1990 SCA CONFERENCE PAPER NUMBER 9020

PETROPHYSICAL APPLICATIONS OF AUTOMATED PROTON HIGH RESOLUTION NMR SPECTROSCOPY

by

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ABSTRACT

A high resolution nuclear magnetic resonance (NMR) spectrometer has been equipped with automated sample changer and off-line spectral processing for rapid, high-accuracy analysis of liquid extracts from cores. Three petrophysical applications are discussed: analysis of oil extracted from polyurethane sponge liners using freon-11, Dean-Stark extracts using xylene, and miscible flooding extracts using chloroform/methanol. In each case, the oil (and water) volumes are measured by ^{1}H NMR. The viscosity of the undiluted oil is estimated from ^{1}H NMR relaxation time measurements on the freon-11 and chloroform/methanol extracts.

INTRODUCTION

Almost all of the procedures used in routine and special core analysis involve extracting fluids from cores with various solvents. In most cases, the core petrophysical quantities are determined by weight and volume measurements, and the extracts are normally discarded. However, automated high resolution proton NMR spectroscopy on these extracts can be used independently to obtain high accuracy measurements of oil and water content as well as estimates of oil properties such as viscosity. With the addition of ^{13}C NMR, further details of oil molecular structure such as aliphatic/aromatic ratio, C/H ratio, and branching can be obtained.

In this paper, we discuss three ^{1}H NMR petrophysical applications on extracts: analysis of oil in freon-extracted polyurethane sponge liners, oil/water in chloroform/methanol miscible flood extracts, and oil in xylene Dean-Stark extracts. In addition to quantifying oil in various extracts, NMR spin-lattice (T1) relaxation time measurements of the oil in freon-11 and chloroform/methanol are used to estimate the viscosity of the undiluted crude.

SOLVENTS FOR ^{1}H NMR

In order to avoid spectral overlap with the oil, the solvent should preferably contain little or no protons in the aliphatic oil band between 0.8-2.0 ppm. (The ppm chemical shift scale is referenced to tetramethysilane (TMS) at 0.0 ppm.) Some overlap can be handled by subtracting the spectrum of the clean solvent from

that of the extract, as described later. However, for maximum accuracy, the solvent background should not overwhelm the oil spectrum.

Noninterfering solvents include all nonprotonated solvents such as the fully halogenated hydrocarbons (freon-11, tetrachloroethylene, carbon tetrachloride, etc.) and the fully halogenated aromatics. Examples of other noninterfering solvents include aromatic hydrocarbons such as xylene and toluene and many other common solvents such as chloroform and methanol. Although these latter solvents may overlap with the aromatic components in the crude, the correction is small because aromatic protons account on average for only 4% of the proton intensity in light and medium gravity crudes (Vinegar et al., 1989). Ideally, any perdeuterated solvent could also be used. However, deuterated solvents are several times more expensive than the normal solvents listed above.

In addition to proton NMR, oil content and molecular structure may also be determined by ^{13}C NMR spectroscopy. This has the advantage of allowing additional solvents whose carbon spectrum is well-resolved from the aliphatic and aromatic oil spectrum. ^{13}C spectroscopy has low signal-to-noise ratio, however, requiring about one hour per analysis compared to minutes for ^{1}H NMR.

APPARATUS

Over the past couple of years, one of the primary goals of the NMR group at Shell has been the automation of standard NMR analyses. The ability to automate NMR analyses stems from the combined use of computer-controlled spectrometers equipped with sample changers and off-line computer workstations.

Each of the automated high resolution solution spectrometers (Bruker AM-360, AMX-400, and AM-500) has a sample changer which accommodates up to 120 NMR tubes. A variety of automated NMR pulse sequences can be set up to run one or more experiments for each sample. Once the data have been acquired, it is transferred to a microVAX 3500 workstation equipped with 8 MB of memory, two hard disks (1 GB total storage capacity), and a 2.2 GB tape drive.

Data are transferred at the completion of a series of analyses using an RS-232 link following SPECNET protocol. Typically, four minutes are required to transfer a 16K NMR free induction decay (FID) file. Data transfer is initiated by the Bruker TRSB file transfer command.

The microVAX has been programmed in-house to perform various tasks such as Fourier transformation, spectral phasing, baseline correction, line fitting, and peak integration. It also recognizes various spectral regions and calculates parameters such as relative molecular composition or, as in the case of petrophysical analyses, absolute concentrations of specific components.

Once an analysis has been automated, minimum operator involvement is required. Following sample preparation and loading in the sample changer, NMR experiments and acquisition parameters are selected

from a standard menu. Data are sent to the microVAX which recognizes the type of analysis to be performed, processes the data accordingly, and finally plots and tabulates results.

SPONGE CORE

Conventional coring procedures result in part of the oil in the core being blown out as the core is brought up to the surface. In order to obtain more accurate estimates of oil content, sponge coring has been introduced recently as a less expensive and operationally simpler alternative to pressure coring to account for these blowdown losses. In sponge coring, the core barrel is lined with a high porosity oil-wet polyurethane sponge which traps the blowdown oil expelled from the core. At the surface, cored sections are frozen and transported to the laboratory to determine the oil content of both core and polyurethane sponge liner. So far the analysis of the polyurethane sponge has proven to be problematical: mechanical extraction (hydraulic press), hot solvent extraction, and retorting have been used but result either in incomplete removal of oil from the sponge or dissolution of the polyurethane and overestimation of oil content.

Recently Shell has developed a practical sponge core analysis method which uses freon-11 (trichlorofluoromethane) for the extraction of oil from the sponge and distillation followed by gas chromatography (GC) for the quantification of oil in the extract (Calkin, 1988; Dangayach, 1988; DiFoggio, 1987). Freon-11 is used because it is a good solvent for oil (Hansen solubility = 15.5) and a poor solvent for polyurethane and because its low boiling point (23.8°C) allows freon distillation to concentrate the oil in the extract prior to gas chromatography.

