

A RAPID METHOD FOR ESTIMATING OIL YIELDS OF OIL SHALES BY BROAD-LINE NMR SPECTROMETRY

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INTRODUCTION

The Bureau of Mines, U.S. Department of the Interior, has been involved for many years in research work on oil shales. One phase of the work is a study of the characteristics, composition, and properties of Green River Formation oil shales in Colorado, Wyoming, and Utah. Of particular interest to a future oil-shale industry is the determination of the quantity of organic matter and of recoverable shale oil that is represented in these deposits.

There are two methods that are the most commonly used to estimate the organic matter and the recoverable shale oil present in oil shales. The standard method for estimating total organic matter is by determining organic carbon contents by the combustion method. The most common method for estimating the recoverable shale oil from oil shales is the modified Fischer assay method (1).² This method involves controlled heating of a sample of oil shale in a small metal retort. Both of these methods have become standard methods of assay for their particular purposes. The methods, however, are time consuming. For example, a typical Fischer assay may take 1-1/2 hours to complete and organic carbon determinations by combustion may take 4 hours to complete. It would be of great utility if a method were available that could increase the number of samples that could be processed per unit time.

Broad-line NMR spectrometry offers advantages for such a method. The NMR instrument may be tuned to observe only proton resonances. The principle of the method is that the quantity of organic hydrogen in the oil shales is related to the organic carbon contents and thus to the potential oil yields. Correlations of the NMR signal strengths can then be made with Fischer assay oil yields and organic carbon contents.

In the present work, it was necessary to test if the correlations of the proton broad-line NMR signal strengths were independent of the depths of the oil-shale samples; that is, is the hydrogen-to-carbon content and the hydrogen-to-potential oil yield sufficiently independent of depth so that the NMR correlations may be used in an analytical method? It was also necessary to show if the correlations hold over the limited area of an oil-shale deposit under development. The usual questions regarding other possible interferences had to be answered, particularly the possible interference from water protons and inorganic protons.

The results of the present research show that the proton broad-line NMR signal strength can be correlated with both the Fischer assay oil yield and the organic carbon contents of five oil shales from Colorado, Utah, Wyoming, and Kentucky. The correlations were shown to be independent of depth. The similarities of correlation parameters for cores of oil shales from the Green River Formation nearly 100 miles apart indicate that only one set of calibration data need be obtained for one oil-shale deposit under commercial development. The method is rapid, and the oil yields and

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² Underlined numbers in parentheses refer to items in the list of references at the end of this report.

organic carbon contents can be estimated on as many as 30 samples per hour. The spectrometric results can be used to supplement the standard methods so that the desired data may be rapidly measured on large numbers of samples expected in a future oil-shale industry.

EXPERIMENTAL PROCEDURE

Oil Shales Studied

Five oil shales from different geographic locations were used in this study. Four of the oil shales were from the Green River Formation in Colorado, Wyoming, and Utah, and one oil shale was from the New Albany Formation in Kentucky. Two oil shales from Wyoming were selected for this study--one from the Green River Basin and one from the Washakie Basin. These two Wyoming shales are designated Wyoming (GRB) and Wyoming (WB) in the discussion that follows.

Samples were selected from one core of each oil shale. Fischer assay oil yields and organic carbon contents were determined on the samples. The samples chosen had a range of Fischer assay oil yield from about 0-50 gal/ton and an organic carbon content range of about 0.5-25 weight percent.

The oil-shale samples were selected so that a test of the correlation of the NMR data with depth could be made. Accordingly, 20 samples of the Wyoming (WB) core were chosen that represented 2,500 feet of the core; 17 samples of the Colorado core were chosen that represented 719 feet of that core; 26 samples were chosen that represented 76 feet of the Utah core; 15 samples of the Kentucky core were chosen that represented 56 feet of that core; and 19 samples were chosen that represented 36 feet of the Wyoming (GRB) core.

Each oil-shale sample was prepared for NMR analysis by grinding it to yield powdered oil shale with the following approximate sieve analysis:

<u>Mesh size³</u>	<u>Wt pct of sample</u>
- 80 + 100	3
-100 + 200	30
-200 + 325	46
-325	21

Preparation of Sample Tubes

Each oil-shale sample was poured into a 4-inch x 1/2-inch-bore test tube. The weight of sample in the tube was approximately 7-8 g. The sample tube was then tapped until the shale sample would settle no further. The oil-shale samples, packed in this way, had bulk densities of about 1.10 g/ml. The sample in the tube completely occupied the sensitive volume of the NMR probe.

