LIQUIFIED-GAS EXTRACTION AND NEAR-INFRARED ANALYSIS OF CORE

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ABSTRACT

This paper describes two new techniques, liquified-gas extraction and near-infrared analysis, which can be used separately or in tandem to analyze core and the crude oil in core.

Liquified-gas extraction of core utilizes solvents such as cyclopropane or vinyl chloride (which boil far below room temperature) to clean core in a pressurized Soxhlet. Because the extraction is conducted at or below room temperature, it can be performed on heat-sensitive core such as those containing gypsum.

After the liquified gas is vented, essentially pure crude oil remains in the boiling flask and recovered water is collected in a desiccant trap. The weights of extracted crude oil and water are obtained from the weight changes of the boiling flask and desiccant, respectively. When sufficient crude is extracted, one can directly measure physical properties such as API gravity (requires $\geq$ 0.1 ml) or viscosity (requires $\geq$ 1.0 ml) as well.

Near-infrared analysis is a powerful technique for estimating properties of crude oils or other materials from their near-infrared spectra. One can perform near-infrared analysis on the liquified-gas extracted crude oil to predict percentage of asphaltenes, gas-oil ratio, API gravity, and viscosity, not only of the extract, but of the corresponding produced crude (before the loss of light ends). Near-infrared analysis can be done using as little as 0.012 ml of sample.

INTRODUCTION

Liquified-gas extraction[1] and near-infrared analysis[2] allow one to directly measure the crude oil content of core samples and to measure or estimate crude properties. Liquified-gas extraction can be used to clean heat-sensitive core[3] in preparation for measuring permeability or other parameters and to remove emulsified water from heavy crudes[1].

With this technology, one may use sidewall samples to determine important crude oil properties such as API gravity, viscosity, or gas-oil ratio. Sidewall samples are much less expensive than production tests. Thus, one can take many more samples spaced shorter distances apart at lower cost and less risk to the well. One can recover an ample amount of crude oil (about 1 ml) to determine basic crude properties from a single 1" diameter by 1.5" long sidewall having 25% porosity and 20% residual oil saturation.

One can also use sidewalls to determine variations in crude content or properties as a function of depth in the well. This is particularly useful in development wells in existing fields where the production of several zones is co-mingled and crude properties of individual zones have not been measured.

It is also useful in zones which have been water flooded where the current brine salinity is variable and uncertain and it is difficult to determine saturations using logs. In such cases, core may be the best way to estimate residual oil saturation.

REVIEW OF DEAN-STARK METHOD

The standard Dean-Stark method for determining oil saturations uses a hot solvent such as toluene or xylene to remove oil and boil off the water in the core. The water is collected in a trap. One calculates the weight of crude oil as the total weight loss of the sample (oil and brine) minus the weight of the brine. One calculates the oil volume as the oil weight divided by its density.

This calculation assumes that the brine salinity is known (so that the volume of brine in the core can be computed from the volume of recovered water) and that the hot solvent has caused no dehydration or degradation of the minerals (as could happen with gypsum or montmorillonite bearing core).

The most curious thing about Dean-Stark analysis is that the extracted crude oil, whose volume is the object of the analysis, remains in the boiling flask with the solvent and is discarded rather than measured. In summary, with Dean-Stark analysis, the extracted crude's volume is never directly measured nor are its chemical or physical properties determined. Furthermore, heat-sensitive core may be damaged.

NEW LIQUIFIED-GAS EXTRACTION METHOD

General

In liquified-gas extraction[1] the core sample is placed inside a glass Soxhlet which in turn is placed inside a steel pressure vessel as shown in Figure 1. A carefully selected liquified gas is introduced under pressure into the Soxhlet's boiling flask. By maintaining the gas at its vapor pressure (typically 2-6 atmospheres at room temperature), liquified gas remains in the boiling flask until the pressure vessel is vented.

The liquified gas cycles in the Soxhlet because of the temperature difference between the "boiling" flask (held at room temperature) and the "cold finger" condenser (held at ice water temperature). After slowly venting the liquified gas, extracted water remains trapped in a desiccant and essentially pure crude oil is left in the boiling flask.

Selection Criteria for a Liquified Gas

Four essential criteria for the liquified gas are:

Low boiling point at room pressure.
Good solvent for crude.
Some solubility in water.
Forms azeotrope with water.

