ loss)	3.85	3.89	2.87	2.91	2.55	2.58
Water	1.15	-	1.38	-	1.27	-
Total	100	100	100	100	100	100
Change in Oil Assay (gal/ton)†		+0.4		+0.3		+0.3

Data Source: Goodfellow[4], Smith[5], Hubbard[7]

A As reported
B Moisture-free
† Calculated using 2.61 times difference in oil present.

Caution must be used in arbitrarily applying a moisture-free basis to MFA data since 'water of pyrolysis' is derived from the pyrolytic decomposition of the organic matter. The quantity of 'pyrolysis water' (X_w) will be proportional to the total organic content; (the author uses the relationship (X_w) $\cong$ 0.077 (X_o) to estimate its value) whereas, the moisture in the shale decreases with increasing organic content (i.e., refer to figures 4, 5, 6). Therefore, it is not uncommon for assay data to show little or no change in MFA water yield as a function of oil yield.

It is therefore suggested that those involved in evaluating or standardizing the MFA procedure take note of this problem. Certainly the relationship between drying technique and water yield needs to be evaluated -- and perhaps a much more detailed study should be made determining the relationship between water yield and retorting temperatures.

INTERPRETATION OF TGA DATA

Figure 7 shows a typical TGA trace for the pyrolysis of a sample of Colorado oil shale in a CO_2 atmosphere. TGA does not give oil yield, and unless the volatiles are recovered and analyzed it is difficult to get such data directly. On the other hand, the data does readily lend itself to analyses on a CD plot since the volatile content is determined rather precisely by TGA. Therefore, if the position of the oil yield line ($\overline{AE}$ in figure 1) is known for the particular shale in question the oil yield can be estimated from the 'x' intercept of that line.

In the event the relationship of the oil yield to the total volatiles is not known for the TGA sample a second data point can be obtained by oxidizing the residual organic matter (Figure 8) at the pyrolysis temperature (to minimize carbonate decomposition). The total volatile data can then be used to establish a point on the oil versus inorganic boundary line ($\overline{AD}$ in figure 1) and the yield estimated again from the 'x' intercept of that line. These data are shown plotted on a compositional diagram as figure 9. The Fischer assay oil yield predicted from the data from figure 7 would be 34.5 gal/ton. That, based on data from figure 8, is 33.4 gal/ton (assuming G/T $\cong$ 2.61 wt %). Fischer assay of four samples of this material averaged 33.38 gal/ton.

CORRELATIONS WITH TOTAL ORGANIC MATTER

Figure 10 shows data for the total organic matter as a function of the oil yield as reported in the literature (3,4,5,8,9) together with the correlation curve derived to fit these data by the investigators of the USBM[3]. Obviously these latter data do not fit the relationship suggested by equation 10, nor do they seem to fit the more precise determinations of Smith[5] and Goodfellow[4]. For this reason care should be used in using the older literature data for total organic content and its correlation particularly as they might apply to making energy balance calculations.

SUMMARY

A compositional diagram has been developed which provides a visual means of evaluating oil shale assay data for the Green River oil shales. Of particular value is the ability to estimate the total organic and organic residue in the pyrolyzed shale from Modified Fischer Assay data. For approximate purposes these relationships are as follows:

1. Total Organic = 1.644 x (MFA oil yield)
2. Organic Residue = 0.361 x (MFA oil yield)
3. (Gas + Water + Losses) = 0.282 x (MFA oil yield)
4. Water (from pyrolysis) = 0.077 x (MFA oil yield)

The compositional diagram can also be used to evaluate TGA (Thermogravimetric Analysis) data for oil shales in order to estimate the oil yield. It is also recommended as a tool for evaluating experimental retorting data, particularly for bench scale and pilot plant retorts where material balance data on the feed and retorted shales can be accurately ascertained.

LITERATURE CITED

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8. Private communications.
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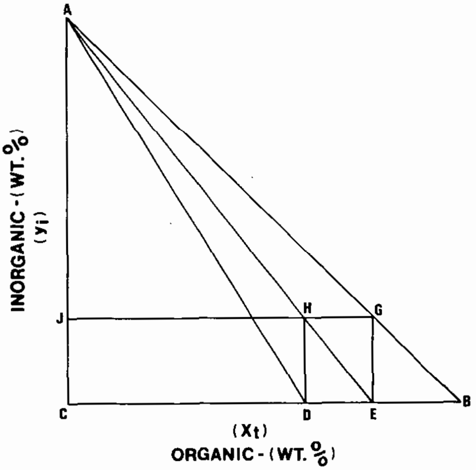

