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Using Broad-Line Nuclear Magnetic Resonance Spectrometry to Estimate Potential Oil Yields of Oil Shales

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Using Broad-Line Nuclear Magnetic Resonance Spectrometry to Estimate Potential Oil Yields of Oil Shales

By A. W. Decora, F. R. McDonald, and G. L. Cook

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USING BROAD-LINE NUCLEAR MAGNETIC RESONANCE SPECTROMETRY TO ESTIMATE POTENTIAL OIL YIELDS OF OIL SHALES

by

A. W. Decora,[1] F. R. McDonald,[2] and G. L. Cook[3]

ABSTRACT

A technique has been developed utilizing proton, broad-line nuclear magnetic resonance spectrometry to estimate the organic carbon contents and the potential oil yields of five domestic oil shales. The quantity of organic hydrogen in the oil shales is mathematically related to the organic carbon contents and to the potential oil yields so that the proton, broad-line nuclear magnetic resonance signal strength can be correlated with both the Fischer assay oil yield and the organic carbon contents of oil shales from Colorado, Utah, Wyoming, and Kentucky. The experimental data indicate that calibration curves need be determined but once for a limited oil shale area under development. The method is rapid, can be applied without extensive calibration, and gives good estimates of oil yields and organic carbon contents on as many as 30 samples per hour.

INTRODUCTION

The Bureau of Mines has been engaged for many years in research on oil shales. One phase of the research is the development of techniques to describe the characteristics, composition, and properties of Green River Formation oil shales in Colorado, Wyoming, and Utah. Of immediate interest for the evaluation of the resource is the determination of the quantities of organic matter and of recoverable shale oil that are 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 method for estimating total organic matter is the measurement of organic carbon content by combustion (11).[4] The most common method for estimating the recoverable shale oil from oil shales is the modified Fischer assay method (9).

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[1] Research chemist, project leader.

[2] Research chemist.

[3] Project coordinator.

All authors are with the Laramie Energy Research Center, Bureau of Mines, Laramie, Wyo.

[4] Underlined numbers in parentheses refer to items in the list of references preceding the appendixes.

The latter method involves controlled heating of a sample of oil shale in a small metal retort. Both of these methods give satisfactory results, but they 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. A more rapid method would have the advantage of increasing the number of samples that could be processed per unit time.

Spectroscopic analyses, where they can be applied, offer many advantages. One of these advantages is usually the rapidity with which analyses may be performed. Broad-line nuclear magnetic resonance (NMR) spectrometry has potential application for estimating oil yields from oil shales. The purpose of the present study was to seek a correlation between proton signal strengths and the Fischer assay oil yields and the organic carbon contents of oil shales. In the present work it was necessary to determine if the correlations of the proton, broad-line NMR signal strengths were independent of the depths of the oil shale samples; that is, the hydrogen-to-carbon content and the hydrogen-to-potential oil yield must be sufficiently independent of depth so that the NMR correlations could be used in an analytical method. It was also necessary to show that the correlations remain valid 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.

In addition to the major thesis of this report, some research was devoted to the preliminary determination of the sensitivities of organic hydrogen of the several oil shales studied. The results indicate that it should be possible to establish absolute sensitivities for the protons that will serve as the basis for future applications of this research. For example, once known, these absolute sensitivities should be valuable in determining the hydrogen-to-carbon ratios (which are related to the potential oil yields) without the need for calibration using any other independent technique.

Results of the present research showed that proton, broad-line NMR signal strengths correlated with the Fischer assay oil yields, the organic carbon contents, and the organic hydrogen contents of five oil shales from Colorado, Utah, Wyoming, and Kentucky. Correlations were shown to be independent of depth. 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 organic carbon contents can be estimated on as many as 30 samples per hour. The spectrometric results can be used to supplement the commonly used methods so that the desired data may be rapidly measured on large numbers of samples expected in a future oil shale industry.

BASIS FOR APPLICATION OF NMR TO OIL SHALE ANALYSIS

Nuclear magnetic resonance spectrometry is a powerful tool for characterizing chemical substances. The resonance technique offers a way in which one may select particular atoms of interest for study. This can be done by choosing an appropriate combination of magnetic field and radio frequency field strengths to "tune-in" to particular atoms of interest--for example, hydrogen. Also, as in other forms of absorption spectroscopy, the absorption signal is proportional to the number of atoms undergoing the magnetic resonance phenomenon. The NMR technique has been extensively used for chemical analysis in the quarter century since its discovery. In the present study, the concern is limited to the use of NMR spectrometry in the study of oil shales.

Broad-line nuclear magnetic resonance signals are obtained when NMR spectra of solid state samples are recorded. Line broadening occurs because of dipole-dipole interactions of nuclear magnets in the rigid environment characteristic of the solid state. The solid sample is usually made into a fine powder to achieve a random distribution of molecular orientations, which has the effect of narrowing the line widths somewhat. Various features of the spectra can then be used to deduce structural features of the solid (1-2, 4).

EXPERIMENTAL PROCEDURES

Geographical Location of the Oil Shales Studied

Five oil shales from different geographic locations were used in this study--four from the Green River Formation in Colorado, Wyoming, and Utah, and one from the New Albany Formation in Kentucky. All of the oil shales were selected from cores upon which other research has been done by the Laramie Energy Research Center (5-8, 10, 12).

For purposes of the present study, one of the oil shales from the Green River Formation was chosen from the Piceance Creek Basin in Colorado (designated "Colorado"); one from the Green River Basin in Wyoming [designated "Wyoming (GRB)"]; one from the Washakie Basin in Wyoming [designated "Wyoming (WB)"]; and one from the Uinta Basin in Utah (designated "Utah"). The approximate locations of these four Green River Formation oil shales are shown in figure 1.

The fifth oil shale, from the New Albany Formation in Kentucky (designated "Kentucky"), has already been shown to be different in composition from the Green River Formation oil shales (7).

Choice of Oil Shale Samples

Several samples were selected from each of the oil shale cores. The samples were chosen after studying Fischer assay data sheets and then selecting samples of different oil yields and from different depths below the surface of the ground. The samples chosen had a range in Fischer assay oil yield from about 0 to 50 gal/ton and an organic carbon content range of about 0.5 to 25 weight-percent.

The number of samples from each core were as follows: 13 samples of the Colorado core were chosen from 821 feet of the core; 17 samples of the Wyoming (GRB) core were chosen from 36 feet of the core; 20 samples of the Wyoming (WB) core were chosen from 332 feet of the core; 25 samples of the Utah core were chosen from 77 feet of the core; and 15 samples of the Kentucky core

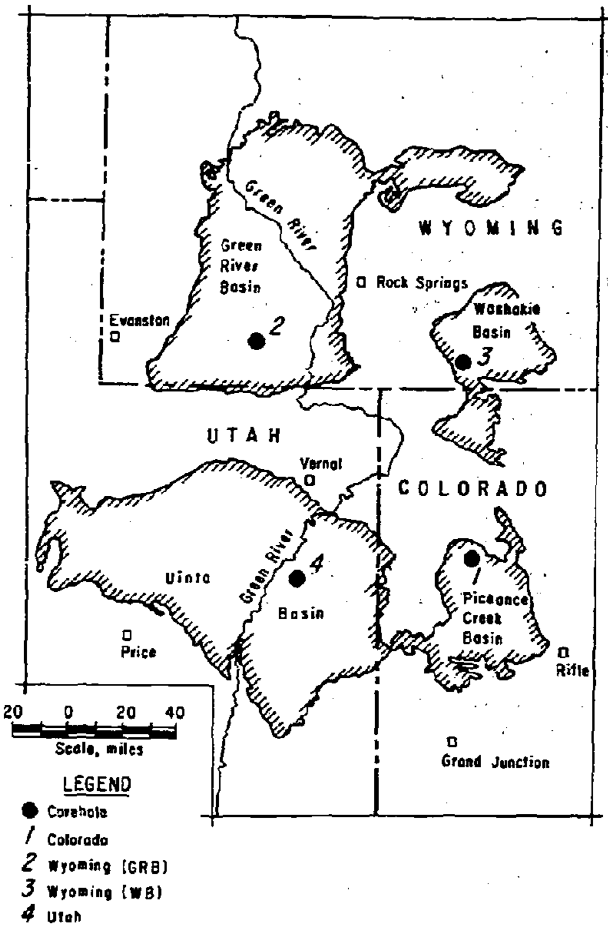

FIGURE 1. - Geographical Location of the Four Green River Formation Oil Shales Studied.

were chosen from 56 feet of the core.[5]

Fischer Assay, Organic Carbon, and Hydrogen Analyses

The modified Fischer assay method was used for estimating the recoverable shale oil from the oil shale samples (9). The method also gives the water yield from the oil shales that is important in another phase of this report. The results from these analyses are reported in gallons per ton of oil shale.