Two desirable criteria for the liquified gas are:

No special safety or handling problems.
Comprised of polar molecules that can dissolve salt.

Basis for Selection Criteria

Low Boiling Point

Upon venting, the low boiling point ensures nearly complete separation of the liquified gas from the extracted crude. Typically, the vented extract contains at most one percent liquified gas.

Because the liquid densities of these gases are about the same as typical crude densities (within ±20%), a small amount of residual gas in the extract has a negligible effect on any directly measured extract densities. It also has negligible effect on directly measured viscosities or the rate at which viscosity changes with temperature (viscosity index).

Solubility in Both Oil and Water

In rock, water frequently surrounds globules of oil or vice-versa. Since this extraction is performed cold, water will not be removed by being boiled away. Thus, if the liquified gas had no solubility in water, it could not clean water from the core nor could it penetrate a water barrier to remove trapped globules of crude oil.

Azeotropes With Water

The objectives of liquified-gas extraction include determination of both oil and water saturations and recovery of nearly pure crude oil from the core for further analysis. By selecting a solvent that azeotropes with water, any water extracted from the core will "attach" itself to the liquified gas.

Thus, as liquified gas cycles in the Soxhlet, evaporated liquified gas will carry its attached water with it to the cooling finger. Both will condense and drop onto the desiccant.

The desiccant (molecular sieve 3A) is specifically chosen to break the azeotrope. It has a very high affinity for water but its pores

are only 3 Angstroms across. The small water molecules quickly enter the desiccant pores but the large liquified-gas molecules cannot. Thus, only pure liquified gas passes through the desiccant and drips back onto the core. The water remains trapped in the desiccant.

The desiccant's weight change equals the weight of extracted water. This is same information that Dean-Stark provides. However, liquified-gas extraction also provides a sample of extracted crude.

Appropriate Gases

Three gases meeting the first four essential criteria include:

Cyclopropane	(BP -32.8°C, -27.0°F)
Vinyl chloride	(BP -13.9°C, 7.0°F)
Freon-152a	(BP -24.7°C, -12.5°F)

Table 1 lists some important chemical, physical, and other properties of these gases.

When safety and handling are factored in, cyclopropane is the overall best choice of the three. As a crude solvent, it was found to be comparable to normal octane. For crudes with API gravities above about 25°, the amount of asphaltenes precipitated is generally so small as not to significantly affect direct measurements of extract API gravity. Of course, one could also utilize near-infrared equations that have been designed to predict API gravity correctly even when significant asphaltenes have been precipitated.

Cyclopropane is a three-carbon triangular ring with two hydrogen attached at each vertex. It has considerable ring strain[4] caused by the fact that its 60° C-C bond angle is much less than the ideal 109.5° bond angle between two sp^3-hybridized orbitals.

Cyclopropane is also the most acidic of the cycloalkanes behaving as a Lewis acid electron pair donor much like the alkyl halides[5]. In crude oils, the resins that peptize asphaltenes are presumed to act as electron pair donors to the asphaltenes[6]. This may explain the good crude solvating ability of cyclopropane and vinyl chloride.

In general, cycloalkanes are remarkably good solvents for asphaltenes and are almost as good as aromatics[7]. According to Hückel's rule[8] (1931), a molecule is aromatic if it has (4n+2) π-bond electrons where n is an integer. Thus, it's aromatic if the number of π-bond electrons is 2, 6, 10, 14, etc. Benzene has 6 π-bond electrons. While cyclopropane is not aromatic, the cyclopropene cation with its double bond is aromatic since it has exactly 2 π-bond electrons. However, cyclopropene is not available in commercial quantities.

A solvent's ability to dissolve asphaltenes correlates fairly well with its solubility parameter, δ, which is defined[5] as

$$\delta = [(H^{\upsilon}-RT)/V]^{1/2}$$

where H^{υ} is the heat of vaporization, R is the gas constant, T is temperature in degrees Kelvin, and V is the molar volume. The correlation is only approximate since solubility parameter theory assumes nonpolar solvents and solutes and does not take into account Lewis acid or base cohesion parameters. Attempts have been made to extend solubility parameter theory to polar compounds using separate terms for dispersion, polar effects and hydrogen bonding.