The sponge, still inside the aluminum liner, is cut into one-foot sections and extracted for up to two days. Following extraction, a distillation column is used to remove most of the freon solvent. The concentrated extract is then treated with aqueous potassium hydroxide and centrifuged in order to separate dissolved polyurethane components. The freon content in the concentrated extract is measured by GC. Finally, the oil volume in the extract is obtained by differencing the total volume of the extract from the GC-determined residual freon volume.

There are two main competing systematic errors in the distillation/GC procedure: loss of light ends from the crude oil during distillation and failure to separate polyurethane completely in the freon extract. Since the oil volume is determined by difference, any residual polyurethane in the concentrated extract is counted as oil. In terms of time, the distillation/GC technique takes about 10 hours per sample. However, batch processing with ten distillation columns translates into roughly one hour labor per sample.

Substitution of NMR for distillation/GC has resulted in a major improvement in the analysis of the sponge extracts (Vinegar, 1989). The NMR method not only avoids the two main sources of error mentioned above for distillation/GC but also requires less than 10 minutes per sample, including sample preparation, data collection, and processing. Up to 120 samples can be analyzed overnight with essentially no operator

involvement. One disadvantage is that NMR instrumentation is more expensive than that required for distillation/GC.

In the NMR method, a 1 ml sample of the initial oil/freon extract (typically 500 to 800 cc) is placed in a 5 mm NMR tube. No distillation is required. Figure 1 shows ^{1}H NMR spectra of a sample of freon-extracted blank polyurethane sponge along with samples of 0.84 and 15.9 vol % oil in freon-extracted blank sponge. The blank sponge spectrum in Figure 1a is consistent with that of a polyurethane obtained from the reaction of an aromatic diisocyanate with a polyester/polyethylene glycol copolymer. Figures 1b and 1c show additional aliphatic and aromatic oil resonances in the 0.8–2.0 ppm and 6.5–8.5 ppm regions, respectively.

The microVAX automatically corrects for the contribution of background urethane sponge resonances which overlap with the aliphatic oil signal. The correction algorithm uses the spectrum of a blank sponge extract to calculate a ratio between sponge resonances which partially or fully overlap oil signals (0.8–4.0 ppm) and sponge resonances which do not overlap oil signals (4.0–4.5 ppm). This ratio is used in the actual sample spectra to back calculate the contribution of polyurethane in the aliphatic oil region. The corrected aliphatic oil signal is then calibrated to that from a standard of known oil concentration. Note that this background correction method does not assume that the amount of polyurethane is constant among samples, but only that the ratio of polyurethane resonances in different portions of the NMR spectrum is constant. The NMR-determined oil concentrations are then multiplied by the total volume of the oil/freon phase measured previously to yield the original oil volume in the sponge.

In order to test the accuracy of the NMR method, blank sponge extracts of 500 to 800 cc were spiked with known amounts of Ventura crude oil and submitted to NMR for quantification of oil volume. The blank sponges were extracted for different lengths of time to obtain different amounts of polyurethane in the extract. Figure 2 and Table 1 show excellent agreement between prepared and NMR-determined volumes of crude oil in various freon extracts of blank sponges. Even though the amount of polyurethane in the extracts varied by a factor of two, the NMR correction algorithm assures no loss in accuracy in determining oil content. The standard error of estimate in the presence of polyurethane background is 0.04 cc or about 2.0%.

Table 1

PREPARED vs NMR AND DISTILLATION/GC-DETERMINED OIL VOLUMES (cc) IN FREON-11

Sample	Prepared	NMR	Distillation/GC
Oil in Pure Freon	0.92	0.87	0.80
Oil in Pure Freon	2.32	2.33	2.30
Oil in 2-Day Freon-Extracted Sponge	2.47	2.51	3.20
Oil in 7-Day Freon-Extracted Sponge	2.49	2.54	3.70

Comparisons between NMR and distillation/GC show that both methods agree at higher oil content but that distillation/GC consistently reads about 1 to 2 cc higher at oil content below 3 cc. As shown in Table 1, double-blind tests confirmed the bias of distillation/GC towards higher oil volumes due to urethane components remaining in the extract even following caustic treatment. The NMR spectra in Figure 3 of the oil/freon phase following caustic addition prove that considerable urethane components are still present in the solution.

As an additional test of the accuracy of the NMR method, several crude oils with widely different API gravity were dissolved in freon-11 at a fixed concentration and measured by NMR. Table 2 shows the standard error of estimate is 0.13 cc or about 1.0%, excluding the 12.1 API sample which left asphaltene components undissolved in freon-11. This data set shows that the accuracy of the NMR analysis is independent of the API gravity of the crude. Therefore, any light or medium gravity crude can be used as a calibration standard, and a sample of the particular oil from the well, although desirable, is not required.

Table 2

PREPARED vs NMR OIL VOLUMES (cc) IN FREON-11 AS FUNCTION OF API GRAVITY OF CRUDE

API Gravity	Prepared	NMR
25.6	13.6	13.7
24.2	13.0	12.8
20.5	13.1	13.2
17.5	13.2	13.1
12.1*	13.5	12.7

*Not fully dissolved.

OTHER SOLVENTS FOR SPONGE CORE ANALYSIS

Freon-11 was initially selected as the sponge solvent because its low boiling point allowed distillation without removing many of the light ends of the crude oil. However, if NMR is used for sponge analysis, the boiling point of the solvent need not be low, which enables use of a much larger number of solvents. In particular, better solvents would shorten the extraction time and result in more complete extraction of the asphaltene components of crude oils. Note that if the solvent boils above room temperature the low temperature condenser used on the Soxhlet extraction unit for freon-11 is not required.