The organic carbon contents of the oil shale samples were determined by a combustion-tube method (11). This method involves total combustion of a weighed sample of oil shale, weighing the carbon dioxide and water combustion products, and calculating organic carbon and total hydrogen as to weight-percent of the oil shale sample.

In the present work, it was necessary to estimate the quantity of organic hydrogen present. Hydrogen chemically combined with the organic carbon in oil shales is difficult to determine because the total hydrogen content is calculated from the weight of water produced from combustion of an oil shale sample. Free water in the oil shale and also lattice water of crystallization in minerals present in the oil shale are also weighed in the water absorbent; therefore, the organic hydrogen was estimated by making a correction for the mineral water and free water in the oil shales. To do this, the Fischer assay water yield was assumed to originate from mineral water and free water. This correction is not entirely correct because some mineral water is obtained at much higher temperatures than at the Fischer assay temperature. As a first approximation, organic hydrogen contents of the oil shales were estimated by converting the

---

[5] Descriptions of the oil shales including Fischer assay oil yields, organic carbon contents, and sample depths may be found in appendixes A and B.

Fischer assay water yields to weight-percent hydrogen and subtracting this figure from the total hydrogen from the combustion analysis.[6]

Preparation of NMR Samples

Solid samples usually are very finely divided to approximate a random distribution of molecular orientations before placing the sample in the NMR probe. In the present work, each oil shale sample was prepared for NMR analysis by grinding it to yield powdered oil shale with the following approximate sieve analysis:

Mesh size[7]	Wt-pct of sample
Minus 80 plus 100...	3
Minus 100 plus 200...	30
Minus 200 plus 325...	46
Minus 325............	21

Each 7- to 8-g oil shale sample was air-dried and then poured into a 4- by 1/2-inch precision-bore test tube. The sample tube was then tapped until the shale sample would settle no further. The oil shale samples, packed in this way, had packed densities of about 1.0 to 1.5 g/cm^3. 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 a Varian V-4200B unit[8] utilizing a 15-inch Varian magnet with a Varian Fieldral Mark III regulator, a Varian Model 4210A, 2- to 16-megahertz (MHz) RF unit; appropriate sweep and detection electronics; a Varian F-80 X-Y recorder, and a Varian V4230B, 8- to 16-MHz probe. A Leeds and Northrup Speedomax G, 0- to 5-mv recorder fitted with a digital integrator (Instron Corp., Quincy, Mass.) was electrically connected to the spectrometer output to give the area under the NMR curves.

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 having ranges of 2 to 4 MHz, 4 to 8 MHz, and 8 to 16 MHz. For the second purpose, an 8- to 16-MHz probe was used.

---

[6] Data from the tables in appendixes A and B were used to perform these calculations.

[7] Plus indicates that the sample is retained by that screen. Minus indicates that the sample passes through the screen. The mesh sizes are those designated by the U.S. Standard Sieve Series.

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

A typical set of conditions for measuring NMR signal areas for the correlation work follows. A sample tube containing an oil shale sample was centered in the 8- to 16-MHz 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 x 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 either the first derivative of the absorption mode or the first derivative of dispersion 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 recorded the positive area of the first derivative of the dispersion mode curve (a base line was chosen that eliminated two 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 conditions. The areas under the broad-line signal of the absorption mode were recorded.

Three correlation runs were made. In run I the paddles of the NMR probe were adjusted to give the first derivative of the absorption mode signal. In this case, the areas under the curve were obtained by counting squares under both the positive and negative areas of the plot on the chart paper. Figure 2 shows an example of this absorption mode NMR signal for the 26.1 gal/ton Colorado oil shale samples. The total area was obtained from the sum of the positive and negative areas between points A and B as shown in the figure.

The paddles of the NMR probe were adjusted to give the first derivative of the dispersion mode in runs II and III. Figure 3 shows an example of this dispersion mode signal for the 26.1 gal/ton Colorado oil shale sample.

Areas for runs II and III were obtained using the electronic integrator and were obtained only of the positive area of the first derivative of the dispersion mode curve (area between points A and B on fig. 3).

The NMR signal areas were expressed as either integrator counts or as "square counts" and were different in each of the three runs owing to changes in integrator constants. These three sets of areas were used to test the repeatability of linear regression correlations of the data.

Tests for Interferences

The three NMR probes described previously were used to determine the location and number of resonance peaks. In the entire sweep field examined, only one peak was found--an absorption peak corresponding to that expected for organic protons.

The nuclear magnetic resonance conditions were set to obtain the proton resonances of the organic protons in the oil shale samples; therefore, it was

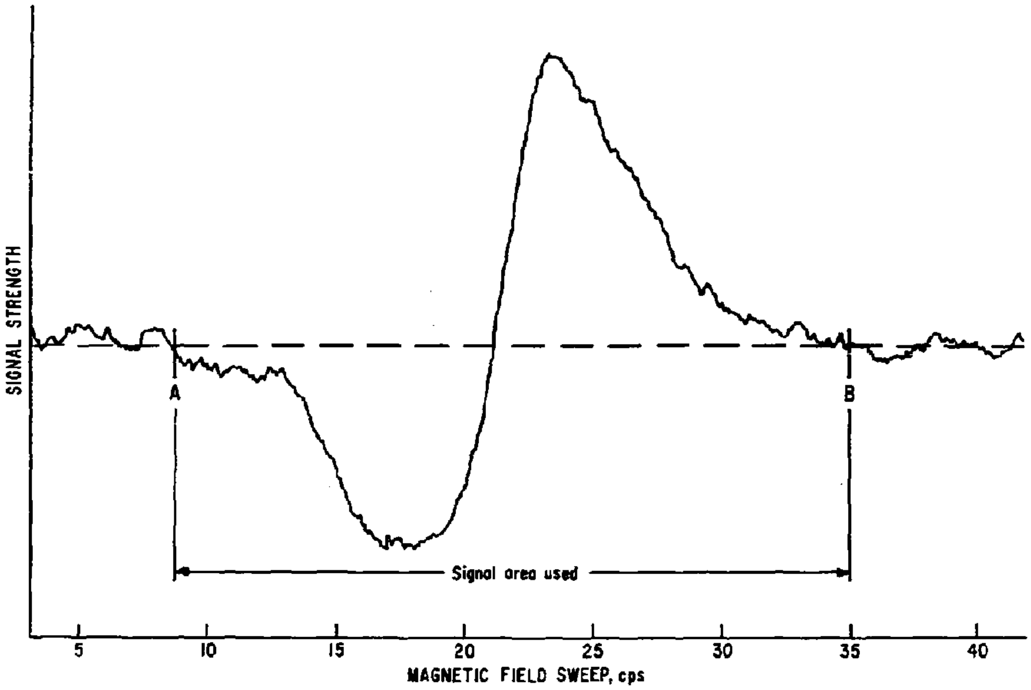

FIGURE 2. - First Derivative of the Absorption Mode Broad-Line NMR Spectrum of 26.1 gal/ton Colorado Oil Shale.

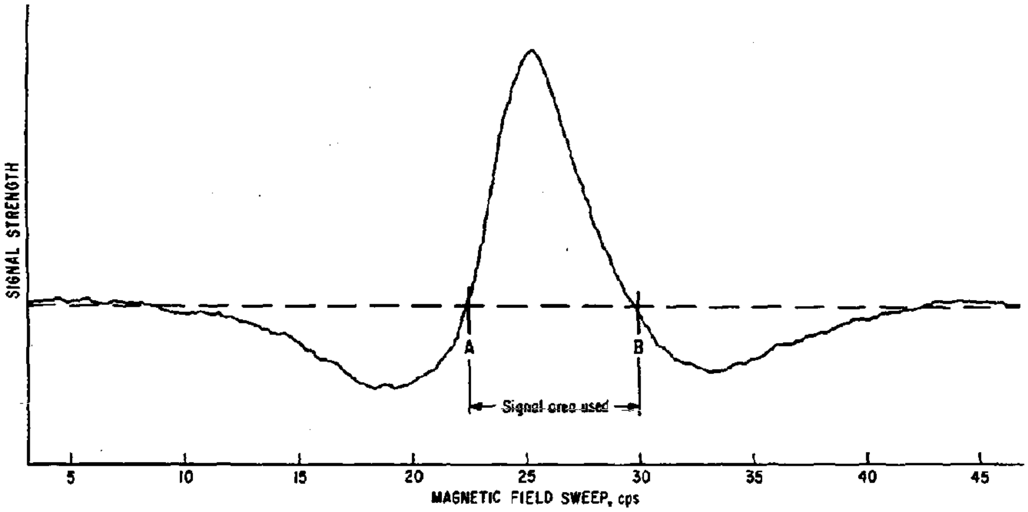

FIGURE 3. - First Derivative of the Dispersion Mode Broad-Line NMR Spectrum of 26.1 gal/ton Colorado Oil Shale.

necessary to prove that the signal measured was due primarily to organic protons. One experiment was performed with a set of oil shale samples having a relatively high concentration of nahcolite ($NaHCO_3$), dawsonite [$NaAl(OH)_2CO_3$], and illite (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 in any significant way with the organic-associated proton resonance that would invalidate the Fischer assay and organic carbon correlations with NMR signal strength.

