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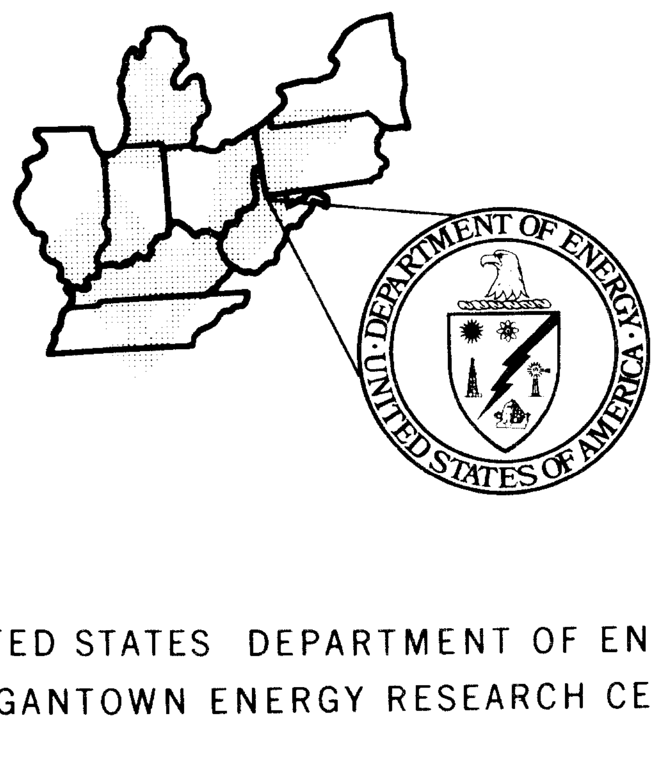
# ORGANIC COMPOSITION OF DEVONIAN SHALE FROM PERRY COUNTY, KENTUCKY

BY

STEVEN C. LAMEY AND EDWARD E. CHILDERS

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## CONTENTS



## ILLUSTRATIONS



## TABLES

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# ORGANIC COMPOSITION OF DEVONIAN SHALE FROM PERRY COUNTY, KENTUCKY

by

Steven C. Lamey[1/] and Edward E. Childers[2/]

## ABSTRACT

Shale samples selected at five foot intervals from a 339 foot section of core in the depth interval from 2369.0 feet to 2708.0 feet of the Devonian Shale from Perry County, Kentucky were studied to determine the quantity of organic matter present, fuel potential, distribution of organic compounds, and the composition of the benzene soluble and insoluble fractions. The methods used consisted of infrared spectroscopy, thermal chromatography, extraction techniques, Fischer Assay, and elemental analysis.

Samples from each five foot interval were ground and then examined by infrared spectroscopy and thermal chromatography. These samples were also subjected to elemental analysis and low temperature ashing. Samples selected at various intervals from the core were then extracted with benzene and each of the two resulting fractions examined further. The benzene soluble portion was checked for functional groups and elemental content, while the insoluble portion was treated with acids to remove mineral matter and infrared spectra of the kerogen material were taken. Resultant depth profiles of total organics, organic to mineral carbon, pyrolytic oil yield, oil carbon number distribution, benzene soluble organic fraction, and major elemental composition of the benzene soluble organics are presented.

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2/ Physical Science Technician

The organic material is contained in several well-defined zones throughout the length of the core, but the individual samples within these zones show variations in the amount of organic material present. The pyrolytic conversion of the organic content to oil is relatively constant which indicates no significant gross compositional changes in the organic components with depth. Thermal chromatographic studies show there is little variation in the chain length of the organic components as a function of depth

## INTRODUCTION

The Morgantown Energy Research Center is participating in a large scale project to characterize the Devonian Shales in the East, determine the magnitude of the resource base, and examine various extraction technologies for recovering the indigenous natural gas. This study is part of that project.

In contrast to the much studied deposits of the Green River Basin in the western United States, relatively little is known of the Devonian Shale deposits of the eastern United States.

A core of the Devonian Shale from Kentucky provided the samples for the present investigation of the organic material in this type sediment. The objectives of this study were to determine the gross composition and quantity of organic material and any differences in content with stratigraphic position.

Knowledge of the composition of the shale is needed to devise recovery methods for extraction of the residual hydrocarbons and to correlate availability of resource with geological data. Determination of the origin of the primary source material can be approached by observing differences in the composition of the organic material present (1,3,8,15). Using similar information, it may be possible to reconstruct the history of the sediment from its deposition through various diagenetic stages (2,4,9,12,13).

## SHALE CORE-LITHOLOGIC DESCRIPTION

The lithology of the core used in this study is described in a report by Byrer and Trumbo (5). The Nicholas Combs Well #7239 in Perry County, Kentucky is located approximately twelve miles north of the town of Hazard. The area contains surface rocks of the Pennsylvanian age associated with the Pennsylvanian Breathitt Formation which contains ten coal beds along with associated shales and limestones. The Lee Formation containing the "Salt Sands" is immediately below the coal section and contains intermittent zones of shale and sandstone. Deeper formations of economic interest includes the massive Maxton sandstone, the Big Lime, the Big Injun and Berea sandstones and the Devonian Shale.

The thickness of the Devonian Shale interval in this region is approximately 400 feet. The total length of the core taken was 339.0 feet beginning at 2369.0 feet and ending at 2708.0 feet. The top portion of the core, approximately 60 feet in length, is medium dark grey shale. A prominent vertical fracture extends almost continuously through this segment along with a number of oblique 60° fractures which are evident throughout the entire core. Numerous pyritic nodules and silty stringers are also present.

A middle section, approximately 240 feet in length, contains zones of darker shale. Intervals reveal slickenside features, many of which are mineral filled. Worm burrows are evident along with many carbonaceous fossil fragments.

The bottom 40 feet of this core is relatively uniform in lithology and appearance. A light medium grey texture is prevalent in this shale segment with no vertical fractures, but numerous bedding plane fractures. This segment is characterized by little pyrite, few organic zones, few slickenside features, few worm burrows, and very little carbonaceous fossil material.

## EXPERIMENTAL

### Sample Preparation

The shale sections for analysis were selected at regularly spaced five foot intervals. Eight inch sections of the four inch diameter oriented core were halved, and one-half removed for petrographic analysis and archiving. The remaining half, after surface sampling, was pulverized to -8 mesh for Fischer Assay analysis. A representative portion of this sample was then ground to -60 mesh for elemental analyses, combustion analysis and chemical separations. A further portion of this material was McCrone ground with ethanol for 15 minutes to -300 mesh. This sample was used for infrared studies, thermal chromatography, and low-temperature ashing.