The solvent should be selected so as to be a good solvent for the oil yet leave the sponge substantially unaffected. As an initial screening procedure, the solvent is selected so as to have a Hansen solubility parameter significantly above or below that of polyurethane (19.2) (Chapiro et al., 1978). (Note that in Chapiro et al. the Hansen solubility parameter scale is 1/2 that utilized in the U.S. literature).

The Hansen solubility parameters for a variety of solvents have been tabulated (Barton, 1983). From this table, several preferred solvents can be chosen, including freon-113 (trichlorotrifluoroethane, commercial trademark Freon-TF), b.p. = 47.6°C, Hansen solubility parameter = 14.9; freon-112 (tetrachlorodifluoroethane), b.p. = 92.8°C, Hansen solubility parameter = 16.0; tetrachloroethylene, b.p. = 121°C, Hansen solubility parameter = 20.3. These nonprotonated solvents are all excellent solvents for crude oil, have low dissolving power for polyurethane sponge, and most important, low to moderate toxicity.

OIL VISCOSITY FROM RELAXATION TIMES IN SPONGE CORE EXTRACTS

In addition to quantifying oil in the extract, the NMR method can estimate the viscosity of the undiluted crude oil by automated spin-lattice (T1) relaxation time measurements on the extracts. Figure 4 plots

T1 measurements on 2 vol % oil-in-freon solutions for a suite of 10 Cannon viscosity standards and 21 light and medium gravity crude oils from Shell fields worldwide. The data show a tight correlation between oil viscosity and NMR T1 relaxation times. Thus, a measurement of T1 for oil in a freon extract can be used to estimate the viscosity of the undiluted oil.

The T1 measurements were made with an inversion-recovery (180-T-90)n pulse sequence with interpulse times varying between 10 and 5000 milliseconds. A simple exponential for T1 provided a good fit to the relaxation data in the extracts. The relaxation times reported are for the repeat chain $-CH_2-$ resonance at 1.08 ppm. The viscosity was measured for each undiluted crude using a shear viscometer at a shear rate of 7.5/sec. Measurements of viscosity and NMR relaxation were performed at 25°C. Several of the crudes had a high wax content and the viscosities at 25°C were extrapolated from three measurements at higher temperatures above the pour point.

In a nonprotonated solvent, the protons on the oil molecules will relax primarily due to intramolecular magnetic dipole-dipole interactions. The major intermolecular contribution to the oil proton relaxation at low concentration will be from the solvent molecules since the probability of interacting with another oil molecule is small. In a fully halogenated solvent, the contributions from unlike chlorine and fluorine spins in relaxing the protons on the oil molecules are reduced relative to other protons by the factor R:

$$R = \frac{2}{3}\left(\frac{\gamma_f}{\gamma_p}\right)^2 \frac{I_f(I_f+1)\ N_f}{I_p(I_p+1)\ N_p} \qquad (1)$$

where γ is the gyromagnetic ratio, I the spin quantum number, N the density of spins per cc, and the subscript p stands for proton and f for fluorine or chlorine (Abragam, 1961). For freon-11, the R factor is 0.0093 for chlorine because of the small chlorine gyromagnetic ratio and 0.057 for fluorine since there is a single fluorine nucleus per freon-11 molecule. Thus, the total intermolecular proton relaxation from freon-11 should be small. Moreover, it should be virtually the same for each crude oil and therefore contribute a small but constant background relaxation.

The intramolecular relaxation from proton-proton interactions within the oil molecule will depend on the rotational motions of the molecule. At low concentrations, the effects of chain entanglement of the oil molecules should be small and use of conventional relaxation theory and the Stoke's hydrodynamic approach leads to the following expression for the intramolecular relaxation rate:

$$(1/T_1)_{intra} = Aa^2\left(\sum_{i>j} R_{ij}^{-6}\right)/nD \qquad (2)$$

where A is a constant, R_{ij} is the proton separation in the proton pair ij, n is the number of protons in the molecule, D is the diffusion coefficient of the oil molecule in the solvent, and a is the effective diameter of the oil molecule. The average of R_{ij}^{-6} is nearly the same for all hydrocarbons since the major contribution to the sum is from nearest neighbor protons. Thus, T1 depends on the size and shape of the oil molecule through the terms a and D. Since these quantities are also related to the viscosity of the undiluted crude oil, one expects a good correlation between T1 and the viscosity of the undiluted crude. At low concentrations, where the oil molecules do not interact, the diffusion coefficient D in Equation (2) should be independent of oil concentration and therefore T1 should be independent of oil concentration.

Table 3 shows that, as expected, at concentrations below 5 vol % there is no dependence of T1 on crude oil concentration for Wasson crude even in a protonated solvent like chloroform/methanol azeotrope. However, for maximum accuracy in using these correlations at 2% concentration, extracts can be adjusted to the 2% concentration by adding or evaporating solvent and using NMR to determine the precise oil concentration.

Table 3

T1 vs CONCENTRATION
WASSON CRUDE IN CHLOROFORM/METHANOL AZEOTROPE

Oil Concentration (vol %)	T1 (ms)
0.625	1215 ± 24
1.25	1254 ± 36
2.5	1270 ± 39
5.0	1276 ± 58
10.0	958 ± 27
100.0	404 ± 20

CHLOROFORM/METHANOL EXTRACTS

In special core analysis of unconsolidated cores, miscible flooding with chloroform/methanol azeotrope is used to extract oil and water prior to performing other measurements. The oil, water, and gas saturations of these special analysis core plugs are normally not determined; rather, saturations are estimated from Dean–Stark extraction on adjacent plugs to avoid altering wettability and disaggregating loosely consolidated cores. In this section, we describe a rapid and accurate method using ^1H NMR to measure crude oil and water directly in chloroform/methanol extracts. Unlike the previous case with nonprotonated freon–11,

chloroform and methanol do contain protons. These protons, however, are located in a portion of the ^1H NMR spectrum which is nonoverlapping with the aliphatic oil components.