In a second experiment, designed to test for the interference of free water, 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 of water in that time. Each wet shale sample was placed in one of the test tubes, the NMR signal area was measured and then compared with the signal area of the sample before wetting. The data showed that the water proton did contribute to the NMR signal strength measured for the organic protons. However, air-drying the sample at room temperature for about 2 hours proved an easy way to avoid this interference caused by free water in the Fischer assay and organic carbon content correlation work.

The contributions to the total NMR signal area due to inorganic-associated or free-water protons are small and the signal is broad and relatively constant. In the work to estimate the hydrogen sensitivities, a correction was made for these signals using data from the Fischer assay water yields of the oil shale samples.

Treatment of Data

The mathematical relationships between five pairs of data were established in this study.

1. Fischer assay oil yield (gal/ton) and organic carbon (wt-pct).
2. Organic hydrogen (wt-pct) and organic carbon (wt-pct).
3. Fischer assay oil yield (gal/ton) and NMR signal area.
4. Organic carbon (wt-pct) and NMR signal area.
5. Organic hydrogen (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 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 [or coefficient of determination (the commercial time-sharing computer program lists this coefficient as the "index of determination")], which is the square of the correlation coefficient (3). This index has the properties that a perfect fit of the pairs of data to the straight line exists when the index of determination equals one. An index of determination of zero means that no linear functional relationship exists.

The regression analyses in some cases were performed on the pairs of data to yield least-squares parameters for two relationships of the pairs of data. For example, in one instance the regression analysis was performed using Fischer assay oil yield as the independent variable and the NMR signal area as the dependent variable, but in the second instance the relationships were reversed.

RESULTS

Regression Analyses

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

$$Y = AX + B,$$

where A is the slope and B is the intercept in the expression.

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 computer program provided the least-squares slopes and intercepts for the pairs of data along with the 95-percent confidence limits for these parameters. The program also provided the correlation coefficient and the index of determination as a test of the "goodness-of-fit" of the pairs of data (3). The index of determination (which is the square of the correlation coefficient) was used in the discussion that follows because it is a more sensitive test-of-fit than is the correlation coefficient.

Relationship of Fischer Assay Oil Yields to Organic Carbon Contents

A linear regression analysis was performed using Fischer assay oil yields (gal/ton) as the dependent variable and organic carbon (wt-pct) as the independent variable. This analysis was performed for two reasons: (1) To compare the relationships between Fischer assay oil yield and organic carbon content for the five oil shales as shown by values for the slopes (A), and (2) to serve as a basis for accepting or rejecting data values in the NMR work. In this latter case, values of Fischer assay oil yield and organic carbon contents were not used in the NMR correlations when they were over three standard deviations away from the least-squares regression line.

Figures 4 to 8 show plots of Fischer assay oil yield (gal/ton) against organic carbon contents (wt-pct) for the five oil shales studied. The figures show that the data for the five oil shales all give excellent linear correlations.

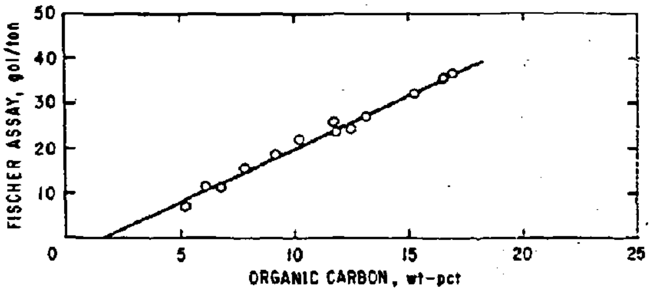

FIGURE 4. - Fischer Assay Oil Yield Versus Organic Carbon for Colorado Oil Shale.

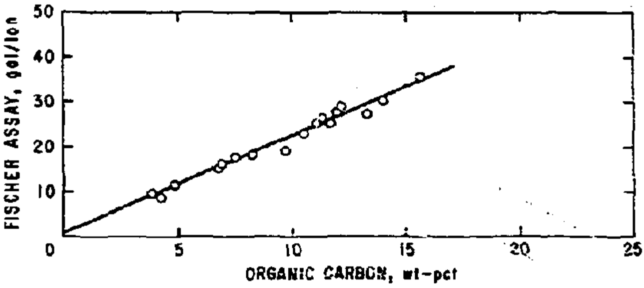

FIGURE 5. - Fischer Assay Oil Yield Versus Organic Carbon for Wyoming (GRB) Oil Shale.

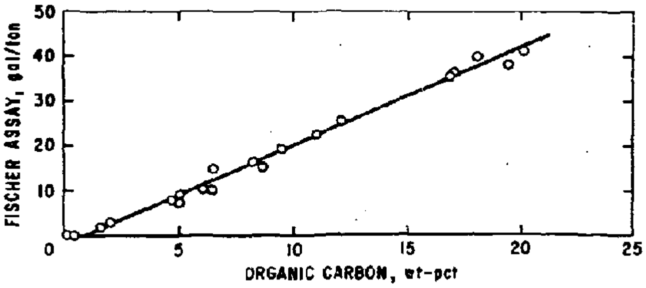

FIGURE 6. - Fischer Assay Oil Yield Versus Organic Carbon for Wyoming (WB) Oil Shale.

The regression equation parameters and the indexes of determination for the five plots are given in table 1. The four Green River Formation oil shales are all quite similar as shown in table 1 by the values for the slopes (A), which are the relationships of potential oil yields to organic carbon contents of the oil shales. The regression of Fischer assay oil yield against organic carbon for the Colorado oil shale has an intercept of -3.7 gal/ton. An explanation for this negative value may be the large amount of gas plus loss obtained in the Fischer assay on this oil shale. The gas plus loss for the Colorado oil shale is nearly four times as much as for the other four oil shales (tables A-1 to A-5, appendix A).

The slope of 0.98 for Kentucky oil shale shows that the Kentucky oil shale yields less than one-half as much Fischer assay oil per unit of organic carbon as the Green River Formation oil shales whose slopes are in the range 2.14 to 2.39. The oil obtained from the Fischer assay of Kentucky oil shale also has a higher specific gravity (~0.96) compared to the specific gravity of oil from the Green River Formation oil shales (specific gravity ~0.92).

TABLE 1. - Regression equation parameters and the indexes of determination for Fischer assay oil yield as a function of organic carbon contents for five oil shales[1]

Oil shale	A[2]	B	Index of determination
Colorado	2.39±0.18	-3.7	0.99
Wyoming (GRB)	2.18± .21	.6	.97
Wyoming (WB)	2.14± .11	-1.4	.99
Utah	2.26± .10	.2	.99
Kentucky	.98± .14	.4	.95

[1] The slopes (A) and the intercepts (B) are for the relationship:

Fischer assay, gal/ton = A x (organic carbon, wt-pct) + B.

[2] The limits shown are the 95-percent confidence limits of each slope.

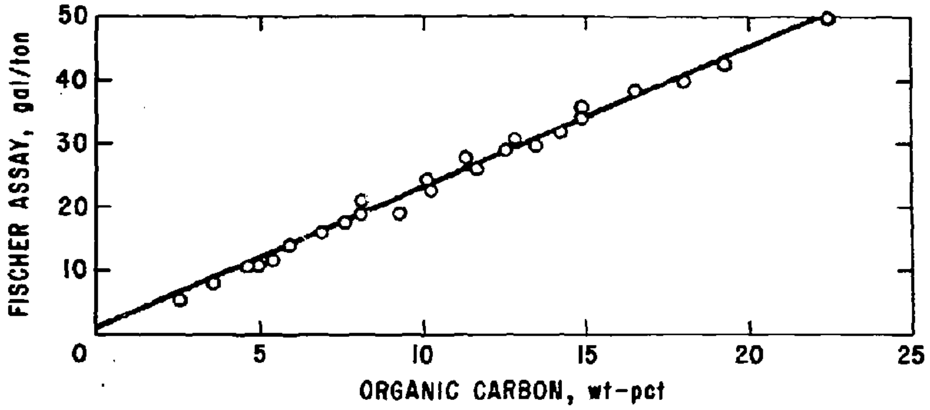

FIGURE 7. - Fischer Assay Oil Yield Versus Organic Carbon for Utah Oil Shale.