Instrumentation

The broad-line NMR spectrometer used in this work was put at our disposal by Major John C. Balogh of the Physics Department of the U.S. Air Force Academy, Colorado Springs, Colorado.

³ Plus signs on mesh sizes indicate that the sample is retained by that screen. Minus signs indicate the sample passes through the screen.

This instrument was a Varian V-4200B unit⁴ utilizing a 15-inch Varian magnet with a Varian Fieldral Mark III regulator; a Varian Model 4210A, 2-16 megahertz RF unit; appropriate sweep and detection electronics; a Varian F-80 X-Y recorder; and a Varian V4230B, 8-16 MHz probe. A Leeds and Northrup Speedomax G, 0-5 mv recorder fitted with a digital integrator (Instron Corp., Quincy, Mass.) was also electrically connected to the spectrometer output to give the area under the NMR adsorption curve.

Measurement of NMR Signal Strengths

NMR spectra were obtained on the various oil shales for two purposes: (1) To determine the location and number of resonance peaks, and (2) to use the absorption peak corresponding to the organic protons for signal strength and oil-yield correlations. For the first purpose, three probes were used: A 2- to 4-megahertz probe, a 4- to 8-megahertz probe, and an 8- to 16-megahertz probe. For the second purpose, an 8- to 16-megahertz probe was used.

A typical set of conditions for measurement of NMR signal areas for the correlation work follows. A sample tube containing an oil-shale sample was centered in the 8- to 16-megahertz probe and placed between the pole faces of the NMR spectrometer. The magnetic field, which had been on for several hours, stabilized at 2.320 kilogauss. The RF unit was turned on and set at a frequency of 10.003 MHz, and the RF field strength was adjusted to a fixed value. The sawtooth modulation unit was adjusted to a frequency of 40 hertz, phasing of 1.7, and field strength of 6.3×100 which corresponds to approximately 2.4 gauss. The output control unit was set at a signal level dependent on signal strength, filter at 40, reference phase 3.8, response 3, and balance at 5.2. The steady-state magnetic field was then swept through 50 gauss centered at 2.320 kilogauss in a sweep time of 2.5 min. The paddles of the probe were adjusted to give the first derivative absorption mode signal. The instrument was adjusted so that the richest oil-shale sample gave a peak of almost full scale on the recorder chart paper. The Instron integrator was used to record the positive area of the absorption curve (a base line was chosen that eliminated two small negative area components of the first derivative curve from the total area). All oil-shale samples in a set were run using constant instrument operating parameters. The areas under the broad-line signal of the absorption mode were recorded.

Three sets of correlation runs were made several months apart. In Run I the paddles of the NMR probe were adjusted to give the dispersion mode signal. In this case, the areas under the dispersion curve were obtained by counting squares under both the positive and negative areas of the dispersion plot on the chart paper. The paddles of the NMR probe were adjusted to give the first derivative of the absorption mode in Runs II and III. Areas for Runs II and III were obtained using the electronic integrator. The NMR signal areas were expressed as either integrator counts or as "square counts" and were different owing to changes in integrator constants. These three sets of areas were used to test the repeatability of linear regression correlations of the data.

Test for Interferences

The nuclear magnetic resonance conditions were set to obtain the proton resonances of the organic protons in the oil-shale samples; therefore, it was necessary to prove that the signal measured was due only to organic protons. One experiment was performed with a set of oil-shale samples having a relatively high concentration of nahcolite (NaHCO_3), dawsonite [$\text{NaAl}(\text{OH})_2\text{CO}_3$], and illite

⁴ Reference to specific brand names is made for identification purposes only and does not imply endorsement by the Bureau of Mines.

(a complex mineral substance containing 4-1/2 to 6 percent water as lattice hydroxyl groups). The experiment showed that the inorganic-associated protons did not interfere with the organic-associated proton resonance.

A second set of experiments was performed to test for the interference of free water. In this set of experiments, three samples of each oil shale were placed in a sealed chamber containing pans of water. The oil-shale samples were allowed to remain in this chamber (75 percent relative humidity) for 48 hours. The samples were found to absorb from 2 to 5 weight percent water in that period. The wet shale was placed in one of the test tubes, and the NMR signal area was measured. The signal area of the wet sample was compared to the signal area of the sample before wetting. The water proton was found to contribute to the NMR signal strength measured for the organic protons. The interference due to water was found to be easily avoided by air-drying the sample at room temperature for about 2 hours.