Cyclopropane is not a polar molecule so it does not dissolve salt. For normal permeability rocks, a salt crust usually forms on the outside of the core that has been cleaned. It appears that initially, inside the rock, some dissolved salts are carried along in a mostly water and partly cyclopropane mixture to the surface of the rock. However, the rock surface is bathed in cyclopropane so the salt drops out of solution since there is insufficient water to keep it dissolved.

If the primary purpose of the liquified-gas extraction is to obtain a sample of crude oil, then cyclopropane's lack of salt solubility doesn't pose a problem. In fact, it is a benefit, for one knows that there is no salt in the boiling flask and that the change in boiling flask weight is due solely to extracted crude. If, however, the extraction is being done to clean heat-sensitive core, then one may need to follow the cyclopropane extraction with another extraction using a polar liquified gas to remove salt.

Cyclopropane is not toxic or carcinogenic although it is highly flammable. It has been used as an anesthetic in medicine since 1933 but has been largely replaced by nonflammable anesthetics except for some use in obstetrics or for seriously-ill patients.[9] It requires only normal handling precautions such as loading and venting the pressurized Soxhlet in a fume hood.

Cyclopropane can dewater even the heaviest crudes without asphaltene precipitation because, in dewatering, the crude is initially placed in the boiling flask and is never as highly diluted by solvent as when the crude is in a core sitting above the boiling flask and is being continuously soaked by freshly distilled solvent.

Vinyl chloride was found to be comparable to cyclopentane as a crude solvent. Thus, it is the best solvent of the three gases. Also, it is a polar molecule so it has some ability to dissolve salt. Vinyl chloride was used as an aerosol propellant in the 1960's until it was discovered that it is a potent carcinogen. This imposes special handling and venting procedures for this gas.

Freon-152a (1,1-difluoroethane) is not a very good crude solvent. It precipitates more asphaltene related material than either pentane or supercritical CO_2. Like CO_2 extracts, Freon-152a extracts are a light golden color similar to motor oil regardless of how black the original crude was.

Freon-152a is polar and does dissolve salt. Traditionally, it was considered safer to breathe than CO_2 although recently those data have been called into question. It could be mixed with cyclopropane or be used after cyclopropane to provide some salt dissolving capability.

NEAR-INFRARED ANALYSIS

Near-infrared analysis grew out of agricultural research in the late seventies[10,11]. It was originally used for rapid determination of properties such as the protein content of wheat or the wool content of textile blends. Among its advantages are that it is fast (seconds), nondestructive, requires no special sample preparation and very little sample, and can predict multiple properties from a single spectrum.

The near-infrared (NIR) region of the spectrum is primarily the overtone and combination region of vibrational spectra of molecules containing hydrogen. Such molecules include hydrogen bonded to oxygen as in water, to carbon as in oil, or to nitrogen as in protein. It is a spectral region that is highly overlapped and thus difficult to use quantitatively without the aid of a computer.

Near-infrared analysis is one of the new "chemometric" or mathematically-based secondary analytical techniques which rely on calibration against primary methods. To do NIR analysis of crudes, one begins by acquiring the NIR spectra (usually over the 1100-2500 nm range) of a training set of crude oils for which various chemical or physical properties have already been measured by some primary technique.

Using a computer, the spectral data are regressed against the sample properties. The resulting regression equations are the keys to this technique and allow one to predict the corresponding properties of unknown crudes or crude extracts directly from their spectra.

Linear multivariate regression equations are some of the more common types of equations used in near-infrared analysis. For example, API gravity can be related to the absorbances A at three wavelengths λ_1, λ_2, λ_3 by an equation of the form:

$$\text{API Gravity} = C_0 + C_1A_{\lambda 1} + C_2A_{\lambda 2} + C_3A_{\lambda 3}$$

where absorbance A is defined as the base ten logarithm of the ratio of light incident on the sample to the light transmitted by the sample.