Various mixtures of chloroform/methanol azeotrope with crude oil and brine were measured, as listed in Table 4. In most cases, two phases are present in the extracts. As shown in Figure 5, the ^1H NMR spectrum of the small upper phase of sample C reveals the presence of methanol and water resonances ($-CH_3$ protons at 3.6 ppm and -OH protons at 5.0 ppm. The water concentration in the upper phase is obtained by subtracting the methanol -OH protons (equal to 1/3 of the integrated area of the methanol $-CH_3$ protons) from the total integrated area of the 5 ppm -OH signal. The water -OH signal is calibrated to that of a standard of known water-in-methanol concentration.

Table 4

PREPARED vs NMR-DETERMINED OIL AND WATER VOLUMES (cc) IN CHLOROFORM/METHANOL AZEOTROPE

	Oil Volume		Water Volume	
Sample	Prepared	NMR	Prepared	NMR
A	1.00	0.93	1.00	1.07
B	0.50	0.46	2.00	1.97
C	2.00	2.04	0.50	0.54

As shown in Figure 6, the lower phase spectrum of sample C reveals the presence of crude oil (aliphatic protons between 0.8 and 2.0 ppm), methanol ($-CH_3$ protons at 3.2 ppm and -OH protons at 4.0 ppm), chloroform ($CHCl_3$ protons at 7.2 ppm), and water (-OH protons at 4.0 ppm). The water concentration in the lower phase is calculated in the same manner as for the upper phase. Note that in the lower phase, the -OH resonance shifts from 5.0 ppm to 4.0 ppm due to a decrease in hydrogen bonding in the presence of chloroform. The lower phase oil concentration is obtained by integrating the aliphatic oil proton region (0.8-2.0 ppm) and calibrating it to that from a standard of known oil-in-chloroform concentration.

The NMR-determined upper and lower phase oil and water concentrations are multiplied by the upper and lower phase total extract volumes measured previously to yield the original oil and water volumes in the extracted core plug. Table 4 compares prepared vs NMR-determined oil and water volumes obtained for various test samples. The standard error of estimate is 0.052 cc for oil and 0.050 cc for water.

NMR analysis is an excellent method for determining the completeness of extraction in chloroform/ methanol miscible core flooding. As an example, oil and water volumes were determined for a core plug

which was subjected to eleven flushes using varying amounts of chloroform and methanol. Passes one through four used pure chloroform, five through nine chloroform/methanol azeotrope, and ten through eleven pure methanol.

Figure 7 plots the oil and water percent by volume concentrations measured in all eleven passes. Figure 8 plots cumulative oil and water volumes extracted from the core plug as a function of cumulative eluted volume. Note that most of the oil is extracted in the first two passes. Subsequent chloroform-only passes show a steady decrease in volume of oil produced. Upon switching to the chloroform/methanol azeotrope, an increase in oil production occurs, which coincides with an increase in water production (no water was detected in the chloroform-only passes). Since chloroform is a poor solvent for water, the increase in oil production on switching to chloroform/methanol may be due to removal of brine-shielding oil. Passes seven through nine show a decrease in water production. The extract in pass nine was clear and NMR showed no oil content. However, passes ten and eleven using pure methanol removed an additional 0.6 cc brine, which is 33% of the initial water volume in the core. This shows that chloroform/methanol azeotrope should be followed by pure methanol to remove residual brine. Extensive air drying without a final methanol flush is not recommended because the salt concentration from the residual brine will remain in the core.

OIL VISCOSITY FROM RELAXATION TIMES IN CHLOROFORM/METHANOL

T1 relaxation times were measured for the Cannon viscosity standards at 2 vol % in chloroform/methanol azeotrope. Figure 9 plots T1 against undiluted Cannon standard viscosity. The correlation is similar to that of the oil-in-freon extracts, but the T1 times are shorter due to intermolecular proton relaxation from solvent molecules.

DEAN-STARK EXTRACTS

Dean-Stark core extraction uses xylene or toluene in a refluxing arrangement where water is removed from the core by hot solvent extraction above the boiling point of water. The water is condensed and trapped and its volume measured. The oil volume is calculated by weight difference assuming a known oil density. In some cases, errors can accrue from this indirect oil determination, for example due to partial salt removal or dehydration of minerals such as gypsum.

As in freon-11 and chloroform/methanol extracts, ^{1}H NMR can be used to measure the oil content directly in Dean-Stark xylene or toluene extracts, thus minimizing errors which can accrue from indirect oil volume determination by weight difference. In addition, the NMR method provides a reliable estimate of oil viscosity of the undiluted crude.

Figure 10 shows ^{1}H NMR spectra of the aliphatic region of a sample of blank o-xylene along with samples of 1.0 and 4.8 vol % oil in o-xylene. The aromatic region of the spectrum is dominated by the o-xylene solvent

peaks. The aliphatic oil signal is detected between 0.8 and 2.0 ppm, while the $-CH_3$ protons of o-xylene are detected between 2.0 and 2.8 ppm. The aliphatic oil signal is corrected for o-xylene background impurities using an approach similar to that of the sponge core extract analysis. Using a blank o-xylene sample, the ratio between o-xylene impurity peaks in the aliphatic oil region and the methyl o-xylene peak is calculated. This ratio is used in actual oil-containing samples to back out solvent impurity signals from the aliphatic oil integral. The corrected oil integral is then calibrated to that from a reference sample of known oil concentration.