Figure 1. Development of the Compositional Diagram

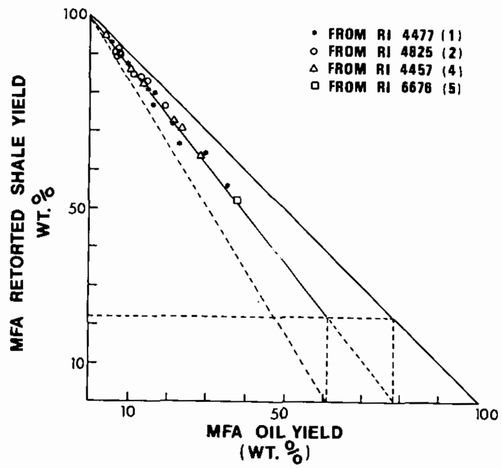

Figure 2. Relationship between Oil Yield and Retorted Shale Yield

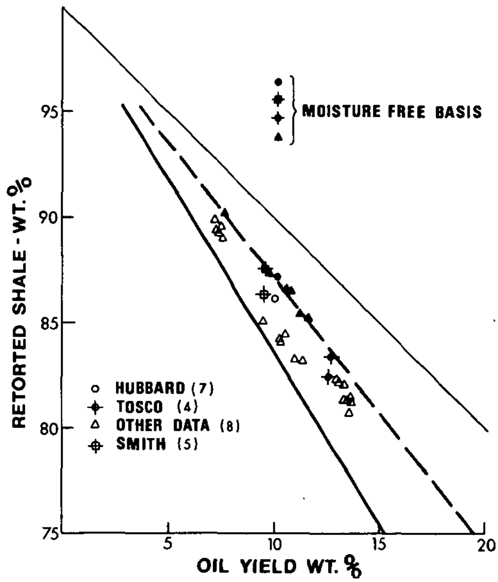

Figure 3. Compositional Diagram Showing Deviation From Ideal Case

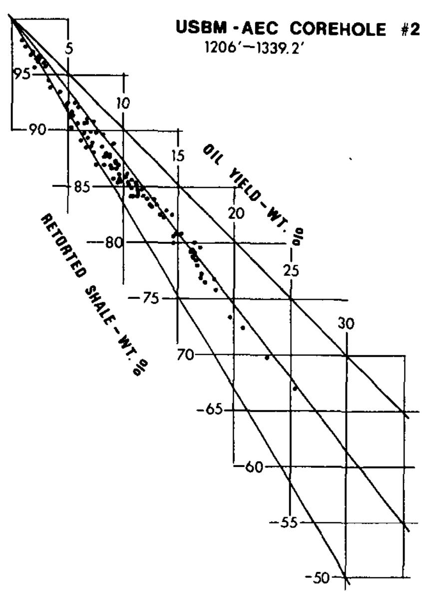

Figure 4. CD Plot for USBM-AEC Corehole #2

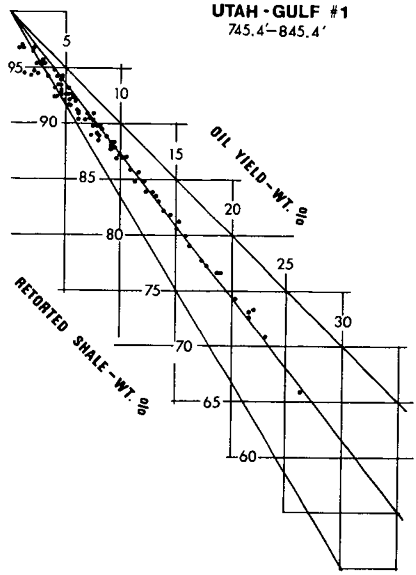

Figure 5. CD Plot of Utah-Gulf Evacuation #1

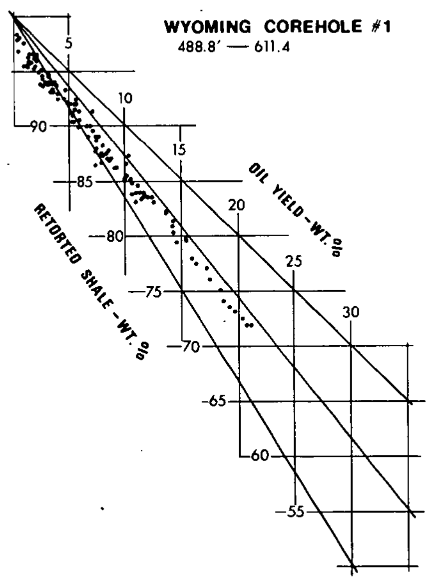