### Extraction

Shale samples, after being ground to -60 mesh, were transferred to a round bottom flask. Spectral-grade benzene was added, and the mixture allowed to stand overnight at room temperature before refluxing for five hours. Ten milliliters of benzene was added for each gram (10:1 v/w) of shale to be extracted. The liquid was then decanted through filter paper and the residue retained in the original flask for further treatment. Additional benzene (10:1 v/w) was added and the material was refluxed for an additional five hours. The mixture was filtered while hot and the residue washed with 100 ml. of benzene. The residue was dried in an oven at 60°C. The extracted portion was heated and evaporated under a nitrogen atmosphere to remove the final traces of solvent. Both extract and residue were weighed and retained for analysis.

## Kerogen Isolation

Kerogen is usually defined as the insoluble organic matter present in sediments. Analysis of the kerogen is inherently difficult because it is bound tightly to the mineral matrix. It is therefore necessary to remove all this mineral material in order to isolate the kerogen as a "concentrate". The concentrate was prepared using essentially the method of Robinson and Cook (11). This method consists of first treating 10 grams of the residue after benzene extraction with an excess of 10% HCl using a 10:1 v/w ratio and allowing to stand overnight at room temperature. Hydrochloric acid dissolves most carbonates, and basic or amphoteric oxides and hydroxides. Excess concentrated HF (49% in a v/w ratio of 5:1) was then added to the dried product and the mixture allowed to stand at room temperature for 24 hours. The HF was used to remove quartz, silicates and clay minerals. At this point, an excess (100 ml.) of saturated boric acid solution was added to dissolve any insoluble fluoride compounds.

The resulting mixture was centrifuged, and the liquid decanted and discarded. Fifty ml. of a 50% HCl solution was added to the residue and the mixture heated to 60°C for two hours to remove any remaining mineral matter. This solution was filtered while still hot, washed chloride free with hot distilled water, and allowed to dry at room temperature.

Pyrite is not removed by this process, and it requires other physical and chemical procedures for removal (7,14).

## ANALYTICAL PROCEDURES

### Elemental Analyses

Total carbon in the shale samples was determined by the standard combustion method while carbonate carbon was determined by absorption of the carbon dioxide evolved upon treatement of the sample with an excess of boiling 10% HCl solution. Organic carbon was determined by difference between total carbon and mineral carbon. Organic hydrogen, carbon, oxygen and nitrogen in the extracts were determined by a Carlo Erba Model 1104 C, H, N, O Elemental Analyzer. (Reference to specific equipment is made to facilitate understanding and does not imply endorsement by DOE).

### Infrared Analysis

The infrared spectra of all samples were obtained on a Perkin-Elmer Model 621 spectrophotometer using cesium iodide pellets. Samples ground to -300 mesh and weighing from 0.000770 grams to 0.000965 grams of sample were uniformly blended into 0.500 grams of cesium iodide and compressed into pellets averaging between .83 mm and .84 mm in thickness (6).

### Thermal Chromatography

Thermal chromatographic analysis was carried out using a Model MP-3 thermal chromatograph (Chromalytics Corp.). Samples ground to -300 mesh were heated from 60°C to 700°C using a temperature program of 12°C/min. The evolved gases were captured on a trap containing Porapak Q and SE-30 held at room temperature and the trap was then heated to 250°C in less than one minute in order to release the adsorbed gases as a "slug". The gases were then back-flushed to a gas chromatograph column packed with Dexsil 300 on Chromosorb WHP. A flame ionization detector and thermal conductivity detector were used to measure the various organic species as they eluted.

## RESULTS AND DISCUSSION

Table 1 in the Appendix shown the organic carbon and mineral carbon content in the core at five foot intervals. The organic carbon ranges from 0.21 weight percent to 11.29 weight percent with an average of 3.99 weight percent. Mineral carbon ranges from 0.005 weight percent to 1.83 weight percent and averages 0.30 weight percent. Mineral carbon occurs primarily as calcite, dolomite, or carbonates.

Figure 1 is a plot of the organic carbon content as a function of depth. The average value for the entire core is represented by the vertical dashed line. With respect to organic carbon content, four distinct regions are apparent. The uppermost 50 feet of the core has much above average organic carbon while the lowest 50 feet has much below average. The largest portion of the core, about 150 feet near the center, is about average in content, while the fourth region, near the bottom of the core, is above average. Figure 2 is a plot of mineral carbon content as a function of depth. Again, the vertical dashed line is the average content. In general, the lower half of the core contains more mineral carbonates than the upper half.

The percent of organic matter which can be converted to oil upon heating can be determined by comparing the oil yield obtained by Fischer Assay to the organic carbon content. Table 2 in the Appendix shows the weight percent oil yield produced and the weight percent organic carbon present in each sample and their ratio. The oil yield range is 0.1

weight percent to 4.0 weight percent and the average value is 1.4 weight percent.

The average percent conversion of the organic carbon to oil is 31%. This agrees with values obtained by Smith and Young for three cores of Devonian Shale in Kentucky (16).

The oil yield/organic carbon ratio may be related to the composition of the hydrocarbons present in the shale (10). A low ratio may indicate that high amounts of condensed aromatic compounds are present which produce low oil yields and high yields of carbon residue on pyrolysis. On the other hand, a high ratio may indicate the presence of a high percentage of aliphatic and alicyclic oil producing compounds. While this has only been proposed for the kerogen fraction of the shale (10) the amount of bitumen, or soluble organics present is so small in this particular core (see Table 4) that the ratios in Table 2 for the shale before benzene extraction is a good approximation to the results for the kerogen alone. This ratio would show significant changes in the overall composition of the organic components within the core. With a few exceptions, this ratio is relatively constant throughout the entire length of the core, indicating little change with depth in the composition of the organic components.