The NMR-determined oil concentrations are multiplied by the total volume of the oil/xylene solution measured previously to yield the total oil volume of each extract. Figure 11 and Table 5 show excellent agreement between prepared and NMR-determined volumes of crude oil in oil-in-xylene test samples. The standard error of estimate is 0.03 cc or about 1.5%.

Table 5

PREPARED vs NMR-DETERMINED OIL VOLUMES (cc) IN O-XYLENE

Sample	Prepared Volume	NMR Volume
A	0.50	0.51
B	0.99	1.04
C	1.96	1.95
D (standard)	4.76	4.76

CONCLUSIONS

Computer-controlled NMR spectrometers equipped with automated sample changers are ideal tools for rapid and accurate quantification of oil and water in core extracts. As an additional benefit, the oil viscosity can be estimated by T1 relaxation time measurements in the extracts. The NMR method has been demonstrated for freon-11 sponge core extracts, chloroform/methanol miscible flood extracts, and xylene Dean-Stark extracts. The method clearly can be extended to many other solvent combinations.

NMR analysis requires about 10 minutes per sample and is fully automated, offering typically one day reporting time for up to 120 samples. Data are acquired and transferred to a microVAX station where it is processed with minimum operator involvement. In the case of freon-11 sponge core extracts, direct comparisons with the distillation/GC technique indicate that the NMR method is more accurate, particularly at low oil content, and about 1/6 the cost. The NMR method is now in routine use at Shell.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of Victor Tong, Barbara Acker, John Ferris, Larry Bielamowicz, Gordon Setser and Rocco DiFoggio in helping develop the methodology presented here.

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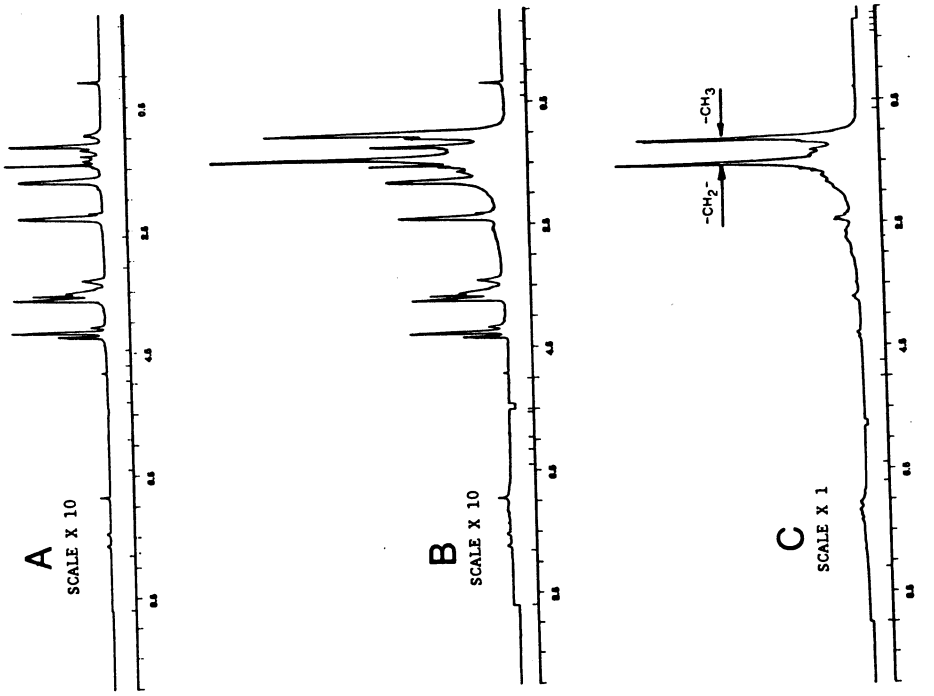

FIGURE 1 - 1H NMR SPECTRA OF (A) FREON-EXTRACTED BLANK SPONGE, (B) 0.84% VOL. AND (C) 15.87% VOL. OIL IN FREON-EXTRACTED BLANK SPONGE. RESONANCES IN (A) ARE CONSISTENT WITH A POLYURETHANE BASED ON THE CURING OF AN AROMATIC DIISOCYANATE WITH A POLYESTER/POLYETHYLENE GLYCOL COPOLYMER. MAJOR OIL RESONANCES APPEAR AT 0.8 AND 1.3 PPM, CORRESPONDING TO METHYL AND REPEAT UNIT METHYLENE PROTONS.

SPONGE CORE ANALYSIS BY NMR
1H NMR, VENTURA 250 CRUDE

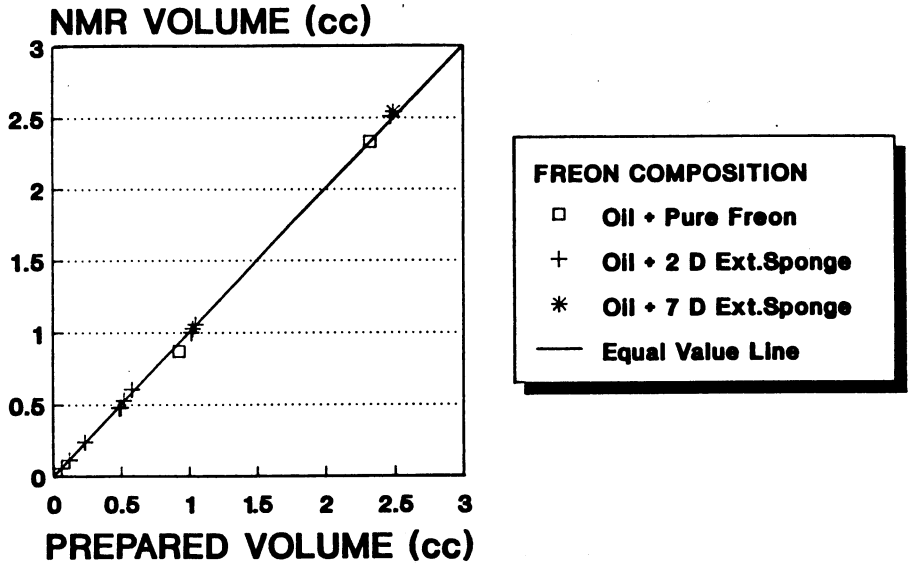

FIGURE 2 - PREPARED VS NMR-DETERMINED OIL CONTENT IN VARIOUS FREON-EXTRACTED BLANK SPONGE SAMPLES.

