SYMPOSIUM ON GEOCHEMISTRY AND CHEMISTRY OF OIL SHALE
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CHARACTERIZATION OF SHALES USING SINK FLOAT PROCEDURES

By

C. J. Vadovic
Exxon Research and Engineering Company, Baytown, Texas 77520

INTRODUCTION

The analysis of the organic fraction in shale leads to important processing insights. However, the analysis is complicated by the presence of a substantial fraction of rock. The rock often contains carbon, as carbonates, and hydrogen, as water of hydration, which make it extremely difficult to obtain a true organic analysis. The route used most often to obtain organic analyses is to isolate the kerogen by acid removal of the inorganics. This poses numerous problems in that the acids used, HCl and HF, can interact with and be incorporated into the organic matrix. Also basic nitrogen compounds are easily extracted from the shale. It has been observed that up to 20% of the organic carbon and up to 50% of the total nitrogen may be removed by acid extraction. To obviate these difficulties a procedure has been developed which utilizes the analyses of raw sink float shale samples to calculate the ratios of organic hydrogen and nitrogen to organic carbon. In addition an estimate of the hydrogen and nitrogen content of the mineral matter is obtained. (Table I)

SINK FLOAT PROCEDURE

The starting point for the procedure outlined here is the floating of material containing rock and mineral matter at a predetermined specific gravity. The principles involved are depicted in Figure 1. At a low media specific gravity essentially all of the material will sink. As the specific gravity increases more of the material floats. At a sufficiently high specific gravity all of the material will float.

In the procedure described here a method analogous to the collection of distillation cuts was employed. The shale was subjected to a low specific gravity and the float fraction collected. The sink fraction was subjected to an incrementally higher specific gravity and the float fraction collected. The procedure was repeated until very little material remained. In this manner a series of samples, differing primarily by organic to rock ratio, was collected.

The nature of the shale plays a role in the selection of the media. Heavy hydrocarbon media may be used on dry, impervious shales such as Colorado. For wet shales, such as Rundle, it is more practical to use an aqueous based heavy media system. The judicious selection of media prevents contamination of the shale and allows accurate analysis.

TABLE I

SINK FLOAT PROCEDURES OFFER ALTERNATIVES
IN SHALE CHARACTERIZATION

- Gravity Separation Analogous to Distillation
  - Samples fractionated by weight fraction of rock and organic
- Characterization Procedure Eliminates Need for Acid Extraction to Obtain Kerogen
  - Atomic ratios determined by analyses of rock containing samples
- H and N Content of Rock Determined

PROCEDURAL DETAILS AND RESULTS

The basis for the procedure presented here is an element balance of the form

$$X_i^{total} = X_i^{organic} + Y_i \cdot X_{mineral}$$

where X_i^{total} and $X_i^{organic}$ are the total and organic weight percent of component i in the raw shale, respectively, $X_{mineral}$ is the weight percent of minerals in the shale, Y_i is the weight percent of component i in the minerals and i is hydrogen or nitrogen.

By algebraic manipulation of the above equation, the details of which are shown in Table II, an equation of the form below is obtained.

$$\frac{100\ X_i^{total}}{Ash + CO_2} = \frac{12\ X_i^{organic}}{MW_i C_{org}} \quad \frac{100\ C_{org}\ NW_i}{(Ash + CO_2)\ 12} + Y_i$$

TABLE II

ELEMENT BALANCES KEY TO SINK FLOAT ANALYSES

$$\cdot\ X_i^{total}\ (wt\%\ of\ shale) = X_i^{organic}\ (wt\%\ of\ shale) + X_i^{inorganic}\ (wt\%\ of\ shale)$$

$$X_i^{inorganic} = Y_i^{minerals}\ (wt\%\ of\ minerals) \times minerals\ (wt\%\ of\ shale)/100$$

Assume: Minerals = Ash + CO_2

$$X_i^{total} = X_i^{organic} + Y_i^{minerals} \times (Ash + CO_2)/100$$

Rearranging Yields

$$\cdot\ \frac{100\ X_i^{total}}{Ash + CO_2} = \frac{100 \times MW_i \times C_{organic}}{(Ash + CO_2)\ 12}\left(\frac{X_i^{organic} \times 12}{C_{organic} \times MW_i}\right) + Y_i^{minerals}$$

where $Y_i^{minerals}$ = Content of ith element in minerals

$$\frac{X_i^{organic} \times 12}{C_{organic} \times MW_i} = \text{Atomic i/C ratio}$$

A simplifying assumption in this derivation is that the mineral content of the shale can be represented by the sum of the ash and carbonate CO_2. The total component X_i and the organic carbon are determined by elemental analyses. To effectively use the above equation, a series of samples containing varying amounts but similar compositions of both organic and inorganic constituents must be obtained.