The regression analysis involves finding the best wavelengths λ_1, λ_2, λ_3, and best constants C_0, C_1, C_2, and C_3, that fit the spectra of the training set of crudes to their known API gravities. For API gravity and density, the best three wavelengths for the training set crudes were 1842, 1898, and 1940 nm. For asphaltenes, the best three wavelengths were 1604, 1744, and 2262 nm.[2]

Notice that if we can correlate a property, X, to absorbances at certain wavelengths ($\lambda_1, \lambda_2, \ldots \lambda_n$), then any other property, F, which is a function of X can also be correlated to the same wavelengths over some interval about X_0. To demonstrate this, simply substitute X into the Taylor series expansion of F(X) about X_0 as shown,

$$X = C_0 + \sum_{i=1}^{n} C_i A_{\lambda i} \quad \text{and} \quad F(X) \approx [F(X_0) - X_0 F'(X_0)] + X\, F'(X_0), \quad \text{so}$$

$$F(X) \approx K_0 + \sum_{i=1}^{n} K_i A_{\lambda i} \quad \text{with} \quad K_0 = [F(X_0) + (C_0 - X_0) F'(X_0)], \quad K_i = C_i\, F'(X_0).$$

This helps explain why density and API gravity can be correlated to absorbances at the same wavelengths and why physical properties (which have no explicit spectral signatures) can be correlated to their NIR spectra through their implicit dependence on chemical composition (which does have a spectral signature).

EXPERIMENTAL TESTS

Liquified-Gas Extraction[1]

To test the extraction efficiency of the liquified gases, Berea or porcelain plugs were saturated with known crudes and/or brines and then extracted. For example, a 33.3° API crude oil was extracted from a plug for 24 hours and the extract's API gravity was measured with a vibrating capillary densitometer and found to be 32.7°.

The API gravity probably declined slightly after extraction because of the loss of some light ends during the process. Had the API gravity gone up, the implication would be that not all of the asphaltenes had been recovered. Gas chromatograms of the original and extracted crude were basically duplicates of one another, with the extracted crude oil chromatogram exhibiting only a trace of cyclopropane.

The plug was next extracted with toluene in a standard Soxhlet for 24 hours and no color was observed in the toluene. This suggests that the cyclopropane had already removed all of the crude.

Vinyl chloride proved to be the best crude solvent, followed by cyclopropane. Freon-152a was a distant third. However, health and safety considerations make the use of vinyl chloride unappealing.

Near-Infrared Analysis of Crudes[2]

The near-infrared spectra of some representative crudes are shown in Figure 2. The peaks around 1700 nm correspond to first overtones of the C-H stretch. The peaks from 2300-2400 nm correspond to combination bands of C-H bending and stretching modes.

The strong absorption that many of the crudes exhibit between 1100 and 1500 nm are due to electronic transitions associated with the asphaltenes. The stronger the absorption in this region, the larger the percentage asphaltenes that the crude oil has.

For comparison, Figure 3 shows the near-infrared spectrum of water. The peaks at 1440 and 1930 correspond to combination bands of O-H vibrational modes. Crude oils that have entrained water exhibit peaks at these wavelengths.

Figures 4 and 5 show transmission spectra of two-millimeter thick slices of dry, water, and water-and-oil saturated Berea sandstone. The NIR spectra of the sandstone matrix (like most minerals) is practically featureless except for some intergranular scattering. Some minerals that do have features in their NIR spectra include carbonates (that have CO_3 bands around 2350 nm and 2550 nm) and clays (that have hydroxyl bands in the 2150-2400 nm region). Eventually, one may be able to use NIR to quantify saturations and crude properties of core without extraction.

Figure 6 shows results of a near-infrared regression for asphaltenes (R=.996) on a training set of crudes. The near-infrared predictions closely match the actual percentage asphaltenes so the data lie close to the 45° or equal value line.

Figures 7 and 8 show the results of near-infrared regressions for API gravity (R=.972) and density (R=.972) on a training set of crudes and Figure 9 shows the predictions of API gravities of three samples (solid squares) that were not in the original training set (open circles). Again, the data lie close to the equal value line.

Near-infrared regressions were performed for these and other parameters of crude oils from other locations with similar results. For example, spectra were taken of crudes from eight states and two foreign countries having API gravities ranging from 13.9° to 60.2° The regression against API gravity had a correlation coefficient of R=.997.

A good near-infrared correlation (R=.96) was also found for liquid-to-gas ratios of condensates having a range of 10 to 98 barrels of condensate per million cubic feet of gas. In addition, good near-infrared correlations have been found for viscosity, asphaltenes, sulfur, nickel, vanadium, total saturates, aromatics and non-hydrocarbon content. Even biodegradation parameters such as acid content, and groups of certain ring, branched ring, chain and branched chain members were correlated to their near-infrared spectra.