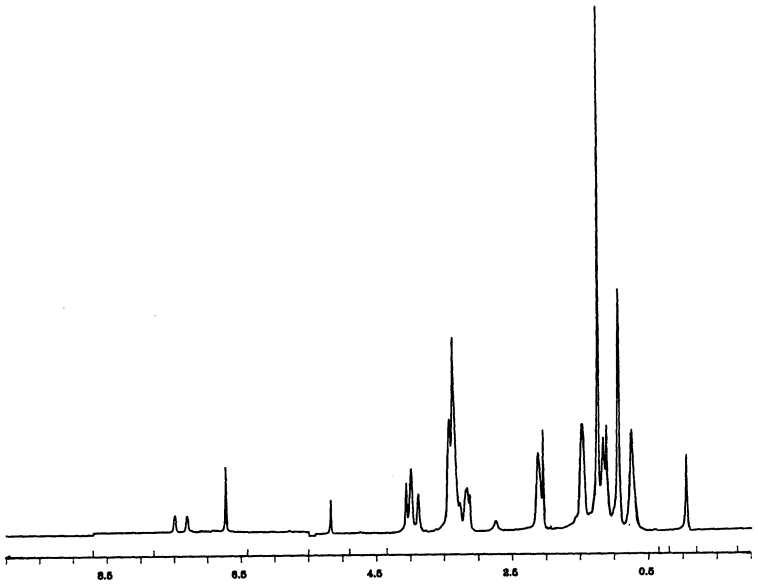

FIGURE 3 - 1H NMR SPECTRA OF THE OIL/FREON PHASE FOLLOWING CAUSTIC TREATMENT. AS IN FIGURE 1, THE SPECTRUM INDICATES THE PRESENCE OF POLYURETHANE RESONANCES WHICH PARTIALLY OVERLAP THE OIL ALIPHATIC SIGNAL. DISTILLATION/GC WOULD COUNT THE POLYURETHANE AS OIL FROM THE SPONGE.

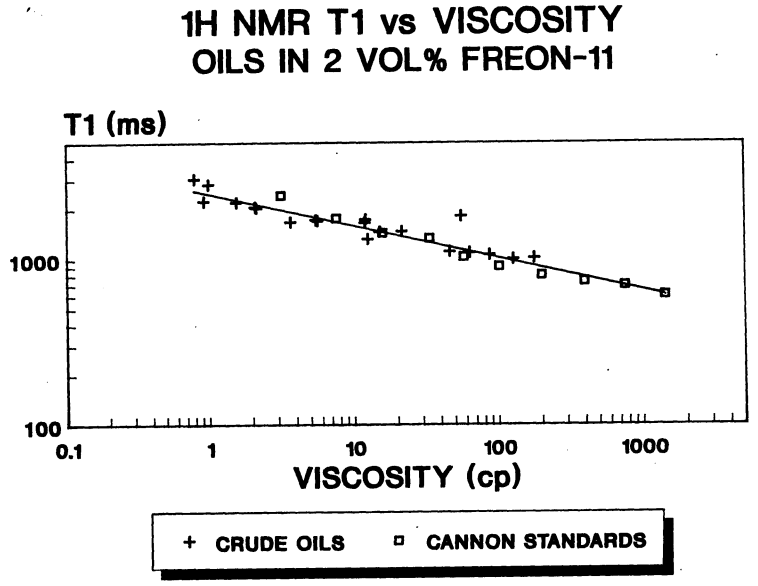

FIGURE 4 - T1 VS VISCOSITY FOR 2 VOL % CRUDE OILS AND CANNON STANDARDS IN FREON-11.

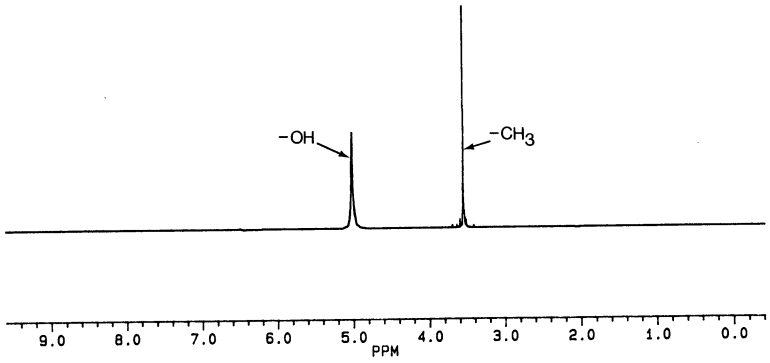

FIGURE 5 - 1H NMR SPECTRUM OF THE UPPER PHASE OF SAMPLE C (SEE TABLE 4).