A subsequent analysis of the organic content with depth was carried out using thermal chromatography. For these studies the gas chromatograph column packing was chosen so that the chromatogram consisted mainly of peaks representing the homologous series of n-alkanes from $C_6$ to about $C_{35}$. This chromatogram served two purposes: First, it was used as a "fingerprint" for each sample, and allowed rapid comparison so that gross differences in organic content between samples could be quickly

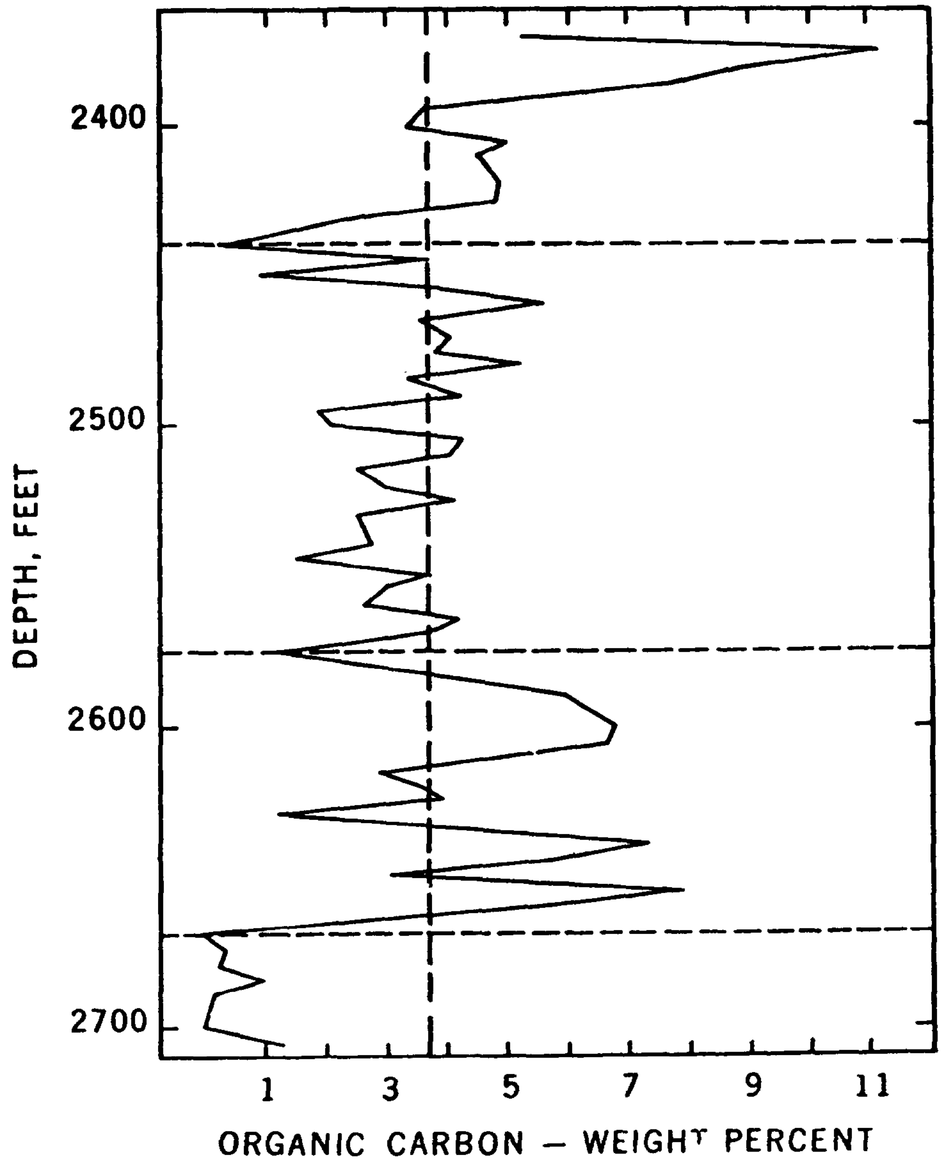


Figure 1: Variation of organic carbon content with depth.