Liquified-Gas Extraction and Near-Infrared Analysis Combined[1,2]

Performing near-infrared analysis on liquified-gas extracts of crudes offers some unique advantages. One can analyze samples of extracted crude as small as 12 microliters (that is, a 1/8 inch diameter droplet). Such samples are generally too small for direct measurements of density or viscosity. Also, one can manipulate the near-infrared technique into predicting the properties of the corresponding produced crude instead of the actual extract being analyzed.

Recall that near-infrared analysis involves regression against a training set of spectra of samples whose properties are known. Suppose one wishes to develop a near-infrared regression for API gravity which is insensitive to the loss of light ends. That is, one wishes to predict what the API gravity of a crude would have been had light ends not been lost.

The stratagem for doing this lies in the construction of the training set of samples and of the corresponding "measured" values of the API gravity. One obtains duplicates of each of the produced crude samples to be included in the training set.

The spectrum of one of the duplicates is obtained and its actual API gravity is recorded for subsequent regression analysis. Next, the other duplicate is deliberately "topped" (has its light ends driven off) by heating in a hood at 60° C for 24 hours. After topping, its spectrum is also obtained; however, its API gravity is recorded as that of the original produced crude instead of its actual (and lower) API gravity.

Upon regressing the spectra, one obtains a near-infrared regression equation which is quite insensitive to the loss of light ends. It predicts the API gravity that a sample would have had before it lost any lights ends.

SUMMARY

Liquified-gas extraction and near-infrared analysis each have some novel and unique capabilities. Liquified-gas extraction allows one to clean heat-sensitive core and to recover essentially pure crude oil samples. Near-infrared analysis allows one to rapidly and nondestructively estimate crude oil properties of both extracts and produced crudes. Combined, they can provide additional information from core samples, such as sidewalls, which have not been fully exploited in the past.

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TABLE 1. Properties of Some Liquified Gases

Name	Formula	Boiling Point °C	Boiling Point °F	Vapor Press (psi)	Liquid Density (gr/cc)	Not Precip Asphaltenes δ/MPa$^{1/2}$	Salt Solvent μ/Debye	Health/ Handling Problems	Weight % Soluble in H_2O
Cyclopropane	C_3H_6	-32.8	-27.0	89.7	0.620	Good 15.0	No 0.00	Std Lab	0.66
Vinyl Chloride	CH_2:CHCl	-13.9	7.0	34.0	0.922	Best 17.8	Yes 1.45	Carcinogen	0.86
R-152a	H_3CCHF_2	-24.7	-12.5	77.7	1.012	Poor 14.3	Yes 2.27	Std Lab	0.54