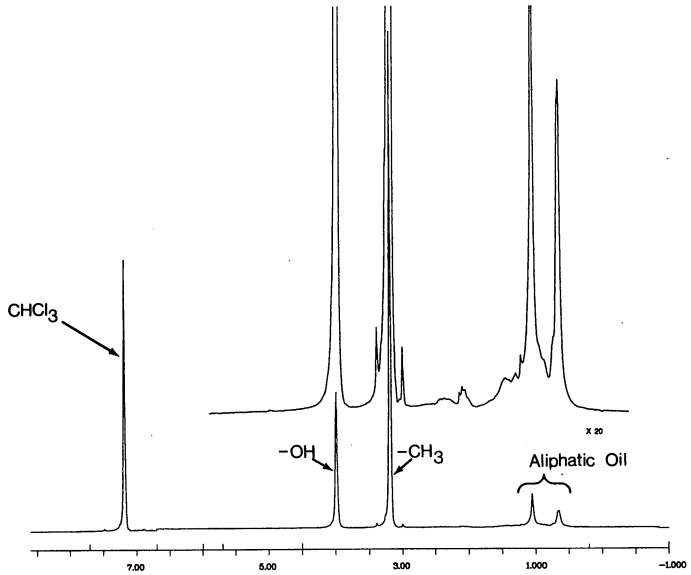

FIGURE 6 - 1H NMR SPECTRUM OF THE LOWER PHASE OF SAMPLE C (SEE TABLE 4).

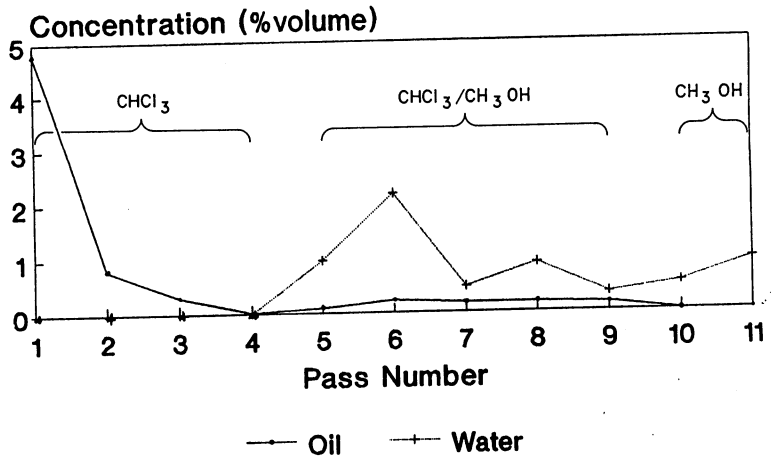

FIGURE 7 - CONCENTRATION OF OIL AND WATER EXTRACTED FROM A CORE PLUG FOLLOWING VARIOUS CHLOROFORM/METHANOL FLUSHES.

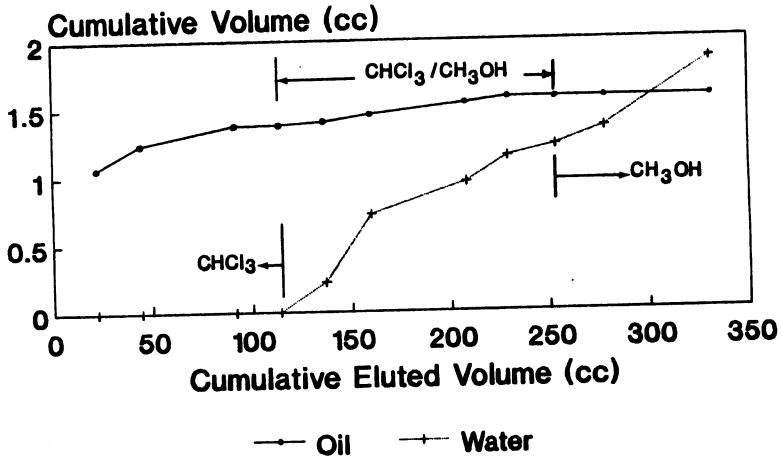

FIGURE 8 - CUMULATIVE VOLUME OF OIL AND WATER FROM CORE PLUG IN FIGURE 7.

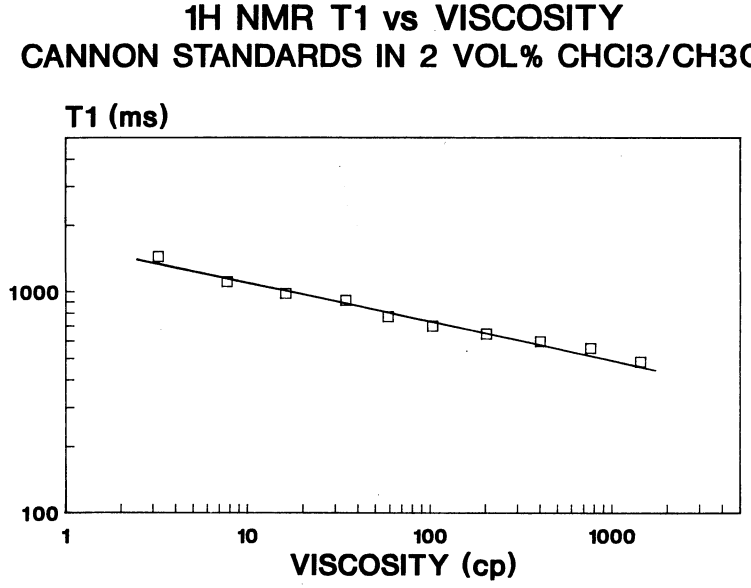

FIGURE 9 - T1 VS VISCOSITY FOR 2 VOL % CANNON STANDARDS IN CHLOROFORM/METHANOL AZEOTROPE.