-------- average content

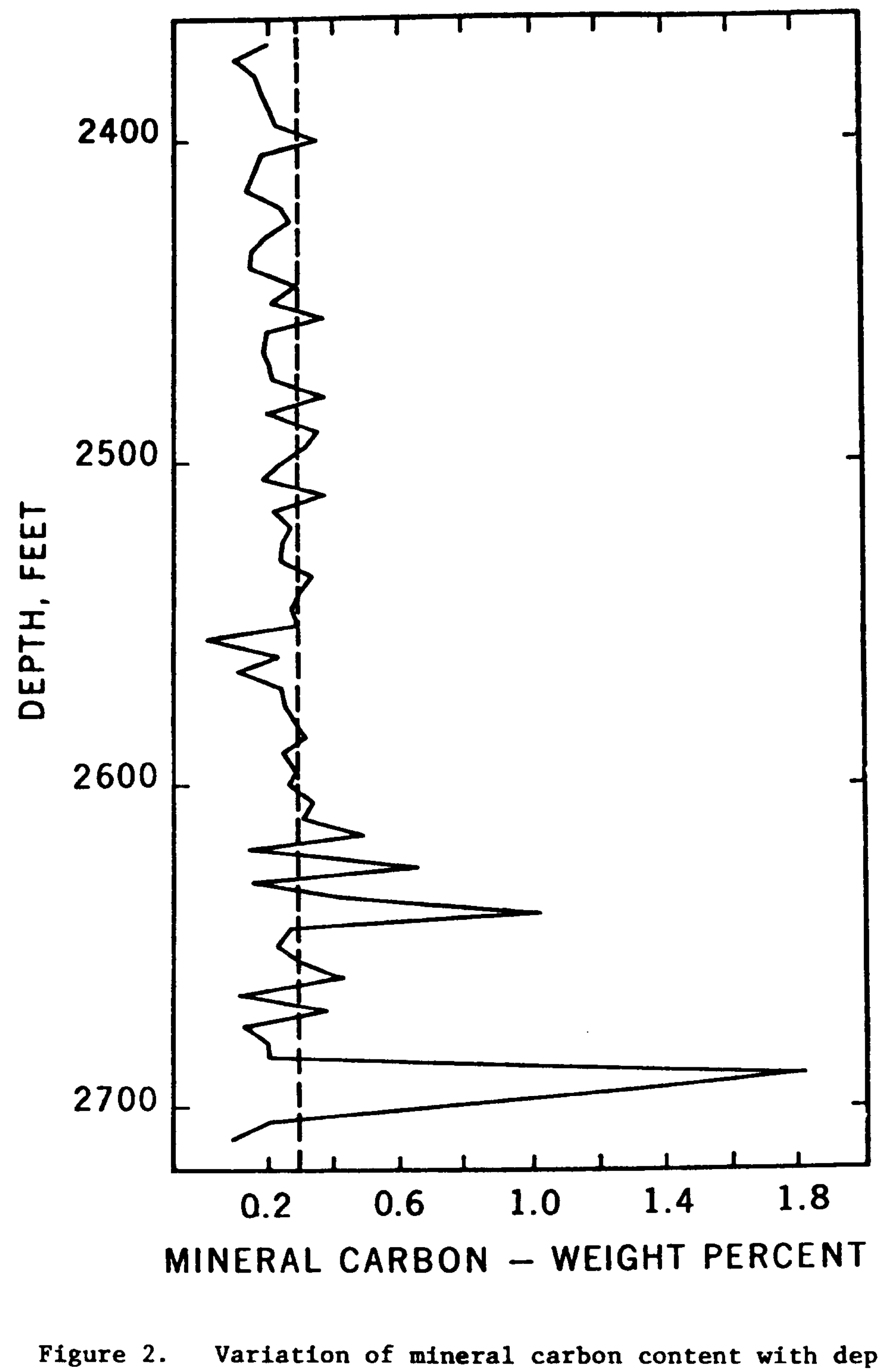


Figure 2. Variation of mineral carbon content with depth.

-------- average content

noted. Secondly, it allows one to assess the distribution, by chain length, of the organic compounds present in the oil derived by pyrolysis.

For analysis, the series of compounds was divided into four carbon number groups: $C_{12}$ and below, $C_{13}$ through $C_{20}$, $C_{21}$ through $C_{26}$, and $C_{27}$ to the end of the chromatogram. These correspond to approximate boiling ranges up to 215°C, 216°C to 361°C, 362°C to 443°C, and above 443°C. The peak height of each component was measured and an assessment of the amount of organic material present in each fraction was made. The results are shown in Table 3.

As shown in Figure 3, all pyrolysis samples had substantial amounts of low molecular weight hydrocarbons. In general, the heavy hydrocarbons represent only a small portion of the total. The composition was about the same at all oil yields. The average value for each fraction obtained by pyrolysis was 48.2%, $C_{12}$ and below; 25.9%, $C_{13}$-$C_{20}$; 16.8%, $C_{21}$-$C_{26}$; 9.1%, $C_{27}$ and above.

The amount of benzene soluble organic matter in these samples is extremely small as illustrated in Table 4. On five samples selected at various depths throughout the core, the average quantity extracted with benzene was about 0.5 weight percent of the total shale. This is essentially the same amount as that reported previously (17) on the New Albany Shale in Illinois which is from the Mississippian-Devonian Period. The extraction ratio (2) is defined as the percent of the soluble extract in oil shale divided by the weight percent of the organic carbon in oil shale. It appears that the percent of total shale mass that is benzene extractable varies directly with the amount of organic carbon present, while the extraction ratio decreases with an increase in

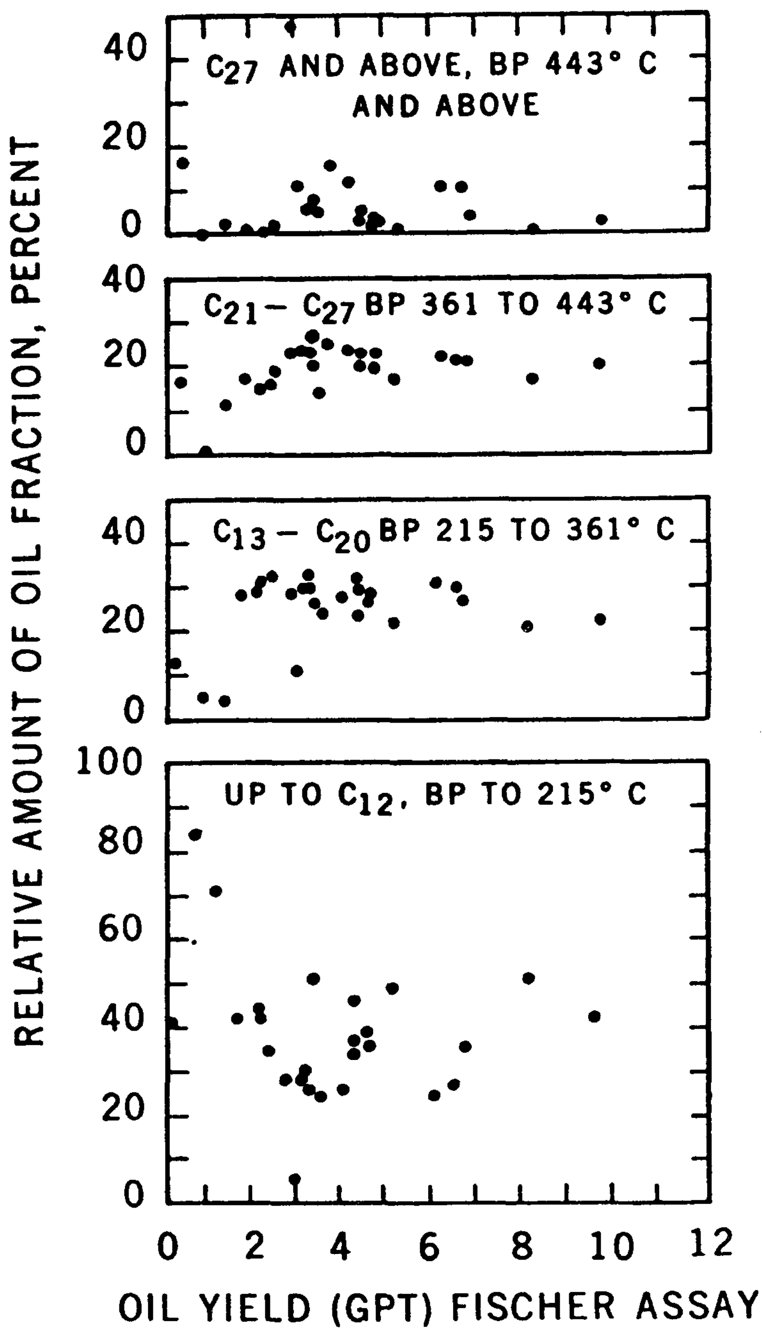


**Figure 3. Variation of Oil Yield with Chain Length of Hydrocarbons, in gallons per ton.**

the amount of organic carbon present. That is, higher organic content shale samples produce more bitumen by extraction, but the bitumen to kerogen ratio decreases. It is not yet clear if this is an experimental technique artifact or a reflection of true compositional differences. This question is being addressed.