Treatment of Data

The mathematical relationships between two pairs of data were established in this study. These pairs were:

1. Fischer assay (gal/ton) and NMR signal area.
2. Organic carbon (wt pct) and NMR signal area.

A curve-fitting computer program was used to test the fit of the pairs of data to six common linear and nonlinear regression equations.

A second linear regression computer program was used to fit the pairs of data to a least-squares straight line and to compute other statistical parameters of the pairs of data. The second computer program also provided statistical data on the "goodness-of-fit" of the pairs of data to the least-squares straight line. The parameter used in this study as the measure of fit is the index of determination which is the square of the correlation coefficient. This index has the property that a perfect fit of the pairs of data to the straight line exists when the index of determination equals 1. An index of determination of zero means that no linear functional relationship exists.

RESULTS

The curve-fitting computer program was used to find which of six common linear and nonlinear regression equations best represented the pairs of data. The pairs of data were found to fit a simple straight line of the form:

$$Y = AX + B.$$

Figures 1 and 2 show representative plots of the two pairs of data for the Colorado oil shale. The figures show plots of Fischer assay and organic carbon contents vs. NMR signal area from Run II. These plots show that good straight-line correlations are obtained from the NMR method. The correlations for the four other oil shales are as good as those for the Colorado oil shale.

A second computer program was used to perform a linear regression analysis on the various pairs of data for each of the oil shales. The results of the regression analysis for the fitting of the Fischer assay oil yields and the organic carbon contents of the five oil shales are given in table 1. Table 1 lists the slopes (A) and the intercepts (B) of the least-squares straight lines together with the indexes of determination for the test of "goodness-of-fit" of the data for one correlation run.

TABLE 1. - Regression equation parameters and the indexes of determination for Fischer assay oil yields and organic carbon contents as a function of NMR signal area for five oil shales¹

Oil shale	Fischer assay vs. area		Index of determination	Organic carbon vs. area		Index of determination
	A	B		A	B	
Colorado	0.068	-1.0	0.91	0.026	1.2	0.95
Wyoming (GRB)	.054	1.7	.92	.021	1.8	.85
Wyoming (WB)	.045	-4.7	.97	.021	-1.5	.98
Utah	.053	-.9	.98	.024	-.7	.99
Kentucky	.045	-6.1	.95	.042	-5.5	.97

¹ The data listed in this table are the parameters calculated for Run III. The dependent variable, Y, in the straight-line equation, $Y = AX + B$, is the Fischer assay oil yield or the organic carbon content. The independent variable, X, is the broad-line NMR signal area.

Table 2 lists the indexes of determination obtained from the linear regression analysis of the Fischer assay vs. area and for the organic carbon vs. area for the five oil shales. The table lists this index for the three runs on the oil shales run several months apart. These three runs were made to test the repeatability of the correlations between the two pairs of data using different instrument operators and different methods (absorption and dispersion curves) of NMR strength integration. Table 2 shows that nearly the same correlations of the data points were obtained from the various pairs of data for the three runs.

TABLE 2. - Repeatability of linear regressions for five oil shales as shown by the index of determination

Oil shale	Index of determination					
	Fischer assay vs. area			Organic carbon vs. area		
	Run I ¹	Run II ²	Run III ²	Run I ¹	Run II ²	Run III ²
Colorado	0.90	0.91	0.91	0.91	0.98	0.95
Wyoming (GRB)	.96	.91	.92	.94	.88	.85
Wyoming (WB)	----	----	.97	----	----	.98
Utah	.96	.95	.98	.95	.97	.99
Kentucky	.89	.92	.95	.91	.97	.97

¹ Using NMR signal strength integrated from counting squares under the dispersion curve.

² Using NMR signal strengths integrated from the positive area under the first derivative of the absorption curve using an electronic integrator.

DISCUSSION OF RESULTS

Summary of the NMR Method

The wide-line NMR instrument in these experiments was adjusted to observe the proton resonance of the organic material of the oil-shale samples. The purpose of the study was to seek a correlation between the proton signal strength and the Fischer assay oil yields and the organic carbon contents of the oil shales. Because the proton signal strength was measured, it is necessary for the proton concentration to be related in some definable way to the Fischer assay oil yields and to the

organic carbon contents of the oil shales for the NMR technique to be useful in estimating the oil yields and organic carbon contents. It is also necessary for the inorganic protons and water protons to be noninterfering in the method. For the correlations to be useful, it is also necessary for the NMR signal strength to be independent of the depth of the oil shales studied and the area of an oil-shale deposit under development.