Figure 6. CD Plot of Wyoming Corehole #1

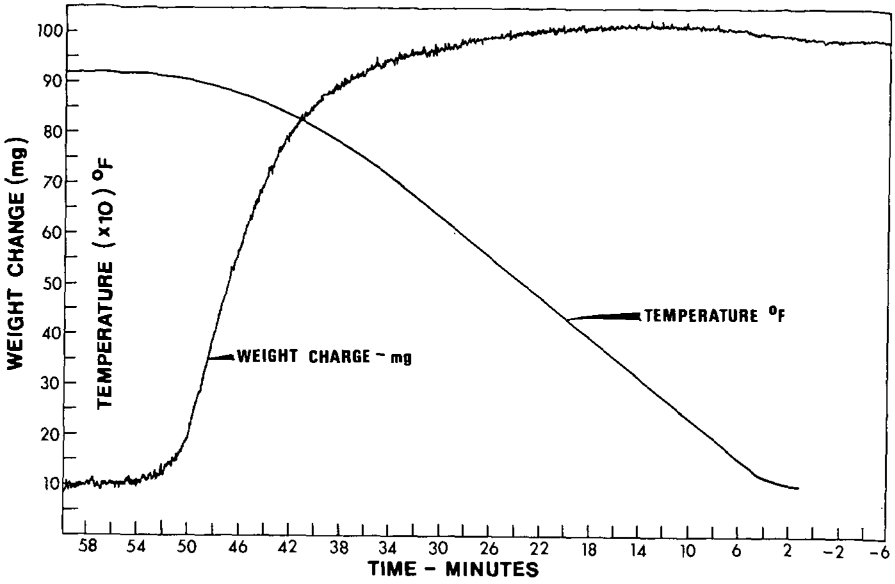

Figure 7. Typical TGA Trace for Colorado Oil Shale

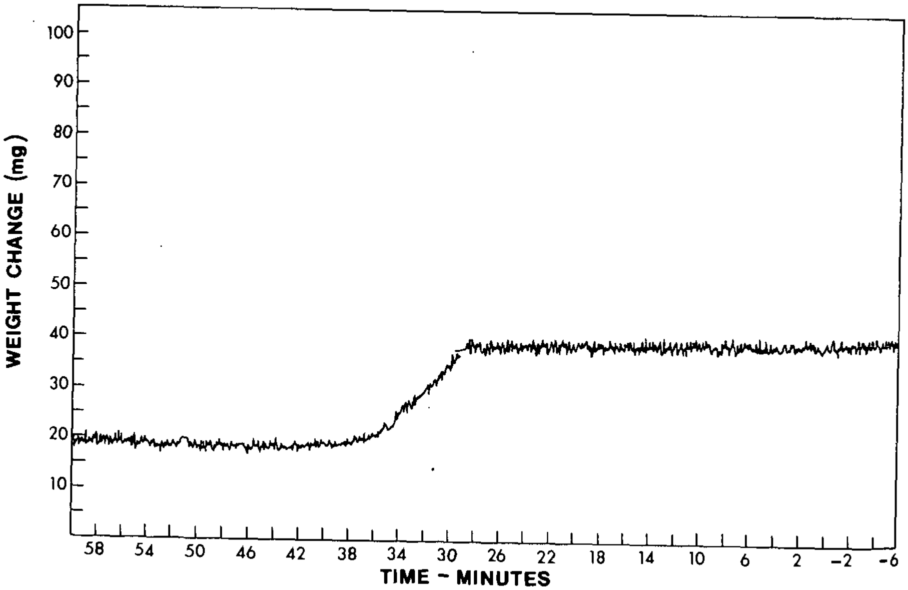

Figure 8. TGA Trace for Oxidation of Residual Organic Matter at 920°F in Air

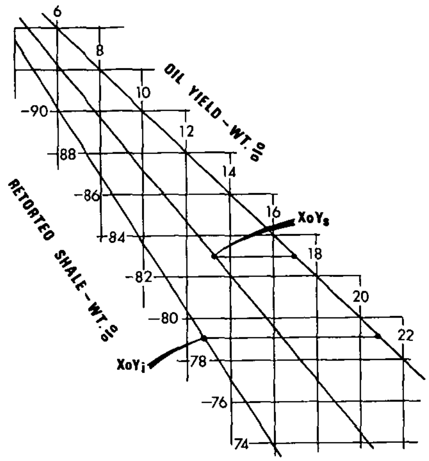

Figure 9. Typical CD Plot for TGA Data of Colorado Oil Shale

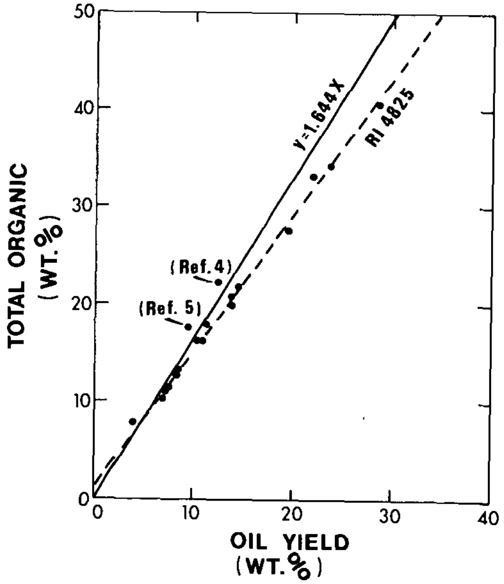

Figure 10. Relationships between Oil Yield and Total Organic Matter