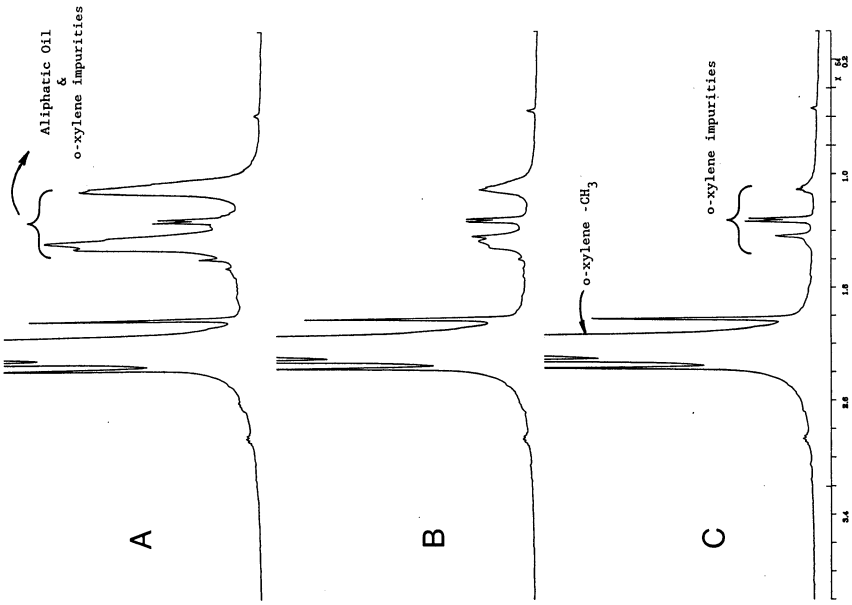

FIGURE 10 - 1H NMR SPECTRA OF THE ALIPHATIC REGION OF (A) BLANK O-XYLENE SOLVENT, (B) 1.0% VOL. AND (C) 4.8% VOL. OIL IN O-XYLENE.

1H NMR of XYLENE DEAN-STARK EXTRACTS

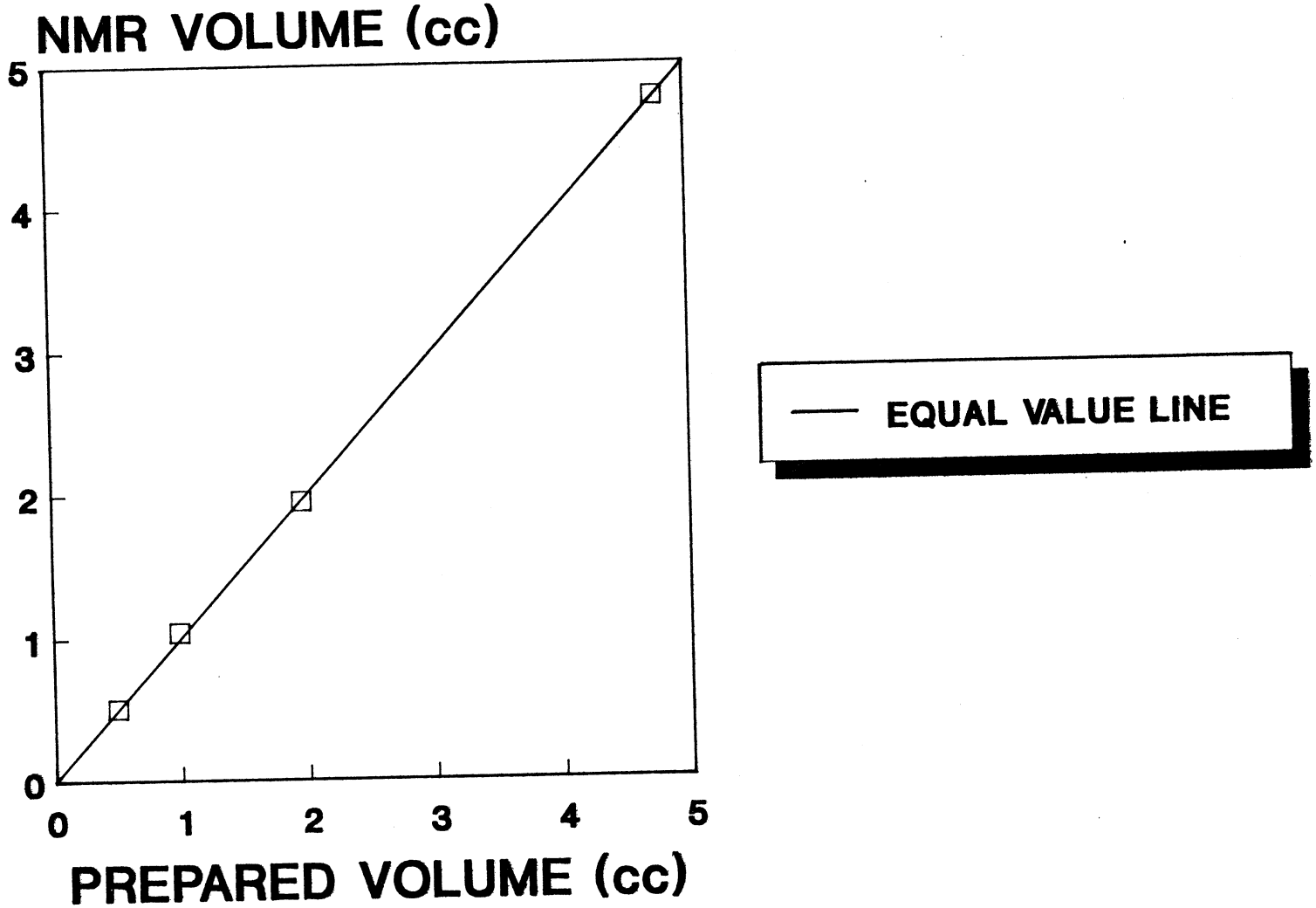

FIGURE 11 - PREPARED VS NMR-DETERMINED OIL CONTENT IN OIL-XYLENE TEST SAMPLES.