The elemental analysis of each of the extracts is shown in Table 5. The composition of each is similar, indicating little change in organic composition with depth.

Infrared spectroscopy aids in evaluating differences in organic composition in terms of functional groups. Spectra taken during and after the application of various analytical techniques was used to ascertain what components in the sample may have been altered by the techniques and to what extent this alteration has taken place. Figures 4,5 and 6 illustrate the types of structural information available through infrared spectroscopy. Figure 4 is a spectrum of the shale ground to -300 mesh before any chemical treatment has occurred. The organic contribution to the total shale spectrum is relatively small. This is due primarily to the composition of the organic material and the relative distribution of the organic and inorganic components. From the spectrum in Figure 4, the predominant mineral is quartz indicated by the bands at 790 $cm^{-1}$, 772 $cm^{-1}$, 452 $cm^{-1}$, 388 $cm^{-1}$ and 363 $cm^{-1}$.

The major clay component is illite as determined by the $OH^-$ stretching vibration at 3597 $cm^{-1}$, and the overall spectral shape. The presence of illite was verified by x-ray diffraction. Figure 5 shows the spectrum of the benzene extract which represents less than 1.0% of the shale. The predominant bands are the following:

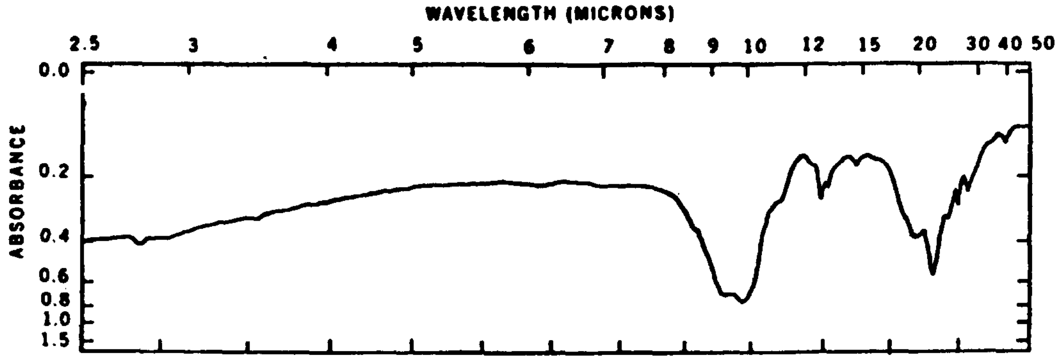


FIGURE 4

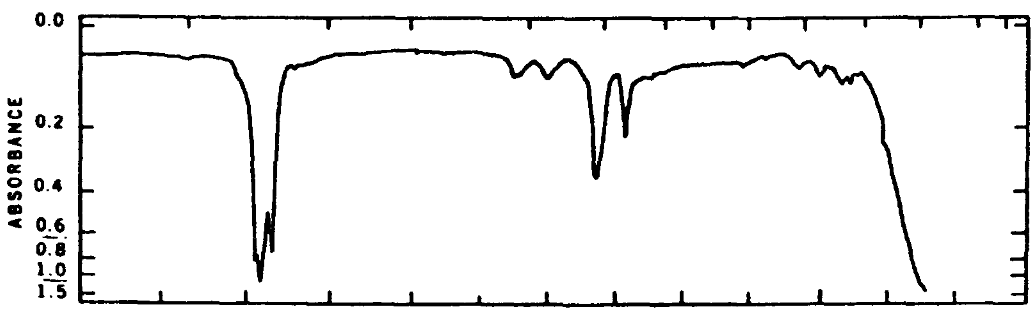


FIGURE 5

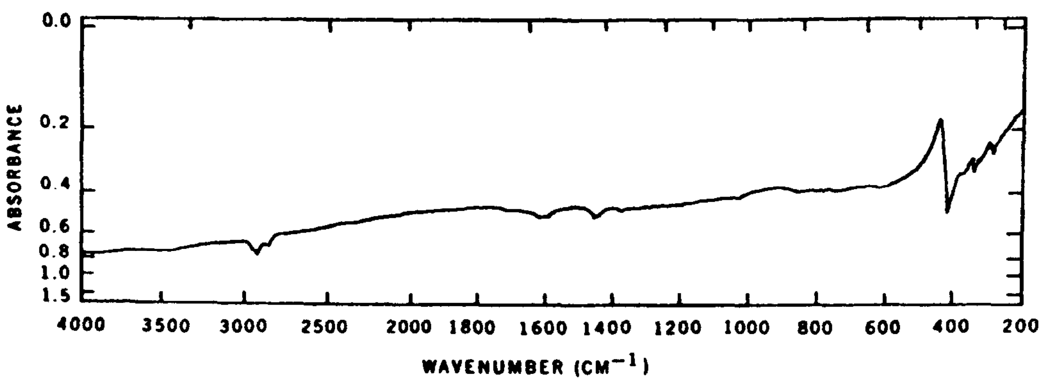


FIGURE 6

Top (Figure 4) Infrared spectrum of untreated shale sample. Middle (Figure 5) Infrared spectrum of the benzene solubles. Bottom (Figure 6) Infrared spectrum of the kerogen concentrate.

(a) The C-H stretching from the aliphatic components at 2850 $cm^{-1}$ and 2960 $cm^{-1}$.

(b) The methyl group bending at 1380 $cm^{-1}$.

(c) The olefinic C-H stretching at 1650 $cm^{-1}$.

(d) The aromatic C-H stretching at 3020 $cm^{-1}$.

(e) The - $CH_2$ - and $CH_3$ - bending at 1460 $cm^{-1}$.

(f) The aromatic out-of-plane bending between 720 $cm^{-1}$ and 900 $cm^{-1}$.

(g) The -C=O stretching at 1715 $cm^{-1}$.

Figure 6 is the spectrum of the kerogen isolate still containing pyrite as indicated by the band at 411 $cm^{-1}$. The organic bands associated with the kerogen are: (1) The aliphatic C-H stretching at 2850 $cm^{-1}$ and 2960 $cm^{-1}$ (2) the aromatic C-H stretching at 3020 $cm^{-1}$ (3) the olefinic C-H stretching at 1650 $cm^{-1}$ (4) the C-H bending at 1380 $cm^{-1}$ and 1460 $cm^{-1}$ (5) the aromatic out-of-plane bending between 720 $cm^{-1}$ and 900 $cm^{-1}$.