The sink float procedure yields a series of samples which contain various levels of organic and inorganic material. It is assumed that in these samples variations in both organic and inorganic composition are minimal (Table III). The variation in ash elements for Brazil and Rundle shale are shown in Figure 2. The variations observed in sink float samples from these clay-containing shales are slight. By plotting 100 X_i^{total}/Ash + CO_2 vs/100 $C_{org}MW_i$/12 (Ash + CO_2) two results are achieved. The slope is the atomic X_i/C_{org} ratio and the intercept is the inorganic content of the element i. The results of such a plot for Brazil and Rundle shales are shown in Figure 3. As can be seen, straight lines with high correlation coefficients result.

The mineralogy of the Colony sink float samples is illustrated in Figure 4. Colorado shale is made up of primarily non-hydrated minerals: calcite, dolomite and quartz. There are, however, measurable quantities of clays which do contain water of hydration. Also there is more variation in mineralogy with specific gravity than has been observed for the Rundle and Brazil samples. The plot of 100 $H_{total}/(Ash + CO_2)$ vs. 100 $C_{organic}/12\ (Ash + CO_2)$ for Colony shale is shown in Figure 5. Again a straight line with a high correlation coefficient results.

TABLE III

IMPLICIT ASSUMPTIONS DO NOT LIMIT TECHNIQUE APPLICABILITY

- Sink float samples are generated based on organic content of rock only
- Organic content is uniform
- Inorganic content is uniform

The method, as outlined here, is also applicable to nitrogen. The approach was applied to Rundle, Brazil and Colony shale samples and the results are plotted in Figure 6. The resultant plots are linear for these three shales. At zero organic content all shales exhibit some nitrogen content. An unexpected result is that the calculated nitrogen content of the mineral matrix of both Rundle and Colony shale is similar. It has been postulated in the literature that compounds composed of ammonia (NH_3) may be present in clay minerals. There are also other naturally occurring ammonia minerals that have been identified. However, the reason for similar levels of inorganic nitrogen in both Rundle and Colony is unclear.

The calculated atomic ratio of H/C and N/C are compared in Table IV with values calculated from analytical results on acid extracted kerogens. The results for raw shale calculated from the procedure suggested here compare quite favorably with the kerogen values. The results show that the H/C ratio for the Rundle shales tested (1.68) is greater than that calculated for Colony (1.55), which in turn is higher than that of Brazil. The N/C ratio for Colony is almost double that of Rundle, 0.029 vs. 0.019. The slight differences between the sink float and the kerogen values suggest that the kerogen extraction procedure is valid despite the loss of both organic carbon and nitrogen during acid extraction.

TABLE IV

H/C AND N/C RATIOS COMPARE FAVORABLY WITH EXTRACTED KEROGEN VALUES

	H/C, Atom/Atom		N/C, Atom/Atom	
	Sink-Float	Kerogen	Sink-Float	Kerogen
Rundle	1.68	1.63	0.017	0.016
Brazil	1.32	1.30	0.024	0.023
Conoly	1.55	1.56	0.029	0.027

The amount of mineral hydrogen and nitrogen relative to the total amount of hydrogen and nitrogen present is shown in Table V. The total levels are representative of the average yield of the shales analyzed. The average yields for Rundle, Brazil and Colony are 25, 20 and 35 gpt respectively. The mineral hydrogen content ranges from 3 to 15% of the total hydrogen, and the mineral nitrogen content ranges from 4 to 31% of the total. Two potential sources of inorganic hydrogen and nitrogen are water of hydration and ammonia. It is obvious that the release of these compounds during retorting can have a measurable effect on retorting yields.

TABLE V

H AND N CONTENT OF MINERALS ARE SMALL BUT SIGNIFICANT

- Levels Representative of Average of Deposit

	Hydrogen			Nitrogen		
Shale	Min, Wt%	Total, Wt%	Min/Total	Min, Wt%	Total, Wt%	Min/Total
Rundle	0.25	2.16	0.11	0.13	0.42	0.31
Brazil	0.28	1.86	0.15	0.02	0.41	0.04
Colony	0.08	2.83	0.03	0.10	0.83	0.12