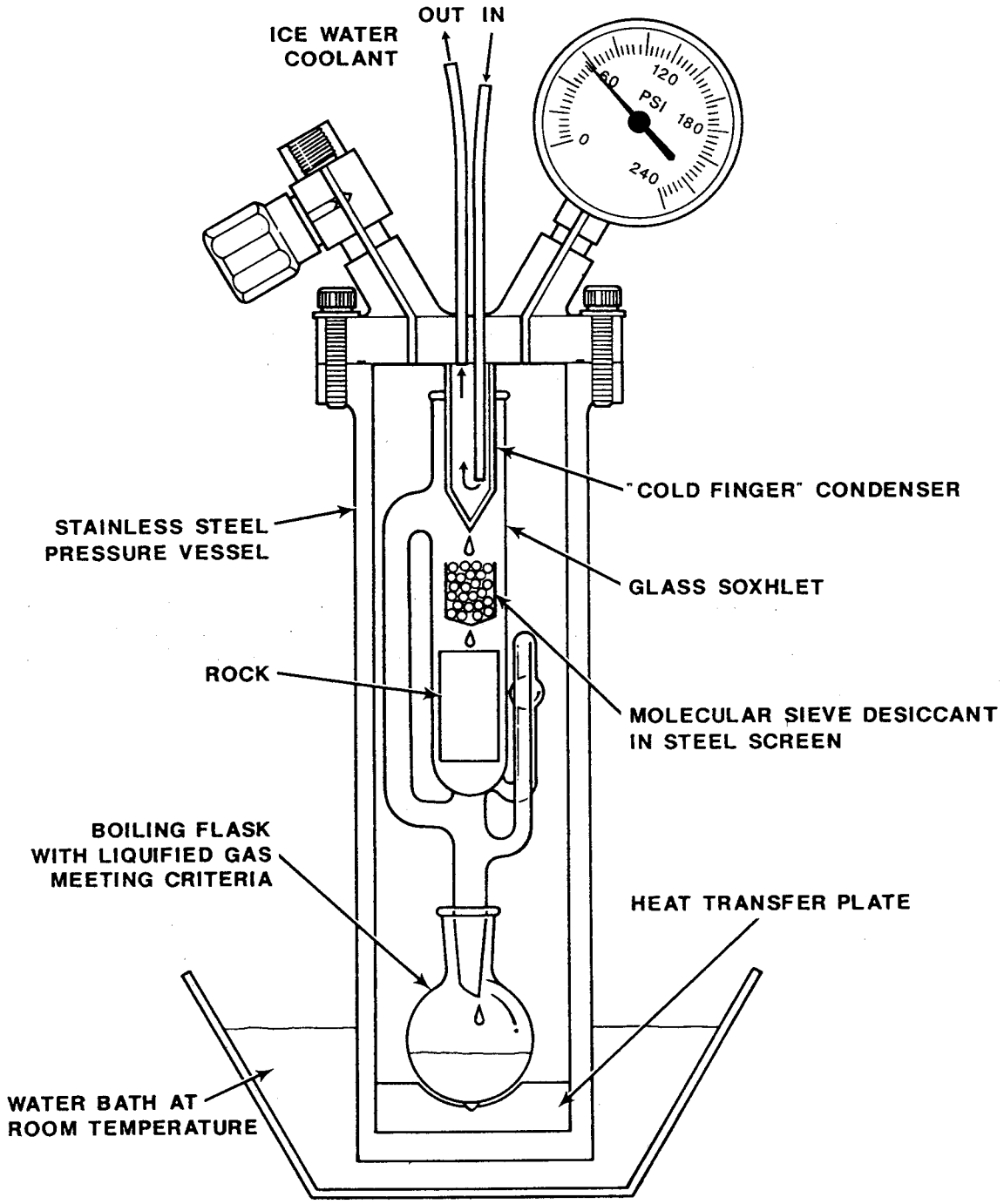

Figure 1 Liquified Gas Extraction Apparatus. Droplets of a liquified gas such as cyclopropane or vinyl chloride fall on a rock sample removing oil and water. As liquified gas evaporates from the boiling flask, it carries extracted water with it. After condensing on a cold finger, droplets hit a desiccant where water is removed and the whole process is repeated. After the rock is cleaned, the liquified gas is slowly vented leaving pure crude oil in the boiling flask and extracted water in the desiccant. Because the rock is not heated, gypsum or other heat-sensitive rock can be cleaned.

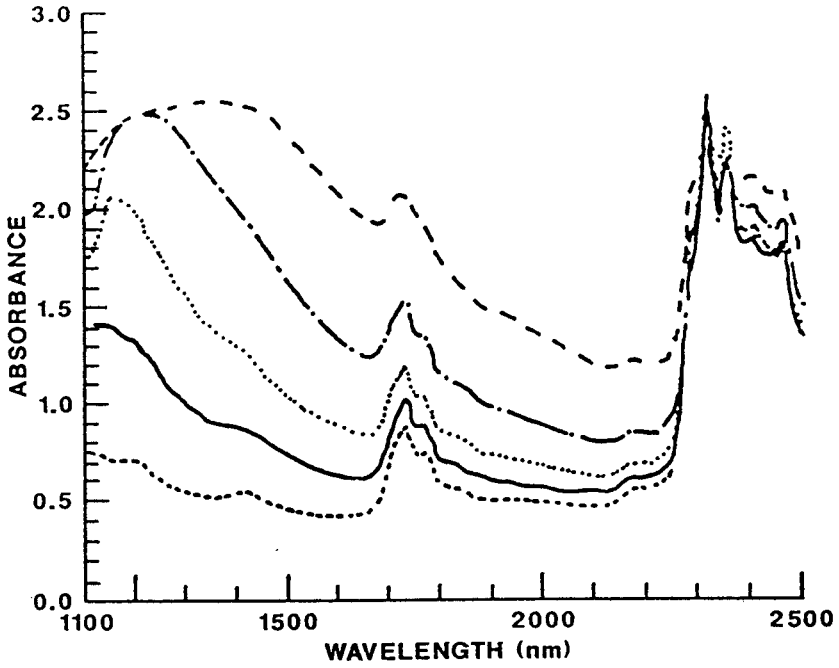

Figure 2 Crude Oil Spectra. The more asphaltenic the crude the greater its absorbance between 1100 and 1500 nm. The absorbance of asphaltenes is primarily due to electronic transitions. The peaks around 1212, 1740, and 2300 nm are due to C-H bond excitations in the crude.