For the purposes of this study, five oil shales were chosen from five different geographic locations. The samples within each of the five sets were selected to give a range of oil yields, organic carbon contents, and depths.

The experiments gave the following results. The wide-line NMR signal strengths correlate well (indexes of determination generally better than 0.90) with the Fischer assay oil yields and the organic carbon contents of the five oil shales. The NMR signal strength is independent of the inorganic protons present in the samples. Free water protons, though interfering with the organic proton NMR signal area, can be effectively removed by air-drying the oil-shale samples for 2 hours at room temperature. The data for these oil shales correlated equally well for samples of oil shale that represented 719 feet of the Colorado oil shale, 36 feet of the Wyoming (GRB) oil shale, 2,500 feet of the Wyoming (WB) oil shale, 76 feet of the Utah oil shale, and 56 feet of the Kentucky oil shale. It was also observed that the correlations were repeatable at time intervals involving several months, utilization of different operators, and integration of NMR strengths by integration of either the absorption or dispersion mode of the NMR signal. These correlations are sufficient to allow the use of wide-line NMR spectrometry to rapidly estimate the potential oil yields and the organic carbon contents of the five oil shales of this study.

In general, the correlation of NMR signal area with organic carbon content was better than with Fischer assay oil yield. This better correlation is most likely due to the better accuracy of the combustion method for measuring organic carbon.

Different NMR correlations were obtained for the five oil shales. That is, least-squares lines of different slopes and intercepts were obtained for the five oil shales studied. Because different correlations were obtained, it is important to obtain calibration data for application to a specific oil-shale area under commercial development. Once calibrations are made, many oil-shale samples can be assayed per unit time to estimate potential oil yields and organic carbon contents. The experimental data indicate that calibration curves need be determined but once for a limited area under development. For example, the correlation parameters for cores of oil shales from the Green River Formation nearly 100 miles apart are similar and indicate that these parameters are probably the same over the limited area that may be involved in a commercial development. Sufficient cores were not available to test this possible similarity more completely.

Use of the NMR Method

Two different sets of oil-shale samples were selected to illustrate the use of the NMR method. Thirteen Colorado oil-shale samples and eight Wyoming (WB) samples were used. Both sets of samples were taken from the same cores that had been used to establish the linear regression parameters.

The NMR signal areas of the samples were obtained during Run III. The linear regression parameters listed in table 1 were used to calculate the Fischer assay oil yields and the organic carbon contents, respectively, from these NMR areas. The calculated results from the NMR method, together with the oil yields by Fischer assay and the organic carbon contents by the combustion method, are listed in tables 3-6. The tables also list the difference between the values calculated from the NMR method and the values obtained from Fischer assay and organic carbon by the combustion method.

TABLE 3. - Comparison of oil yields for 13 samples of Colorado oil shale determined by the broad-line NMR method and by the Fischer assay method

Fischer assay	Oil yield, gallons per ton	
	NMR ¹	Difference
7.2	8.4	0.8
11.6	11.2	.4
11.8	12.7	.9
15.8	18.1	2.3
22.1	21.5	.6
23.9	28.2	4.3
24.5	29.1	4.6
26.1	27.5	1.4
27.4	26.1	1.3
32.3	39.0	6.7
35.9	39.4	3.5
36.9	34.0	2.9
48.3	45.6	2.7

¹ The oil yields were calculated from the relationship:

$$\text{Oil yield, gallons per ton} = 0.068 \times (\text{NMR signal area}) - 1.0.$$

TABLE 4. - Comparison of organic carbon contents for 13 samples of Colorado oil shale determined by the broad-line NMR method and by the combustion method

Combustion	Organic carbon contents, wt pct	
	NMR ¹	Difference
3.8	4.8	1.0
5.8	6.4	.6
6.2	5.9	.3
7.8	8.5	.7
10.2	9.8	.4
11.6	12.1	.5
11.8	12.7	.9
12.6	11.6	1.0
13.2	12.4	.8
14.9	16.5	1.6
15.0	14.6	.4
15.7	16.6	.9
20.6	19.0	1.6

¹ The organic carbon contents were calculated from the relationship:

$$\text{Organic carbon, wt pct} = 0.026 \times (\text{NMR signal area}) + 1.2.$$

TABLE 5. - Comparison of oil yields for eight samples of Wyoming (WB) oil shale determined by the broad-line NMR method and by the Fischer assay method