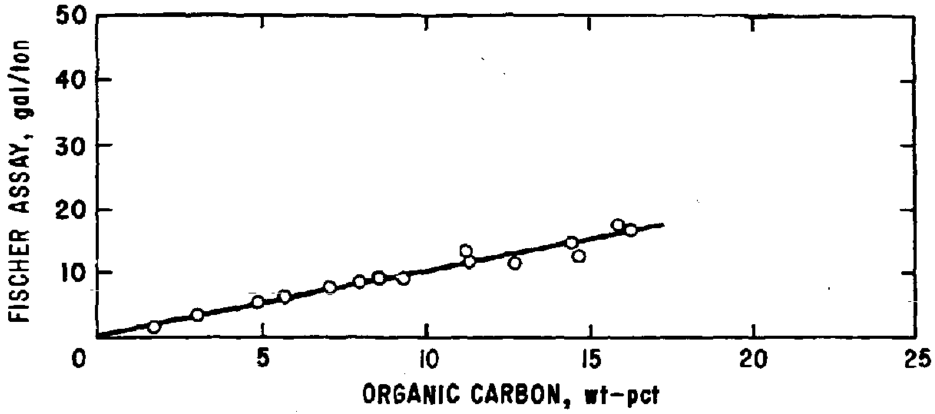

FIGURE 8. - Fischer Assay Oil Yield Versus Organic Carbon for Kentucky Oil Shale.

Relationship of NMR Signal Strengths to Fischer Assay Oil Yields and Organic Carbon Contents

Linear regression analyses were performed to establish the relationships of Fischer assay oil yields and organic carbon contents with NMR signal areas for all of the five oil shales. Figures 9 and 10 show representative plots of the two pairs of data for the Utah oil shale. The figures show plots of Fischer assay oil yield and organic carbon contents versus NMR signal areas from run III. These representative plots show that good straight-line correlations were obtained. The correlations for the four other oil shales were as good as those for the Utah oil shale.

The results of the regression analysis for the Fischer assay oil yields and organic carbon contents against NMR signal area are given in table 2. The table lists the slopes (A) and the intercepts (B) of the least-squares regression lines together with the indexes of determination for the test of "goodness-of-fit" of the data for run III. Again, the similarities of the four Green River Formation oil shales can be seen from the similar slopes (A) for these oil shales.

The value for the slope of organic carbon versus area for the Kentucky oil shale is different from the four Green River oil shales indicating that the hydrogen-to-carbon ratio for this oil shale is different than for the Green River Formation oil shales.

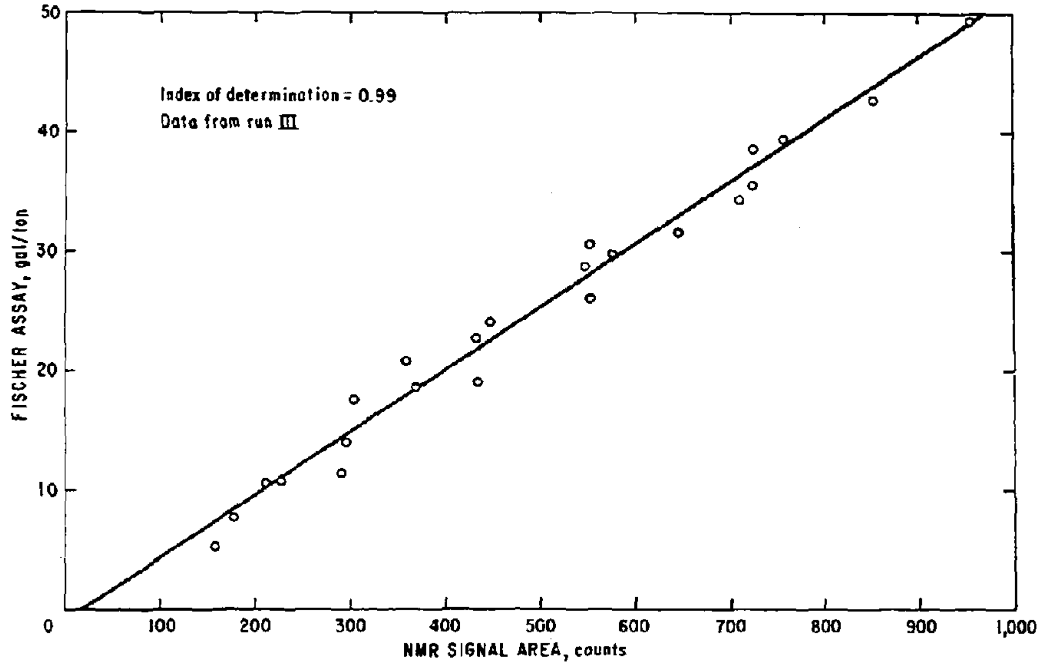

FIGURE 9. - Fischer Assay Oil Yield Versus NMR Signal Area for Utah Oil Shale.

TABLE 2. - 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 shales[1]

Oil shale	Fischer assay versus area		Index of determination	Organic carbon versus area		Index of determination
	A	B		A	B	
Colorado.........	0.058	0.7	0.96	0.023	2.27	0.95
Wyoming (GRB)....	.053	1.7	.92	.024	.67	.90
Wyoming (WB).....	.045	-4.7	.97	.021	-1.51	.98
Utah.............	.054	-1.9	.99	.024	-.56	.99
Kentucky.........	.043	-5.1	.95	.040	-4.71	.98

[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 (gal/ton) or the organic carbon content (wt-pct). The independent variable, X, is the broad-line NMR signal area.

Table 3 lists the indexes of determination obtained from the linear regression analysis of the Fischer assay oil yield versus area and the organic carbon versus area for the five oil shales. The table lists the indexes for three runs on the oil shales. These three runs were made to test the repeatability of the correlations between the two pairs of data using different instrument operators and recording first derivatives of either absorption or

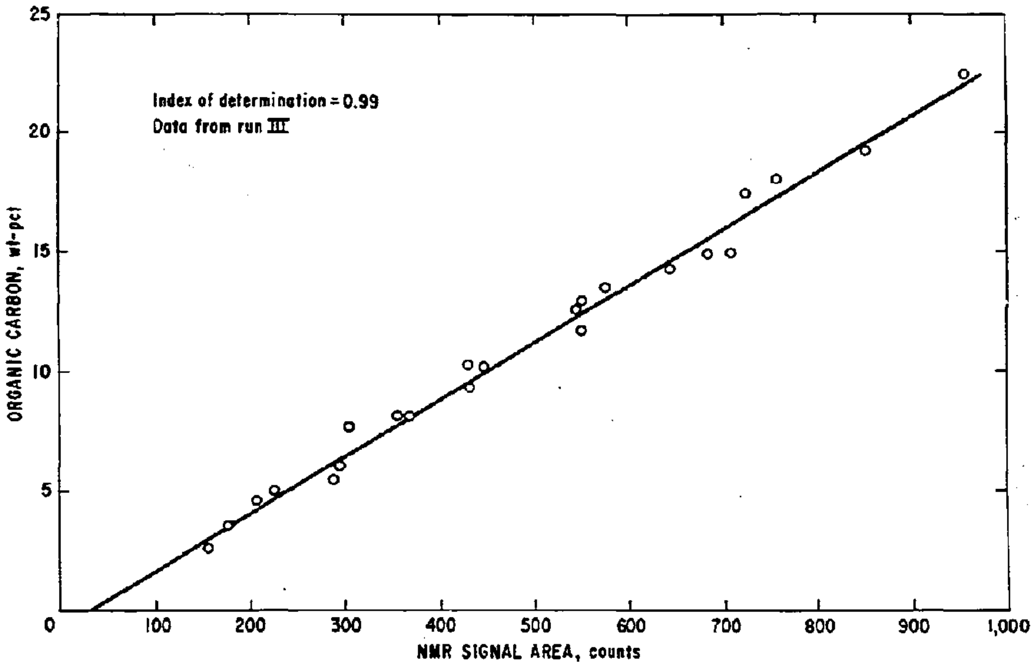

FIGURE 10. - Organic Carbon Content Versus NMR Signal Area for Utah Oil Shale.

dispersion curves. Table 3 shows that nearly the same correlations of the data points were obtained from the various pairs of data for the three runs.