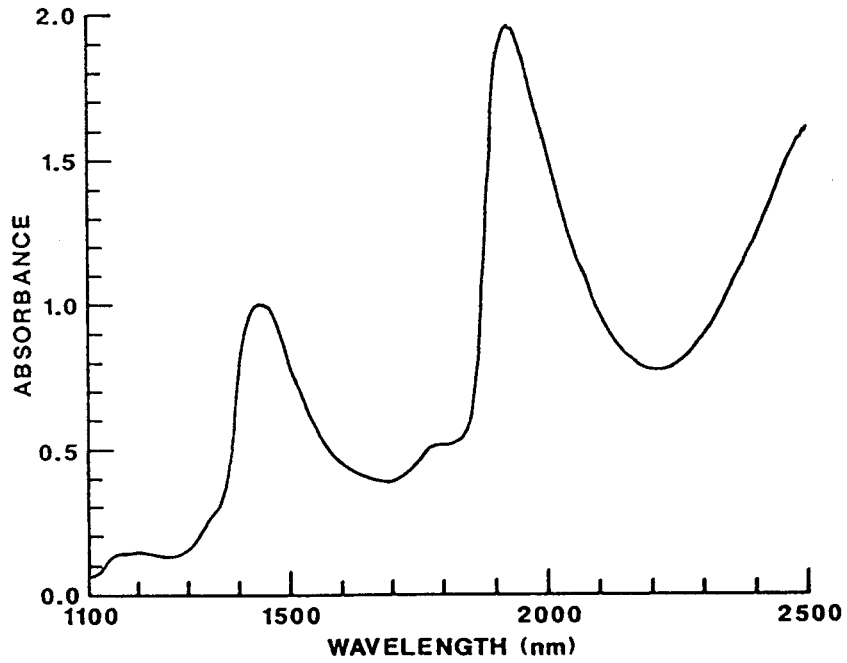

Figure 3 Water Spectrum. The spectrum of water has peaks at 1440 and 1930 nm corresponding to O-H bond excitations. Notice that these peaks are clearly shifted and easily discernible from oil peaks.

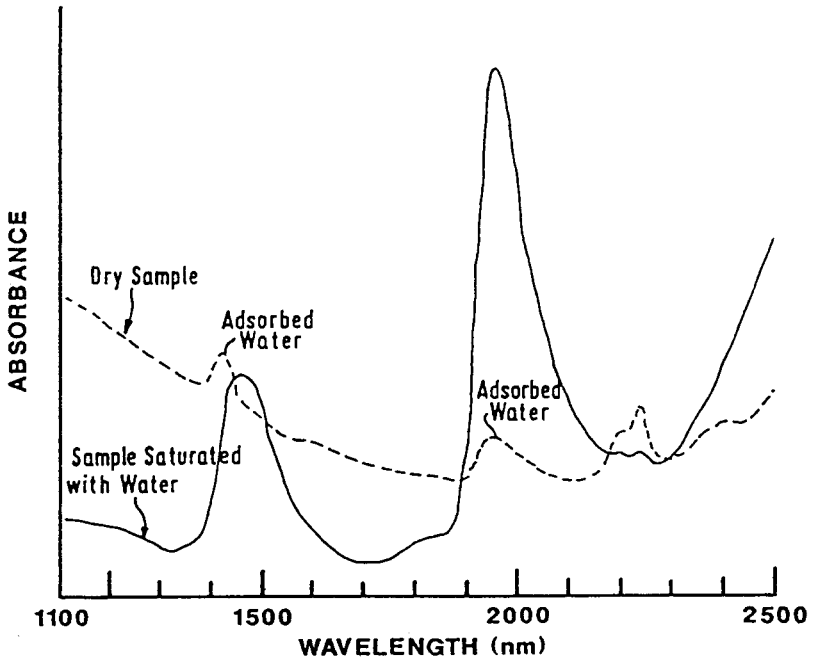

Figure 4 Spectra of "Dry" and Water-Saturated Slices of Rock. Transmission spectra through two-millimeter thick slices of Berea sandstone show that the spectrum of the small amount of adsorbed water in the "dry" samples is shifted relative to the spectrum of bulk water as seen in the 100% water saturated sample. The increase in absorbance at short wavelengths is a physical effect due to intergranular light scattering. It is less pronounced for the water saturated sample because water's refractive index is closer to that of the grains than is air's refractive index.