## CONCLUSION

It is apparent, based upon all the parameters examined, that the quantity of organic material and the oil yield vary significantly in various zones throughout the core, but little difference in the composition of the organic matter, with depth, was observed.

There is very little apparent difference in the composition of the organic components throughout the core section examined, but further analyses of composition are planned. This is the first Devonian Shale core examined for organic content at the Morgantown Energy Research Center. Other wells are being studied at this time and further reports of these cores are anticipated.

Appendix

Table 1 - Organic and Mineral Carbon Content of The Devonian Shale Samples

| Depth, ft. | Organic Carbon wt. % | Mineral Carbon wt. % |
|---|---|---|
| 2369.05-2369.67 | 5.51 | 0.18 |
| 2375.10-2375.50 | 11.29 | 0.08 |
| 2379.61-2380.27 | 9.08 | 0.13 |
| 2384.87-2385.28 | 7.89 | 0.16 |
| 2390.47-2391.15 | 6.14 | 0.18 |
| 2395.15-2395.78 | 3.88 | 0.20 |
| 2400.55-2401.15 | 3.62 | 0.34 |
| 2405.60-2406.18 | 5.23 | 0.16 |
| 2416.00-2416.70 | 4.72 | 0.11 |
| 2418.78-2419.48 | 5.11 | 0.22 |
| 2424.85-2425.23 | 5.10 | 0.25 |
| 2429.45-2430.12 | 2.89 | 0.18 |
| 2434-85-2435.23 | 0.52 | 0.13 |
| 2439.14-2439.79 | 4.40 | 0.49 |
| 2440.20-2440.50 | 0.31 | 0.13 |
| 2443.78.2444.35 | 3.89 | 0.26 |
| 2449.62-2450.29 | 1.20 | 0.19 |
| 2454.75-2455.48 | 4.23 | 0.35 |
| 2459.97-2460.63 | 5.82 | 0.18 |
| 2463.94-2464.42 | 3.80 | 0.17 |
| 2468.58-2469.24 | 4.30 | 0.19 |
| 2474.70-2475.17 | 4.05 | 0.20 |
| 2479.60-2480.26 | 5.50 | 0.35 |
| 2484.90-2385.85 | 3.58 | 0.19 |
| 2489.78-2490.46 | 4.49 | 0.34 |
| 2495.00-2495.57 | 2.17 | 0.30 |
| 2499.17-2499.79 | 2.35 | 0.22 |
| 2504.60-2505.28 | 4.46 | 0.17 |
| 2509.69-2510.30 | 4.26 | 0.36 |
| 2514.90-2515.37 | 2.83 | 0.21 |
| 2519.33-2520.04 | 3.27 | 0.26 |
| 2525.10-2525.45 | 4.35 | 0.24 |
| 2529.49-2530.15 | 2.81 | 0.24 |
| 2534.80-2535.43 | 2.89 | 0.32 |
| 2538.86-2539.53 | 3.03 | 0.29 |
| 2545.30-2545.80 | 1.75 | 0.27 |
| 2549.69-2550.37 | 3.00 | 0.29 |
| 2555.60-2556.65 | 3.27 | 0.005 |
| 2559.58-2560.26 | 2.91 | 0.24 |
| 2565.10-2565.85 | 4.48 | 0.11 |

Appendix

Table 1 - Organic and Mineral Carbon Content of the Devonian Shale Samples (continued)

| Depth, Ft. | Organic Carbon wt. % | Mineral Carbon wt. % |
|---|---|---|
| 2570.06-2570.69 | 3.96 | 0.24 |
| 2574.85-2575.45 | 1.48 | 0.25 |
| 2579.81-2580.49 | 3.26 | 0.28 |
| 2585.35-2586.00 | 4.20 | 0.31 |
| 2589.80-2590.47 | 5.23 | 0.25 |
| 2594.60-2595.25 | 7.10 | 0.28 |
| 2599.88-2600.54 | 6.97 | 0.26 |
| 2604.50-2605.12 | 6.85 | 0.33 |
| 2609.68-2610.34 | 8.71 | 0.30 |
| 2615.12-2615.74 | 3.06 | 0.48 |
| 2618.12-2619.39 | 3.75 | 0.11 |
| 2624.00-2625.48 | 4.14 | 0.65 |
| 2628.79-2629.50 | 1.52 | 0.13 |
| 2634.45-2635.10 | 5.32 | 0.41 |
| 2639.38-2640.03 | 7.52 | 1.02 |
| 2644.65-2645.10 | 5.98 | 0.26 |
| 2648.88-2649.55 | 3.38 | 0.22 |
| 2654.80-2655.35 | 8.12 | 0.28 |
| 2659.19-2659.88 | 6.11 | 0.41 |
| 2665.80-2666.20 | 1.38 | 0.10 |
| 2669.26-2669.94 | 0.21 | 0.37 |
| 2674.90-2675.45 | 0.58 | 0.12 |
| 2678.92-2679.59 | 0.80 | 0.19 |
| 2684.75-2685.32 | 1.35 | 0.20 |
| 2688.95-2689.62 | 0.41 | 1.83 |
| 2694.80-2695.45 | 0.38 | 1.30 |
| 2699.41-2700.07 | 0.29 | 0.67 |
| 2704.80-2705.50 | 1.59 | 0.21 |
| 2707.87-2708.60 | 4.37 | 0.10 |