TABLE 3. - Repeatability of linear regressions for five oil shales as shown by the index of determination

Oil shale	Fischer assay versus area			Organic carbon versus area		
	Run I[1]	Run II[2]	Run III[2]	Run I[1]	Run II[2]	Run III[2]
Colorado............	0.95	0.98	0.96	0.97	0.98	0.95
Wyoming (GRB).......	.96	.96	.92	.96	.93	.90
Wyoming (WB)........	-	-	.97	-	-	.98
Utah................	.97	.97	.99	.96	.97	.99
Kentucky............	.89	.95	.95	.91	.97	.98

[1] Using NMR signal strength integrated from counting squares under the first derivative of the absorption made curve.

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

Relationship of NMR Signal Strengths to Organic Hydrogen Contents

The underlying principle of the NMR analysis work is that the NMR signal strength is proportional to the quantity of total hydrogen present in the oil shales. A linear regression analysis was performed on the NMR signal areas from run III and the quantity of organic hydrogen present in each oil shale

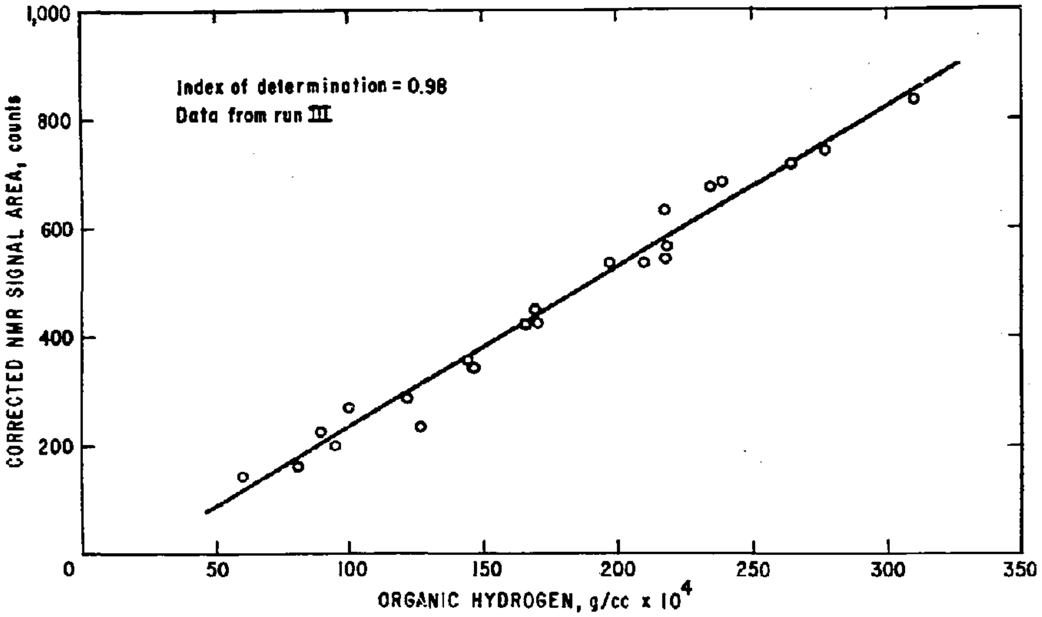

FIGURE 11. - Corrected NMR Signal Area Versus Organic Hydrogen for Utah Oil Shale.

sample. As already mentioned in the experimental section, the actual quantity of hydrogen chemically combined to organic carbon in the oil shales is difficult to determine. A correction (as shown in the experimental section) was applied to estimate the quantity of organic hydrogen, and then the packed densities of the oil shales in the NMR sample tubes were used to correct for the weight of hydrogen in the effective volume of the NMR probe.

A linear regression analysis was performed using corrected NMR signal areas and organic hydrogen values.[9] Figure 11 shows a typical plot of the results for one of the oil shales. A good linear correlation was obtained as shown in the figure. The correlations for the other oil shales were as good as the one shown.

The regression equation parameters for the NMR signal areas as a function of organic hydrogen for the five oil shales are given in table 4. The table shows (as shown by values of the slopes A) that the NMR sensitivity for hydrogen was nearly the same for the five oil shales. Refinement of the method should yield hydrogen sensitivities that more closely approach the excepted equality.

TABLE 4. - Regression equation parameters and 95-percent confidence limits for NMR signal areas as a function of organic hydrogen for five oil shales[1]

Oil shale	$A^1 \times 10^{-3}$	B^1	Index of determination
Colorado................	25.0±2.9	-158	0.98
Wyoming (GRB)..........	25.7±4.2	-51	.93
Wyoming (WB)...........	29.1±1.3	-34	.99
Utah....................	29.5±2.0	-64	.98
Kentucky...............	24.8±2.7	8	.97

[1] The slopes (A) and the intercepts (B) are for the relationship:

NMR signal area = A X (organic hydrogen, g/cm^3) + B.

Determination of Average Atomic Hydrogen-to-Carbon Ratios for the Five Oil Shales

A study was made of the relationship of organic hydrogen to organic carbon of the samples of the five oil shales to support the NMR data. Accordingly, linear regression analyses were made between weight-percent organic hydrogen and weight-percent organic carbon.[10] The slopes (A) from these analyses were multiplied by 12 (the atomic weight of carbon) to give the average atomic hydrogen-to-carbon ratios for the five oil shales. The results are given in table 5.

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[9] Data in appendixes A, B, and C were used to derive values for the regression analysis.

[10] The values for organic hydrogen and organic carbon used in these regression analyses are from tables C-1 to C-5 in appendix C.

TABLE 5. - Regression equation parameters and indexes of determination for organic hydrogen as a function of organic carbon for five oil shales and atomic hydrogen-to-carbon ratios derived from the slopes A

Oil shale	A	B	Index of determination	H/C, atomic[1]
Colorado............	0.141±0.015	0.02	0.980	1.69±0.18
Wyoming (GRB).......	.130± .009	.06	.986	1.56± .11
Wyoming (WB)........	.124± .006	.14	.991	1.49± .07
Utah................	.125± .003	.12	.997	1.50± .04
Kentucky............	.084± .008	.28	.976	1.01± .10

[1] Obtained by multiplying the slopes A by 12, the atomic weight of carbon.

The regression of organic hydrogen against organic carbon gave excellent straight lines as shown by high values of the index of determination (0.98 to 0.99). This regression shows that the atomic H/C ratio for all of the oil shale in each particular core is remarkably constant. It is the constancy of this relationship of organic hydrogen to organic carbon for each of the five oil shales that allows the use of broad-line NMR spectrometry for the application presented in this report.

DISCUSSION OF RESULTS

Application of the NMR Method

The present work is sufficient to apply to practical oil shale analysis problems without extensive independent calibration work. The applications can give good estimates of the quantities mentioned above. More extensive calibration (that is, the determination of absolute sensitivities) will give more accurate values.

As an example, two different sets of oil shale samples were selected to illustrate the use of this NMR method. Twelve 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 2 were used to calculate the Fischer assay oil yields and the organic carbon contents 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 6 to 9. The tables also list the difference between the values calculated by the NMR method and the values obtained from Fischer assay and organic carbon by the combustion method.

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 6 to 9 indicate the amount of spread that may be obtained in estimations of the sought values by the NMR method when compared with the standard methods. The

NMR method gives values that compare favorably with those used to obtain the correlations.

TABLE 6. - Comparison of oil yields for 12 samples of Colorado oil shale determined by the Fischer assay method and by the broad-line NMR method (gal/ton)

Oil yield		
Fischer assay method	NMR method[1]	Difference
7.2	8.7	1.5
11.6	11.1	.5
11.8	12.4	.6
15.8	17.0	1.2
22.1	19.9	2.2
23.9	25.6	1.7
24.5	26.4	1.9
26.1	25.0	1.1
27.4	23.9	3.5
32.3	34.8	2.5
35.9	35.2	.7
36.9	30.5	6.4

[1] The oil yields were calculated from the relationship:

$$\text{Oil yield, gal/ton} = 0.058 \times (\text{NMR signal area}) + 0.7.$$

TABLE 7. - Comparison of organic carbon contents for 12 samples of Colorado oil shale determined by the combustion method and by the broad-line NMR method (wt-pct)

Organic carbon		
Combustion method	NMR method[1]	Difference
5.2	5.5	0.3
6.7	6.4	.3
6.1	6.9	.8
7.8	8.8	1.0
10.2	9.9	.3
11.8	12.2	.4
12.5	12.5	.0
11.7	11.9	.2
13.1	11.5	1.6
15.3	15.8	.5
16.6	16.0	.6
16.9	14.1	2.8

[1] The organic carbon contents were calculated from the relationship:

$$\text{Organic carbon, wt-pct} = 0.023 \times (\text{NMR signal area}) + 2.3.$$

TABLE 8. - Comparison of oil yields for eight samples of Wyoming (WB) oil shale determined by the Fischer assay method and by the broad-line NMR method (gal/ton)

Oil yield		
Fischer assay method	NMR method[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	.8

[1] The oil yields were calculated from the relationship:

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

TABLE 9. - Comparison of organic carbon contents for eight samples of Wyoming (WB) oil shale determined by the combustion method and by the broad-line NMR method (wt-pct)

Organic carbon		
Combustion method	NMR method[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 closer agreement of the NMR results with Fischer assay 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 than for the Colorado oil shale.