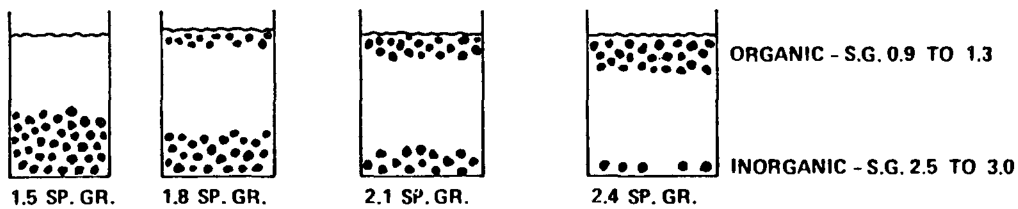
EXTENSION TO SULFUR AND OXYGEN

The method developed here is only applicable to hydrogen and nitrogen. This is primarily because it assumed that the mineral form is uniform and the H and N in the mineral matter are proportional to the amount of mineral matter present. These assumptions are not true for sulfur and oxygen (Table VI). A major source of sulfur is pyrite, which seems to be randomly distributed through the sink float fractions. Consequently, a procedure to back out pyrite prior to mathematical analysis would be desirable. However, an accurate method for pyrite analyses in shales is not yet

FIGURE 1

HOW PHYSICAL SHALE BENEFICIATION WORKS

NOTE: EACH PARTICLE CONTAINS SOME ROCK OR MINERAL MATTER



LABORATORY FLOAT/SINK TESTS

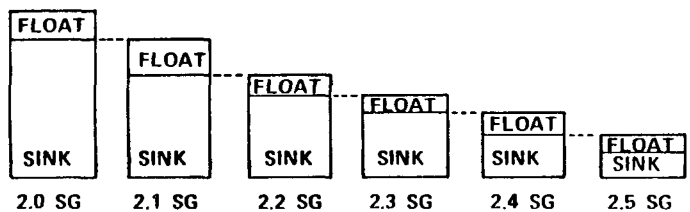


FIGURE 2

ASH ELEMENTS ARE UNIFORM IN SINK FLOAT FRACTIONS

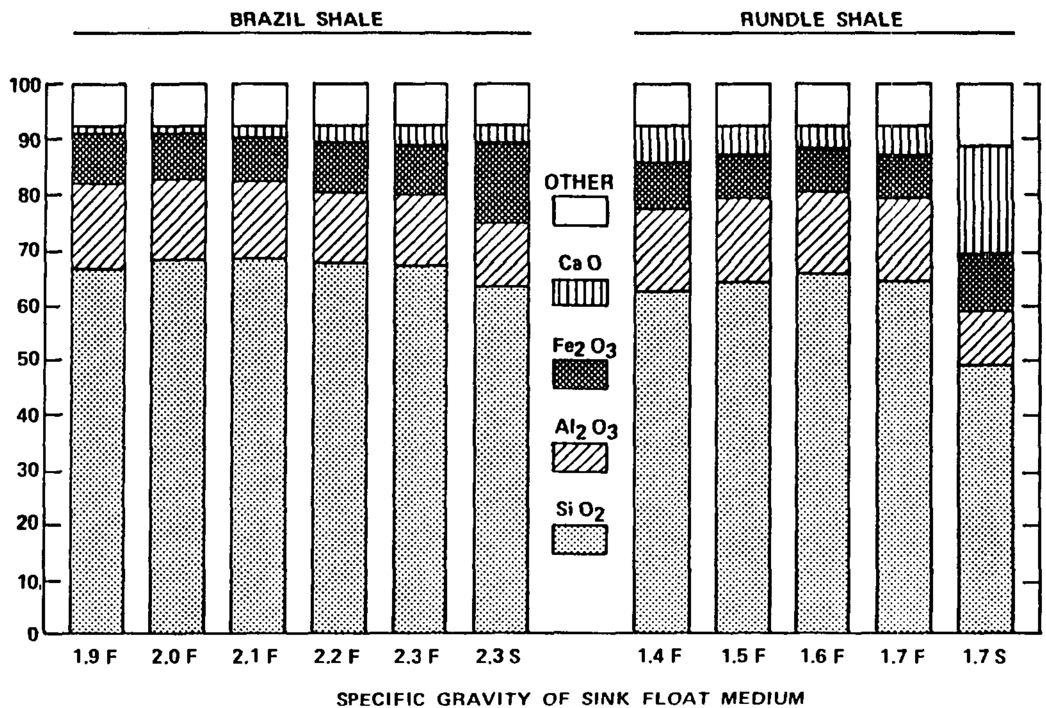


FIGURE 3