Appendix

Table 2 - Relation of Oil Yield by Fischer Assay to Organic Carbon in the Shale

| Depth, Ft. top btm. | Organic Carbon Wt. % | Oil yield gal/ton | Oil Yield Wt. % | Oil Yield / Org. Carbon |
|---|---|---|---|---|
| 2369.05-2369.67 | 5.51 | 4.0 | 1.5 | 0.27 |
| 2375.10-2375.50 | 11.29 | 10.5 | 4.0 | 0.35 |
| 2379.61-2380.27 | 9.08 | 8.1 | 3.1 | 0.34 |
| 2384.87-2385.28 | 7.89 | 7.6 | 2.9 | 0.37 |
| 2390.47-2391.15 | 6.14 | 6.1 | 2.3 | 0.37 |
| 2395.15-2395.78 | 3.88 | 3.3 | 1.2 | 0.31 |
| 2400.55-2401.15 | 3.62 | 2.6 | 1.0 | 0.28 |
| 2405.60-2406.18 | 5.23 | 5.2 | 2.0 | 0.38 |
| 2416.00-2416.70 | 4.72 | 3.6 | 1.4 | 0.30 |
| 2418.78-2419.48 | 5.11 | 4.3 | 1.6 | 0.31 |
| 2424.85-2325.23 | 5.10 | 3.8 | 1.5 | 0.29 |
| 2429.45-2430.12 | 2.88 | 2.1 | 0.8 | 0.28 |
| 2439.14-2439.79 | 4.41 | 3.2 | 1.2 | 0.27 |
| 2443.78-2444.35 | 3.89 | 1.7 | 0.6 | 0.15 |
| 2454.75-2455.48 | 4.23 | 2.9 | 1.1 | 0.26 |
| 2459.97-2460.63 | 5.82 | 4.5 | 1.7 | 0.29 |
| 2463,94-2464.42 | 3.80 | 3.0 | 1.1 | 0.29 |
| 2468.58-2469.24 | 4.30 | 3.4 | 1.3 | 0.30 |
| 2474.70-2475.17 | 4.05 | 3.1 | 1.2 | 0.30 |
| 2479.60-2480.26 | 5.51 | 4.6 | 1.8 | 0.33 |
| 2484.90-2485.85 | 3.58 | 2.7 | 1.0 | 0.28 |
| 2489.78-2490.46 | 4.49 | 4.3 | 1.6 | 0.36 |
| 2495.00-2495.57 | 2.17 | 0.4 | 0.1 | 0.05 |
| 2499.17-2499.79 | 2.35 | 2.2 | 0.8 | 0.34 |
| 2504.60-2505.28 | 4.46 | 3.1 | 1.2 | 0.27 |
| 2509.69-2510.30 | 4.26 | 3.6 | 1.4 | 0.33 |
| 2514.90-2515.37 | 2.83 | 4.6 | 1.8 | 0.64 |
| 2519.33-2520.04 | 3.27 | 2.8 | 1.1 | 0.34 |
| 2525.10-2525.45 | 4.35 | 2.9 | 1.1 | 0.25 |
| 2539.49-2530.15 | 2.81 | 1.7 | 0.6 | 0.21 |
| 2534.80-2535.43 | 2.89 | 2.0 | 0.7 | 0.24 |
| 2538.86-2539.53 | 3.03 | 2.4 | 0.9 | 0.30 |
| 2545.30-2545.80 | 1.75 | 1.1 | 0.4 | 0.23 |
| 2549.69-2550.37 | 3.00 | 1.5 | 0.6 | 0.20 |
| 2555.60-2556.65 | 3.28 | 2.1 | 0.8 | 0.24 |
| 2559.58-2560.26 | 2.91 | 3.3 | 1.3 | 0.45 |
| 2565.10-2565.85 | 4.48 | 2.4 | 0.9 | 0.20 |
| 2570.06-2570.69 | 3.98 | 3.0 | 1.2 | 0.30 |
| 2574.85-2575.45 | 1.50 | 2.4 | 0.9 | 0.60 |
| 2579.81-2580.49 | 3.26 | 3.2 | 1.2 | 0.37 |

## Appendix

Table 2 - Relation of Oil Yield by Fischer Assay to Organic Carbon in the Shale (continued)

| Depth, Ft. top btm. | Organic Carbon Wt. % | Oil yield gal/ton | Oil Yield Wt. % | Oil Yield / Org. Carbon |
|---|---|---|---|---|
| 2585.35-2586.00 | 4.20 | 3.3 | 1.3 | 0.31 |
| 2589.80-2590.47 | 5.23 | 4.6 | 1.8 | 0.34 |
| 2594.60-2595.25 | 7.10 | 7.4 | 2.7 | 0.38 |
| 2599.88-2600.54 | 6.97 | 6.7 | 2.5 | 0.36 |
| 2604.50-2605.12 | 6.85 | 4.2 | 1.6 | 0.23 |
| 2609.68-2610.34 | 8.91 | 6.5 | 2.4 | 0.27 |
| 2615.12-2615.74 | 3.14 | 2.9 | 1.1 | 0.35 |
| 2618.12-2619.39 | 3.75 | 4.3 | 1.6 | 0.43 |
| 2624.00-2625.48 | 4.15 | 3.0 | 1.2 | 0.29 |
| 2628.79-2629.50 | 1.52 | 0.8 | 0.3 | 0.20 |
| 2634.45-2635.10 | 5.32 | 3.8 | 1.5 | 0.28 |
| 2639.38-2640.03 | 7.52 | 9.6 | 3.6 | 0.48 |
| 2644.65.2645.10 | 5.98 | 5.1 | 1.9 | 0.32 |
| 2648.88-2649.55 | 3.34 | 3.4 | 1.3 | 0.39 |
| 2654.80-2655.35 | 8.12 | 5.4 | 2.1 | 0.26 |
| 2659.19-2659.88 | 6.11 | 5.1 | 2.0 | 0.33 |
| 2684.75-2685.32 | 1.36 | 0.4 | 0.1 | 0.07 |
| 2704.80-2705.50 | 1.60 | 0.5 | 0.2 | 0.13 |
| 2707.87-2708.60 | 4.38 | 4.1 | 1.6 | 0.37 |

Appendix

Table 3 - Thermal Chromatographic Analysis and Relative Composition of the Pyrolytic Oil Fractions for the Shale Core