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, thus effectively supplementing the standard methods in a future oil shale industry where many samples will need to be assayed per day.

Summary of the NMR Method

The broad-line NMR instrument used 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 was necessary for the proton concentration to be related in some definable way to the Fischer assay oil yields and the organic carbon contents of the oil shales for the NMR technique to be useful in estimating the oil yields and organic carbon contents. Another requirement was that the inorganic protons and water protons be noninterfering in the method. For the correlations to be useful, it was 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 include a range of oil yields, organic carbon contents, and depths.

The experiments gave the following results. The broad-line NMR signal strengths correlated well (indexes of determination all better than 0.90) with the Fischer assay oil yields and the organic carbon contents of the five oil shales. The inorganic protons present in the samples did not interfere in the analyses. Free water protons, though interfering with the organic proton NMR signal, were 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 from 821 feet of the Colorado oil shale, 36 feet of the Wyoming (GRB) oil shale, 332 feet of the Wyoming (WB) oil shale, 77 feet of the Utah oil shale, and 56 feet of the Kentucky oil shale. It was observed that the correlations were repeatable at time intervals involving several months, use of different instrument operators, and integration of NMR strengths by integration of the first derivatives of either the absorption or of the dispersion mode. These correlations are sufficient to allow the use of wide-line NMR spectrometry for rapid estimation of the potential oil yields and the organic carbon contents of the five oil shales of this study.

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.

The correlation parameters for cores of oil shales from the Green River Formation nearly 100 miles apart are similar. The similarities of these Green River Formation samples indicate that in the much smaller area that would be involved in a commercial development, one calibration would probably serve for that limited area. Sufficient cores were not examined to fully test this postulate.

The NMR method shows possible utility in determining atomic hydrogen-to-carbon ratios of various oil shales. The present work (column 2, table 4) shows that NMR values obtained for the sensitivities of organic hydrogen of the five oil shales were nearly the same. Refinement of the method should yield hydrogen sensitivities that more closely approach the expected equality. This refinement of the research work should lead to absolute sensitivities for hydrogen that can be related to any oil shale. When this is accomplished one should be able to make only one calibration run (involving independent analyses) and then apply only broad-line NMR spectrometry to the estimation of potential oil yields, organic carbon contents, organic hydrogen contents, and atomic hydrogen-to-carbon ratios.

NEED FOR FURTHER STUDY

The present research has shown that broad-line NMR spectrometry can be used to advantage in oil-yield estimation of oil shales. In the present work, it was necessary to make calibrations for each oil shale studied. The indications were that the sensitivity of the NMR instrument for hydrogen was nearly constant, but the research results included sources of error that should be sought in a future study. The present research should serve as a basis for extended research that will seek the fundamental quantitative factors responsible for the NMR technique. Also, broad-line NMR spectrometry should be employed to distinguish different proton environments in oil shale kerogen. This proton environmental characterization could give some insight into kerogen structural features that could be used to predict the nature of the shale oil formed from the kerogen. The future research should improve the broad-line NMR method to the point of being universally applicable to all oil shales without the need for extensive calibrations in oil-yield estimation work, and also will provide kerogen structure information.

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APPENDIX A.--FISCHER ASSAY DATA FOR FIVE OIL SHALES

Tables A-1 to A-5 in this appendix list the results obtained from Fischer assay on the five oil shales of this study. The tables list the sample numbers of the various oil shales together with the Fischer assay oil and water yields in gallons per ton of oil shale; material balance as shown by gas plus loss of sample during the Fischer assay; the specific gravity of the shale oil produced; and the depth in feet of the sample in the core.

TABLE A-1. - Fischer assay data for samples of Colorado oil shale

Sample No.	Yields, gal/ton		Gas and loss, wt-pct	Oil, specific gravity	Sample depth, ft
	Oil	Water			
SBR-68-249X	24.5	2.3	6.5	0.92	1,900-1,910
SBR-68-251X	15.8	2.2	4.3	.91	1,920-1,930
SBR-68-255X	18.9	7.4	10.2	.90	1,959-1,970
SBR-68-256X	22.1	5.8	9.0	.90	1,970-1,980
SBR-68-261X	32.3	2.0	6.4	.90	2,021-2,031
SBR-68-268X	26.1	4.1	7.5	.90	2,089-2,100
SBR-68-272X	11.6	10.5	16.3	.91	2,129-2,135
SBR-68-278X	7.2	11.0	13.7	.90	2,179-2,191
SBR-68-282X	11.8	9.6	12.5	.91	2,219-2,231
SBR-68-301X	36.9	9.1	13.7	.91	2,411-2,422
SBR-68-304X	27.4	6.0	8.6	.92	2,440-2,449
SBR-68-317X	23.9	8.1	13.8	.91	2,570-2,581
SBR-68-331X	35.9	2.4	4.8	.90	2,712-2,721

TABLE A-2. - Fischer assay data for samples of Wyoming (GRB) oil shale

Sample No.	Yields, gal/ton		Gas and loss, wt-pct	Oil, specific gravity	Sample depth, ft
	Oil	Water			
SBR-67-7539	23.0	1.4	2.9	0.91	3,170.3-3,171.5
SBR-67-7541	25.3	1.9	3.0	.91	3,171.5-3,172.6
SBR-67-7542	25.3	1.9	1.8	.92	3,172.6-3,174.0
SBR-67-7545	19.1	1.9	1.3	.93	3,175.6-3,176.6
SBR-67-7547	28.0	2.5	2.8	.91	3,177.6-3,178.1
SBR-67-7551	18.0	1.2	2.3	.91	3,180.5-3,181.7
SBR-67-7553	15.3	1.1	2.4	.92	3,182.8-3,183.3
SBR-67-7555	8.8	1.9	1.2	.92	3,183.9-3,185.0
SBR-67-7557	17.9	2.2	2.1	.92	3,186.0-3,187.0
SBR-67-7561	9.9	.8	.7	.89	3,189.5-3,190.0
SBR-67-7562	16.2	1.7	1.6	.90	3,190.0-3,190.9
SBR-67-7567	35.9	2.6	3.6	.92	3,193.9-3,194.9
SBR-67-7568	30.5	3.4	3.6	.92	3,194.9-3,195.6
SBR-67-7570	11.7	3.2	2.5	.90	3,196.1-3,196.7
SBR-67-7575	27.3	1.7	2.2	.93	3,200.2-3,201.3
SBR-67-7578	29.0	3.4	2.3	.92	3,203.4-3,204.6
SBR-67-7580	26.5	3.7	2.3	.92	3,205.0-3,206.0

TABLE A-3. - Fischer assay data for samples of Wyoming (WB) oil shale

Sample No.	Yields, gal/ton		Gas and loss, wt-pct	Oil, specific gravity	Sample depth, ft
	Oil	Water			
SBR-69-2413	8.1	7.2	1.6	0.92	320-321
SBR-69-2417	41.2	5.3	4.8	.94	324-325
SBR-69-2418	36.2	5.5	3.9	.94	325-326
SBR-69-2419	38.2	6.5	4.3	.94	326-327
SBR-69-2423	9.1	6.5	1.8	.91	330-331
SBR-69-2427	7.7	4.3	2.9	.93	334-335
SBR-69-2428	10.5	4.8	2.2	.93	335-336
SBR-69-2430	10.2	3.5	3.5	.93	337-338
SBR-69-2431	15.1	4.4	2.4	.92	338-339
SBR-69-2447	19.4	4.8	2.6	.91	355-357
SBR-69-2448	40.0	6.5	3.8	.93	357-358
SBR-69-2449	35.5	5.8	3.4	.93	358-360
SBR-69-2450	16.8	4.3	2.3	.90	360-361
SBR-69-2452	25.8	4.8	3.6	.91	362-363
SBR-69-2453	22.7	3.4	3.8	.91	363-365
SBR-69-2456	15.6	3.4	3.1	.91	368-370
SBR-69-2516	2.0	5.0	.9	-	433-434
SBR-69-2521	0	5.3	.2	-	448-452
SBR-69-2534	3.0	3.4	1.4	-	493-495
SBR-69-2662	0	3.7	1.0	-	650-652