Oil yield, gallons per ton		
Fischer assay	NMR ¹	Difference
5.8	9.5	3.7
6.9	9.5	2.6
10.5	11.5	1.0
15.0	12.9	2.1
16.8	15.7	1.1
26.8	25.1	1.7
30.2	30.9	.7
42.7	41.9	.3

¹ The oil yields were calculated from the relationship:

$$\text{Oil yield, gallons per ton} = 0.045 \times (\text{NMR area signal}) - 4.7.$$

TABLE 6. - Comparison of organic carbon contents for eight samples of Wyoming (WB) oil shale determined by the broad-line NMR method and by the combustion method

Organic carbon content, wt pct		
Combustion	NMR ¹	Difference
3.7	5.1	1.4
4.1	5.1	1.0
5.6	6.1	.5
8.0	6.7	1.3
8.2	8.0	.2
13.2	12.4	.8
14.9	15.1	.2
20.8	20.3	.5

¹ The organic carbon contents were calculated from the relationship:

$$\text{Organic carbon, wt pct} = 0.021 \times (\text{NMR signal area}) - 1.5.$$

The NMR method is not independent of the Fischer assay and combustion organic carbon methods because the latter two methods are used to establish the correlations with broad-line NMR signal strengths. Therefore, the oil yields and organic carbon contents calculated by NMR and listed in tables 3-6 indicate the amount of spread that may be obtained in estimations of the sought values by the NMR method when compared to the standard methods. The NMR method gives values that compare favorably to those used to obtain the correlations.

The closer comparison of the NMR results for the Wyoming (WB) oil shale than for the Colorado oil shale is directly related to the better correlation curves obtained for the Wyoming (WB) oil

shale (Fischer assay vs. area = 0.97; organic carbon vs. area = 0.98) than for the Colorado oil shale (Fischer assay vs. area = 0.91; organic carbon vs. area = 0.95).

The broad-line NMR method can be used to estimate the oil yields and the organic carbon contents many times faster than the conventional methods. The broad-line NMR method can be used to supplement the standard methods in a future oil-shale industry where many samples will need to be assayed per day.

CONCLUSION

Broad-line NMR spectrometry can be used to give a rapid estimation of the Fischer assay oil yields and organic carbon contents of oil shales. The broad-line NMR data give results that are a little less precise than the Fischer assay method and the combustion method, but the NMR method is many times faster than the other methods. The broad-line NMR method will have utility in a future oil-shale industry where many samples must be assayed in an area under development.

ACKNOWLEDGMENT

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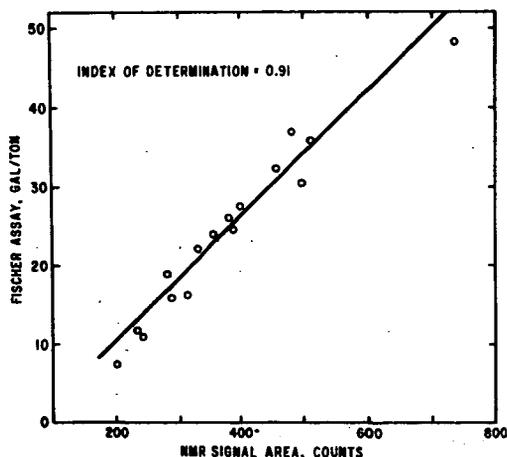


FIGURE 1.-Plot of Fischer Assay Oil Yield Vs NMR Signal Area for Colorado Oil Shale.

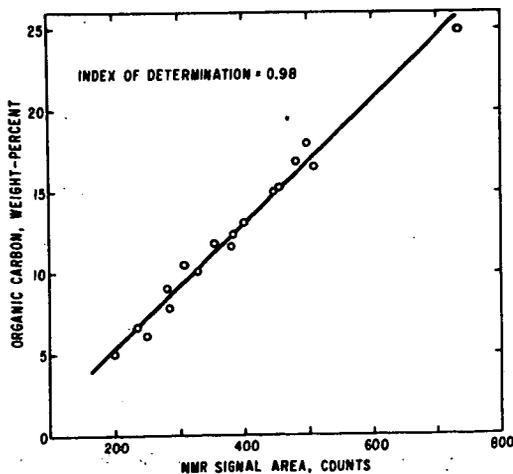


FIGURE 2.-Plot of Organic Carbon Content Vs NMR Signal Area for Colorado Oil Shale.