| Depth Ft. | | Relative Amount of Oil Fractions % | | | |
|---|---|---|---|---|---|
| TOP | BTM. | $C_{12}$ and below | $C_{13}$-$C_{20}$ | $C_{21}$-$C_{26}$ | $C_{27}$ and above |
| 2369.05 | 2369.67 | 36.4 | 28.4 | 23.3 | 11.9 |
| 2375.10 | 2375.50 | 41.7 | 27.4 | 19.6 | 11.3 |
| 2379.61 | 2380.27 | 61.2 | 20.9 | 17.0 | 0.9 |
| 2384.87 | 2385.28 | 43.1 | 30.4 | 16.8 | 9.7 |
| 2390.47 | 2391.15 | 34.8 | 31.2 | 23.3 | 10.7 |
| 2395.15 | 2395.78 | 37.7 | 29.7 | 19.8 | 12.8 |
| 2400.55 | 2401.15 | 36.6 | 31.2 | 19.0 | 13.2 |
| 2405.60 | 2406.18 | 32.7 | 28.4 | 21.2 | 17.7 |
| 2416.00 | 2416.70 | 37.5 | 33.2 | 18.2 | 11.1 |
| 2418.78 | 2419.48 | 42.9 | 32.4 | 21.0 | 3.7 |
| 2424.85 | 2425.23 | 49.4 | 24.0 | 15.0 | 11.6 |
| 2429.45 | 2430.12 | 52.8 | 30.9 | 16.2 | 0.1 |
| 2439.14 | 2439.79 | 38.9 | 34.1 | 20.7 | 6.3 |
| 2443.78 | 2444.35 | 54.5 | 24.1 | 14.5 | 6.9 |
| 2454.75 | 2455.48 | 45.6 | 27.0 | 14.9 | 12.5 |
| 2463.94 | 2464.42 | 45.2 | 28.8 | 16.0 | 10.0 |
| 2468.58 | 2469.24 | 60.1 | 25.9 | 14.0 | 0.0 |
| 2474.70 | 2475.17 | 61.4 | 23.6 | 11.3 | 3.7 |
| 2479.60 | 2480.26 | 49.6 | 28.3 | 19.7 | 2.4 |
| 2484.90 | 2485.85 | 29.6 | 30.5 | 16.7 | 13.2 |
| 2489.78 | 2490.46 | 42.7 | 30.5 | 22.7 | 4.1 |
| 2495.00 | 2495.52 | 47.6 | 34.1 | 10.1 | 8.2 |
| 2499.17 | 2499.79 | 53.5 | 30.5 | 15.7 | 0.3 |
| 2504.60 | 2505.28 | 61.2 | 20.8 | 11.4 | 6.6 |
| 2509.69 | 2510.30 | 43.0 | 24.3 | 26.4 | 15.3 |
| 2514.90 | 2515.37 | 48.6 | 27.6 | 13.3 | 10.6 |
| 2519.33 | 2520.04 | 33.8 | 28.2 | 24.2 | 13.8 |
| 2529.49 | 2530.15 | 52.0 | 28.8 | 18.1 | 1.1 |
| 2534.80 | 2535.45 | 44.6 | 28.8 | 17.0 | 9.6 |
| 2538.86 | 2539.53 | 44.4 | 33.6 | 19.5 | 2.5 |
| 2545.30 | 2545.80 | 44.5 | 27.3 | 14.6 | 13.6 |
| 2555.60 | 2556.05 | 54.5 | 22.9 | 12.8 | 9.8 |
| 2559.58 | 2560.26 | 36.6 | 30.2 | 28.2 | 5.0 |
| 2565.10 | 2565.85 | 50.8 | 30.7 | 12.9 | 5.6 |
| 2570.06 | 2570.69 | 15.2 | 11.2 | 24.1 | 49.5 |
| 2574.85 | 2575.45 | 51.7 | 25.6 | 16.6 | 6.1 |
| 2579.81 | 2580.49 | 38.5 | 29.9 | 23.6 | 7.9 |
| 2589.90 | 2590.47 | 46.9 | 26.9 | 23.3 | 2.9 |
| 2594.60 | 2595.25 | 76.1 | 15.3 | 5.1 | 3.5 |
| 2599.88 | 2600.54 | 46.5 | 27.5 | 21.7 | 4.3 |
| 2604.50 | 2605.12 | 52.9 | 25.8 | 15.4 | 5.9 |
| 2609.68 | 2610.34 | 37.0 | 29.7 | 22.5 | 10.8 |

Appendix

Table 3 - Thermal Chromatographic Analysis and Relative Composition of the Pyrolytic Oil Fractions for the Shale Core (continued)

| | | | | | |
|---|---|---|---|---|---|
| 2615.12 | 2615.74 | 59.5 | 13.9 | 7.7 | 18.9 |
| 2618.12 | 2619.39 | 55.5 | 23.1 | 19.7 | 1.7 |
| 2624.00 | 2625.48 | 37.6 | 27.6 | 18.6 | 16.2 |
| 2634.45 | 2535.10 | 56.6 | 18.7 | 14.4 | 10.2 |
| 2639.38 | 2640.03 | 53.2 | 23.7 | 20.2 | 2.9 |
| 2644.65 | 2645.10 | 49.9 | 24.0 | 17.5 | 8.6 |
| 2654.80 | 2655.35 | 49.3 | 28.0 | 15.6 | 7.1 |
| 2665.80 | 2666.20 | 31.9 | 25.8 | 11.0 | 31.3 |
| 2669.26 | 2669.94 | 81.0 | 4.0 | 12.0 | 3.0 |
| 2674.90 | 2675.45 | 48.9 | 21.5 | 13.5 | 16.0 |
| 2678.92 | 2679.59 | 94.0 | 5.2 | 0.7 | 0.0 |
| 2684.75 | 2685.32 | 61.3 | 18.7 | 12.3 | 7.7 |
| 2688.95 | 2689.62 | 50.6 | 13.6 | 18.8 | 17.0 |
| 2704.80 | 2705.50 | 49.5 | 43.9 | 2.9 | 3.7 |

## Appendix

Table 4 - Percentage of Extractable Organics for Selected Segments of the Shale Core

| Depth, ft. | Weight % of total shale extracted with benzene | Weight % of organic carbon | Extraction ratio x 100 |
|---|---|---|---|
| 2379.61-2380.27 | 0.63 | 9.08 | 6.9 |
| 2468.58-2469.24 | 0.35 | 4.30 | 8.1 |
| 2559.58-2560.26 | 0.38 | 2.91 | 13.1 |
| 2599.88-2600.54 | 0.54 | 6.97 | 7.7 |
| 2654.80-2655.35 | 0.51 | 8.12 | 6.2 |

Appendix

Table 5 - Chemical Analysis of the Benzene Soluble Material For Selected Segments of the Shale Core

| Depth, ft. | % Carbon | % Hydrogen | % Nitrogen | % Oxygen | H/C |
|---|---|---|---|---|---|
| 2379.61-2380.27 | 85.72 | 11.76 | 0.33 | 1.71 | 1.65 |
| 2468.58-2469.24 | 85.72 | 11.80 | 0.23 | 1.39 | 1.65 |
| 2559.58-2560.26 | 86.02 | 11.84 | 0.18 | 1.48 | 1.65 |
| 2599.88-2600.54 | 86.23 | 11.73 | 0.36 | 1.42 | 1.63 |
| 2654.80-2655.35 | 86.22 | 11.43 | 0.40 | 1.17 | 1.59 |

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