TABLE A-4. - Fischer assay data for samples of Utah oil shale

Sample No.	Yields, gal/ton		Gas and loss, wt-pct	Oil, specific gravity	Sample depth, ft
	Oil	Water			
SBR-69-7163	18.6	0.7	1.5	0.91	2,268-2,269
SBR-69-7164	11.4	1.3	1.5	.92	2,269-2,270
SBR-69-7165	34.2	1.3	2.1	.91	2,270-2,271
SBR-69-7166	20.8	.5	1.5	.92	2,271-2,272
SBR-69-7169	13.9	.7	.8	.91	2,273-2,274
SBR-69-7172	28.6	.6	1.7	.92	2,276-2,277
SBR-69-7174	42.7	1.0	3.3	.91	2,278-2,279
SBR-69-7175	38.5	.4	2.3	.90	2,279-2,280
SBR-69-7176	22.6	.4	2.2	.90	2,280-2,281
SBR-69-7178	15.8	.4	1.5	.92	2,282-2,283
SBR-69-7183	10.5	.7	1.3	.91	2,287-2,288
SBR-69-7192	24.0	.1	1.9	.90	2,296-2,297
SBR-69-7194	17.7	.4	1.9	.90	2,298-2,299
SBR-69-7195	30.5	.5	2.2	.90	2,299-2,300
SBR-69-7198	49.8	.8	3.7	.90	2,305-2,306
SBR-69-7201	27.6	.1	1.4	.89	2,317-2,318
SBR-69-7205	29.7	1.0	1.3	.92	2,321-2,322
SBR-69-7210	39.7	.8	2.0	.90	2,326-2,327
SBR-69-7211	35.7	.4	1.8	.89	2,327-2,328
SBR-69-7213	31.8	.6	2.2	.90	2,329-2,330
SBR-69-7214	26.0	1.1	2.5	.90	2,330-2,331
SBR-69-7217	19.0	.5	2.5	.92	2,333-2,334
SBR-69-7220	5.2	.8	.4	.92	2,336-2,337
SBR-69-7222	7.8	1.1	1.5	.90	2,338-2,339
SBR-69-7225	10.6	.2	1.5	.92	2,344-2,345

TABLE A-5. - Fischer assay data for samples of Kentucky oil shale

Sample No.	Yields, gal/ton		Gas and loss, wt-pct	Oil, specific gravity	Sample depth, ft
	Oil	Water			
SBR-67-4359	12.7	5.0	3.5	0.96	47- 48
SBR-67-4360	16.4	5.3	3.4	.96	48- 49
SBR-67-4362	10.8	5.5	1.7	.97	50- 51
SBR-67-4364	8.9	5.3	2.2	.96	52- 53
SBR-67-4367	14.6	4.3	4.4	.96	55- 56
SBR-67-4370	17.3	3.6	4.7	.95	58- 59
SBR-67-4373	11.2	2.6	4.5	.97	61- 62
SBR-67-4380	9.0	3.6	2.2	.96	68- 69
SBR-67-4382	13.3	3.6	2.5	.96	70- 71
SBR-67-4385	8.6	3.2	3.0	.96	73- 74
SBR-67-4388	6.4	3.4	1.8	.95	76- 77
SBR-67-4389	7.7	3.1	2.3	.96	77- 78
SBR-67-4400	5.4	3.4	1.5	.95	88- 89
SBR-67-4413	3.3	3.8	.7	Est. .92	101-102
SBR-67-4414	1.3	2.3	.8	Est. .92	102-103

APPENDIX B.--DATA FOR REGRESSION ANALYSIS OF FISCHER ASSAY OIL YIELDS, ORGANIC CARBON CONTENTS, AND TOTAL HYDROGEN WITH NMR SIGNAL AREAS FOR FIVE OIL SHALES

This appendix lists the integrated NMR signal strengths from the three runs together with the organic carbon and total hydrogen contents of the various oil shale samples. The Fischer assay oil yields, organic carbon contents, and the NMR signal areas from these tables were used in the linear regression analyses.

The hydrogen content listed in the tables is the total hydrogen from combustion analysis and consists of the organic hydrogen, mineral hydrogen, and water hydrogen in the oil shale samples.

TABLE B-1. - Fischer assay oil yields, organic carbon and total hydrogen contents, and NMR signal areas for samples of Colorado oil shale

Oil yield, gal/ton	Organic carbon, wt-pct	Total hydrogen, wt-pct	NMR signal area		
			Run I	Run II	Run III
7.2	5.22	1.10	307	200	154
11.6	6.73	1.50	489	236	156
11.8	6.12	1.38	467	247	209
15.8	7.83	1.24	483	287	268
18.9	9.13	1.58	461	281	223
22.1	10.23	1.64	544	327	315
23.9	11.84	2.16	568	356	411
24.5	12.47	1.89	598	387	400
26.1	11.71	1.81	560	379	390
27.4	13.08	•	618	397	429
32.3	15.26	2.26	724	455	562
35.9	16.55	2.41	769	508	588
36.9	16.91	2.80	866	480	506

TABLE B-2. - Fischer assay oil yields, organic carbon and total hydrogen contents, and NMR signal areas for samples of Wyoming (GRB) oil shale

Oil yield, gal/ton	Organic carbon, wt-pct	Total hydrogen, wt-pct	NMR signal area		
			Run I	Run II	Run III
8.8	4.32	0.62	150	154	109
9.9	3.82	.62	180	202	207
11.7	4.84	.88	339	195	217
15.3	6.86	.98	252	302	231
16.2	6.91	1.09	305	357	339
17.9	7.48	1.12	300	227	262
18.0	8.25	1.12	308	324	345
19.1	9.69	1.35	351	355	313
23.0	10.54	1.52	483	528	-
25.3	11.04	1.56	450	493	490
25.3	11.61	1.59	471	551	504
26.5	11.34	1.80	456	493	416
27.3	13.27	1.86	546	585	485
28.0	11.97	1.65	447	536	519
29.0	12.07	1.85	431	448	432
30.5	13.99	2.00	595	632	549
35.9	15.83	2.22	567	684	615

TABLE B-3. - Fischer assay oil yields, organic carbon and total hydrogen contents, and NMR signal areas for samples of Wyoming (WB) oil shale

Oil yield, gal/ton	Organic carbon, wt-pct	Total hydrogen, wt-pct	NMR signal area, run III[1]
0	0.20	0.32	80
0	.28	.26	61
2.0	1.80	.56	148
3.0	2.02	.54	127
7.7	5.09	1.00	376
8.1	4.77	.96	339
9.1	5.04	1.08	376
10.2	6.45	1.13	342
10.5	6.06	1.10	387
15.1	6.52	1.12	395
15.6	8.61	1.34	408
16.8	8.22	1.42	453
19.4	9.56	1.52	527
22.7	11.08	1.88	649
25.8	12.08	2.00	700
35.5	16.94	2.46	837
36.2	17.08	2.42	885
38.2	19.40	2.81	1,052
40.0	18.06	2.64	904
41.2	20.83	2.90	991

[1] Data for the Wyoming (WB) oil shale were obtained only in run III.

TABLE B-4. - Fischer assay oil yields, organic carbon and total hydrogen contents, and NMR signal areas for samples of Utah oil shale

Oil yield, gal/ton	Organic carbon, wt-pct	Total hydrogen, wt-pct	NMR signal area		
			Run I	Run II	Run III
5.2	2.56	0.46	108	140	156
7.8	3.60	.60	-	201	175
10.5	4.61	.76	-	177	207
10.6	4.99	.72	-	274	225
11.4	5.40	.84	196	250	289
13.9	5.94	.92	313	248	294
15.8	6.97	1.03	230	232	236
17.7	7.59	2.28	232	275	302
18.6	8.06	1.18	355	321	366
19.0	9.31	1.28	399	426	432
20.8	8.10	1.24	348	320	355
22.6	10.24	1.46	387	330	429
24.0	10.12	1.42	356	365	445
26.0	11.67	1.64	458	448	551
27.6	11.35	1.61	360	425	-
28.6	12.57	1.68	473	505	546
29.7	13.52	1.80	492	564	575
30.5	12.88	1.76	508	491	551
31.8	14.27	1.91	524	566	644
34.2	14.87	2.02	549	570	708
35.7	14.90	1.98	600	650	684
38.5	16.54	2.28	672	620	723
39.7	18.00	2.41	691	705	755
42.7	19.22	2.58	719	806	851
49.8	22.50	2.62	994	895	954