HYDROGEN ANALYSIS FOR CLAY CONTAINING SHALES

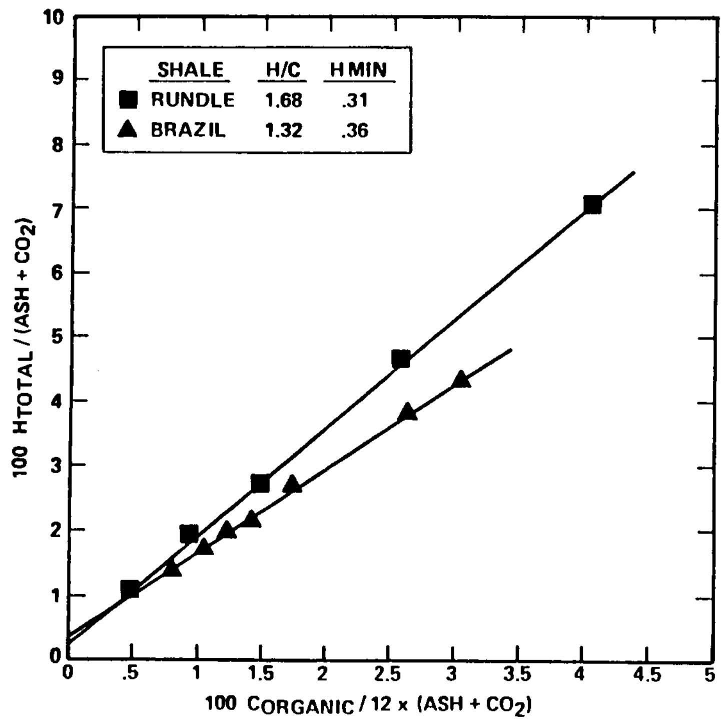


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FIGURE 4

MINERALOGY OF COLONY SINK FLOAT SAMPLES

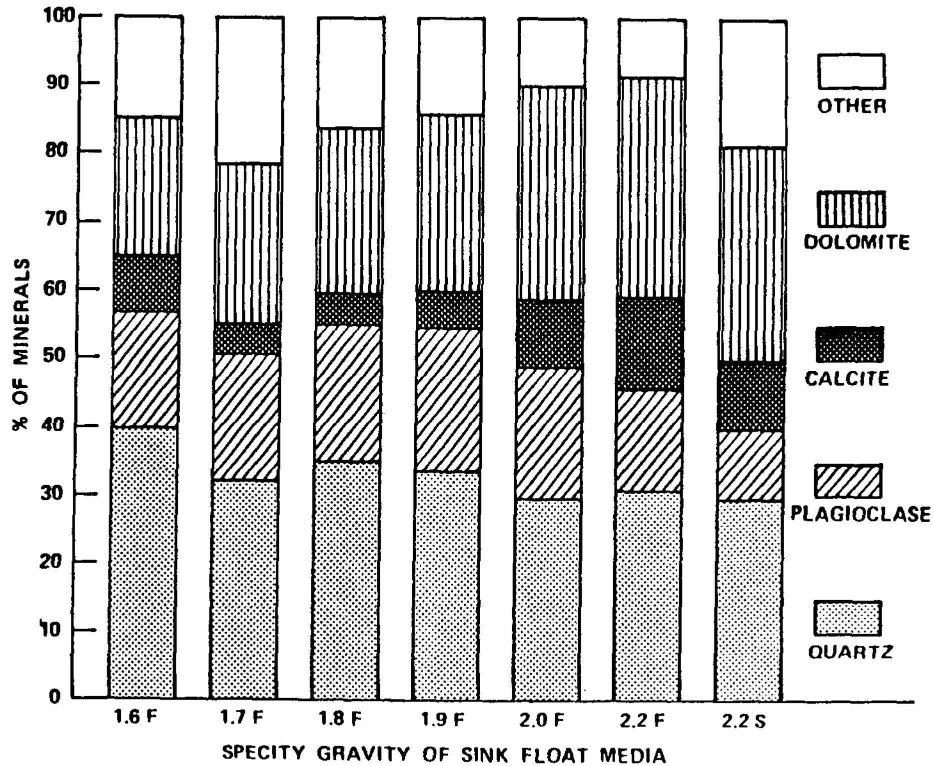


FIGURE 5

HYDROGEN ANALYSIS FOR COLONY SHALE

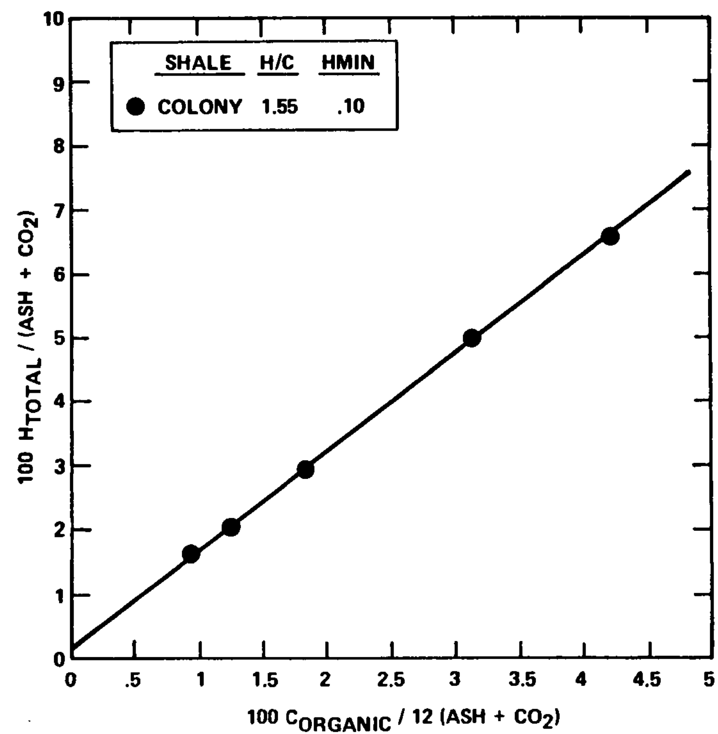
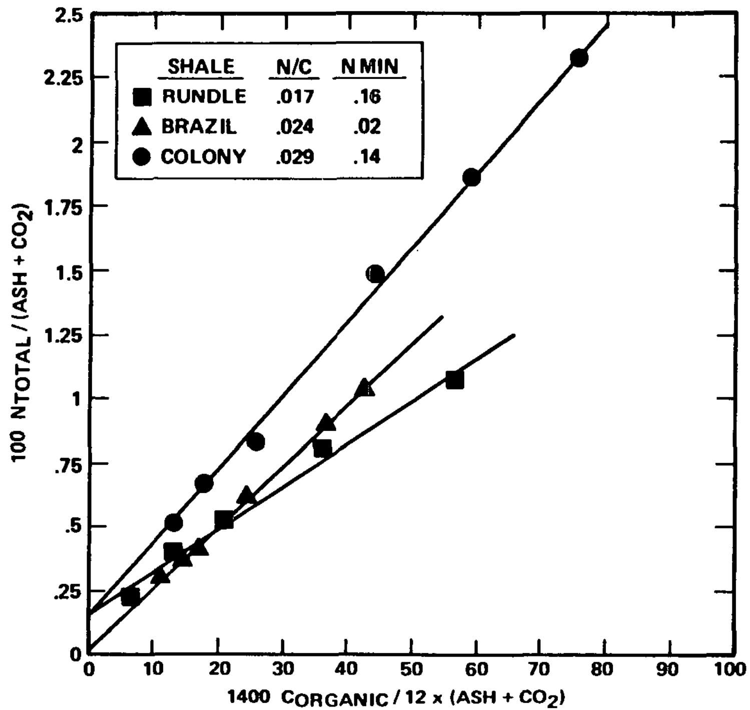


FIGURE 6

SHALE NITROGEN DISTRIBUTION ALSO DETERMINED FROM SINK/FLOAT ANALYSIS



available. A similar situation exists for oxygen. There are three major sources of oxygen: organic, carbonate, and metal oxides. The carbonate can be analyzed and backed out. It is not clear, however, that the high level of oxygen as metal oxides will allow the accurate calculation of either the slope or the intercept. The extension of the procedure to sulfur and oxygen must be evaluated as more accurate data become available.

TABLE VI

TECHNIQUE APPLICABLE TO SULFUR AND OXYGEN

- Overall Balances Slightly Different
  - $O_{total} = O_{organic} + O_{Ash} + O_{CO_2}$
  - $S_{total} = S_{organic} + S_{SO_4} + S_{pyrite}$
- Analyses Complicated by Analytical Difficulties
  - Pyritic and sulfate sulfur difficult to measure in shale
  - Oxygen analyses not straightforward
- Extension to Spent Shale also Possible

TABLE VII

ALTERNATIVE CHARACTERIZATION PROCEDURE INITIATED

- Sink Float Techniques Useful as Characterization Tool
- H/C and N/C Atomic Ratios Calculated
  - Good agreement with extracted kerogen values achieved
- H and N Content of Mineral Matter Calculated
  - Inorganic H and N are significant fractions of total element
- Procedure Applicable to other Elements

CONCLUSIONS

A method has been developed, utilizing sink float procedures, which:

- calculates the H/C and N/C ratios in raw shales
- eliminates the need for acid extraction
- estimates the H and N content of the mineral matrix.

The procedure has been tested on several shales with good results.