TABLE B-5. - Fischer assay oil yields, organic carbon and total hydrogen contents, and NMR signal areas for samples of Kentucky oil shale

Oil yield, gal/ton	Organic carbon, wt-pct	Total hydrogen, wt-pct	NMR signal area		
			Run I	Run II	Run III
1.3	1.70	0.56	148	208	207
3.3	3.08	.66	184	198	204
5.4	4.82	.88	168	277	225
6.4	5.65	.88	257	259	268
7.7	7.01	1.10	209	312	321
8.6	7.97	1.10	237	365	323
8.9	9.33	1.24	279	351	339
9.0	8.55	1.16	311	362	329
10.8	11.33	1.42	334	433	390
11.2	12.74	1.55	325	498	411
12.7	14.61	1.66	360	498	408
13.3	11.18	1.43	316	431	395
14.6	14.39	1.64	407	520	488
16.4	16.16	1.86	464	516	464
17.3	15.81	1.84	395	548	525

APPENDIX C.--DATA FOR REGRESSION ANALYSIS OF ORGANIC HYDROGEN WITH CORRECTED NMR SIGNAL AREA FROM RUN III

The data in this appendix are those derived for the regression analyses using corrected hydrogen, carbon, and NMR areas. The NMR areas are those corrected from run III. The tables C-1 to C-5 identify oil shale samples by the Fischer assay oil yields.

The tables also list the packed densities of oil shale in the NMR tubes. These packed densities were obtained by dividing the weight in grams of oil shale in the NMR tube by the volume of the tube occupied by the oil shale. The assumption was made that the packed density for the oil shale in the NMR probe was the same as that for the entire tube.

Two listings for hydrogen are found in the tables. The first, H_{org}, was obtained in the following way: The Fischer assay water yield in gallons per ton (columns 3, tables A-1 to A-5) was assumed to have its origin in mineral water and free water in the oil shales. The water yield was converted to pounds of hydrogen per ton of the oil shale. The weight of mineral and free water hydrogen was then calculated as weight-percent hydrogen and subtracted from the total hydrogen (columns 3, tables B-1 to B-5) to yield the hydrogen corrected for water content in weight-percent.

The relative weights of hydrogen in the NMR probe were then calculated by multiplying the packed densities (columns 2, tables C-1 to C-5) by the H_{org} (columns 3, table C-1 to C-5). These weights of hydrogen in the NMR probe are listed as H_{org} in tables C-1 to C-5.

The relative weights of organic carbon in the NMR probe were calculated by multiplying the packed densities by the appropriate organic carbon contents (columns 2, tables B-1 to B-5). These weights of organic carbon are listed as C_{org} in tables C-1 to C-5.

The last columns in the tables in this appendix list corrected areas for run III. This correction assumes that the NMR sensitivities for organic hydrogen and mineral and free water hydrogen were the same. The NMR signal areas from run III (tables B-1 to B-2) were multiplied by the ratio H_{org}/H_{total} to approximate the fraction of the NMR area due to organic hydrogen.

TABLE C-1. - Table of data corrected for Fischer assay water yield and for packed density in the NMR sample tube for Colorado oil shale

Fischer assay oil yield, gal/ton	Packed density, g/cm^3	H_{org}, wt-pct	H_{org}, g/cm^3 X 10^4	C_{org}, g/cm^3 X 10^4	Area$_{corr}$
7.2	1.34	0.62	83	699	87
11.6	1.22	1.04	127	821	108
11.8	1.29	.96	124	789	145
15.8	1.31	1.14	149	1,026	246
18.9	1.11	1.25	139	1,013	176
22.1	1.23	1.38	170	1,258	252
23.9	1.14	1.80	205	1,350	359
24.5	1.21	1.79	217	1,509	378
26.1	1.20	1.63	196	1,405	351
32.3	1.27	2.17	276	1,938	540
35.9	1.25	2.30	288	2,069	561

TABLE C-2. - Table of data corrected for Fischer assay water yield and for packed density in the NMR sample tube for Wyoming (GRB) oil shale

Fischer assay oil yield, gal/ton	Packed density, g/cm^3	H_{org}, wt-pct	H_{org}, $g/cm^3 \times 10^4$	C_{org}, $g/cm^3 \times 10^4$	$Area_{corr}$
8.8	1.26	0.54	68	544	95
9.9	1.34	.58	78	512	195
11.7	1.36	.74	101	658	182
15.3	1.17	.93	109	803	219
16.2	1.29	1.02	132	891	319
17.9	1.18	1.02	120	883	238
18.0	1.26	1.07	135	1,040	331
19.1	1.29	1.27	164	1,250	294
25.3	1.22	1.48	181	1,347	466
25.3	1.27	1.51	192	1,474	479
26.5	1.11	1.64	182	1,259	379
27.3	1.17	1.79	209	1,553	466
28.0	1.22	1.54	188	1,460	483
29.0	1.12	1.70	190	1,352	397
30.5	1.20	1.85	222	1,679	511
35.9	1.17	2.11	247	1,852	584

TABLE C-3. - Table of data corrected for Fischer assay water yield and for packed density in the NMR sample tube for Wyoming (WB) oil shale

Fischer assay oil yield, gal/ton	Packed density, g/cm^3	H_{org}, wt-pct	H_{org}, $g/cm^3 \times 10^4$	C_{org}, $g/cm^3 \times 10^4$	$Area_{corr}$
0	1.45	0.09	13	29	22
0	1.46	.10	15	41	23
2.0	1.40	.34	48	252	90
3.0	1.37	.39	53	277	92
7.7	1.27	.81	103	646	305
8.1	1.23	.64	79	587	226
9.1	1.27	.79	100	640	275
10.2	1.25	1.02	128	806	309
10.5	1.36	.89	121	824	313
15.1	1.23	.93	114	802	328
15.6	1.26	1.19	150	1,102	362
16.8	1.31	1.23	161	1,077	392
19.4	1.29	1.31	169	1,233	454
22.7	1.33	1.73	230	1,474	597
25.8	1.30	1.79	233	1,570	627
35.5	1.23	2.20	271	2,084	748
36.2	1.25	2.18	273	2,135	797
38.2	1.29	2.52	325	2,503	944
40.0	1.24	2.35	291	2,239	805
41.2	1.21	2.67	323	2,520	912

TABLE C-4. - Table of data corrected for Fischer assay water yield and for packed density in the NMR sample tube for Utah oil shale

Fischer assay oil yield, gal/ton	Packed density, g/cm³	H_{org}, wt-pct	H_{org}, $g/cm^3 \times 10^4$	C_{org}, $g/cm^3 \times 10^4$	$Area_{corr}$
5.2	1.40	0.42	59	358	142
7.8	1.46	.55	80	526	160
10.5	1.29	.73	94	595	199
10.6	1.25	.71	89	624	223
11.4	1.27	.78	99	686	269
13.9	1.37	.89	121	814	285
15.8	1.25	1.01	126	871	231
18.6	1.25	1.15	144	1,008	355
19.0	1.31	1.26	165	1,220	423
20.8	1.20	1.22	146	972	348
22.6	1.18	1.44	170	1,208	425
24.0	1.19	1.42	169	1,204	445
26.0	1.24	1.59	197	1,447	534
28.6	1.27	1.65	210	1,596	535
29.7	1.24	1.76	218	1,676	564
30.5	1.25	1.74	218	1,610	545
31.8	1.16	1.88	218	1,655	631
34.2	1.22	1.96	239	1,814	687
35.7	1.20	1.96	235	1,788	677
38.5	1.17	2.26	264	1,935	716
39.7	1.17	2.37	277	2,106	740
42.7	1.22	2.54	310	2,345	834

TABLE C-5. - Table of data corrected for Fischer assay water yield and for packed density in the NMR sample tube for Kentucky oil shale

Fischer assay oil yield, gal/ton	Packed density, g/cm³	H_{org}, wt-pct	H_{org}, $g/cm^3 \times 10^4$	C_{org}, $g/cm^3 \times 10^4$	$Area_{corr}$
3.3	1.14	0.49	56	351	151
5.4	1.13	.73	82	545	187
6.4	1.16	.73	82	655	222
7.7	1.10	.96	106	771	277
8.6	1.13	.96	108	901	282
8.9	1.07	1.01	108	998	276
9.0	1.11	1.00	111	949	284
10.8	1.08	1.18	127	1,224	324
11.2	1.09	1.44	157	1,389	382
12.7	.98	1.44	141	1,432	354
13.3	1.10	1.27	140	1,230	351
14.6	1.11	1.45	161	1,597	431
16.4	1.07	1.63	174	1,729	406
17.3	1.07	1.68	180	1,692	479