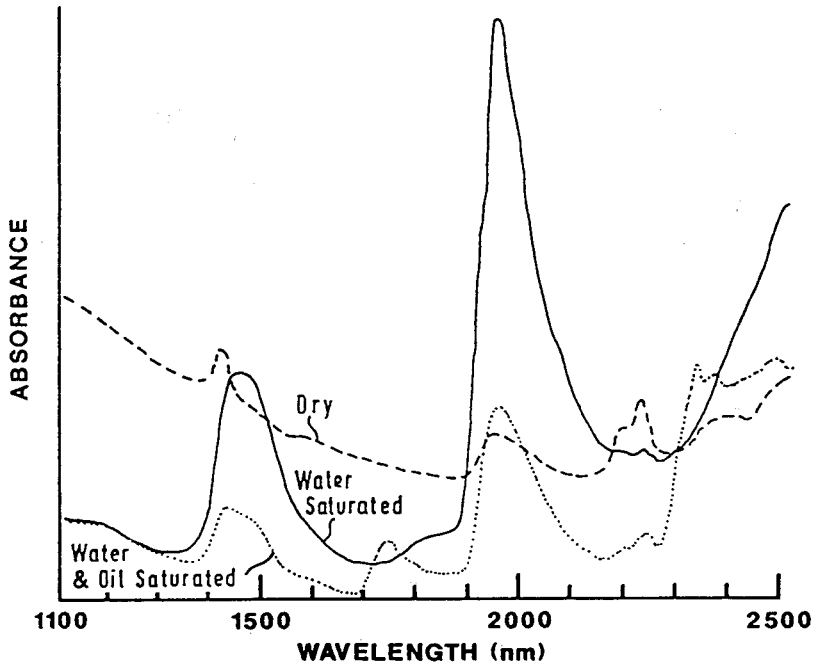

Figure 5 Spectra of "Dry", Water, and Water-and-Oil Saturated Slices of Rock. Transmission spectra through two-millimeter thick slices of Berea sandstone as shown above but including a sample partially saturated with water and partly with refined mineral oil. Notice that both the oil and water peaks are visible.

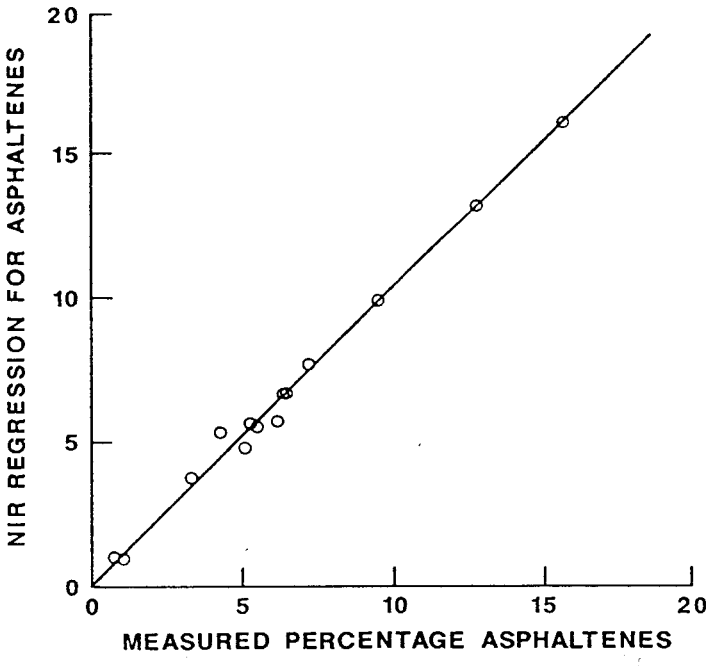

Figure 6 NIR Regression for Asphaltenes. A good correlation (R = .996) was found between the percentage of asphaltenes of this training set of crudes and the corresponding near-infrared spectra. In a perfect correlation, all the points would lie exactly on the 45° equal value line. The regression equation was based on the absorbances at three wavelengths, 1604, 1744, and 2262 nm.

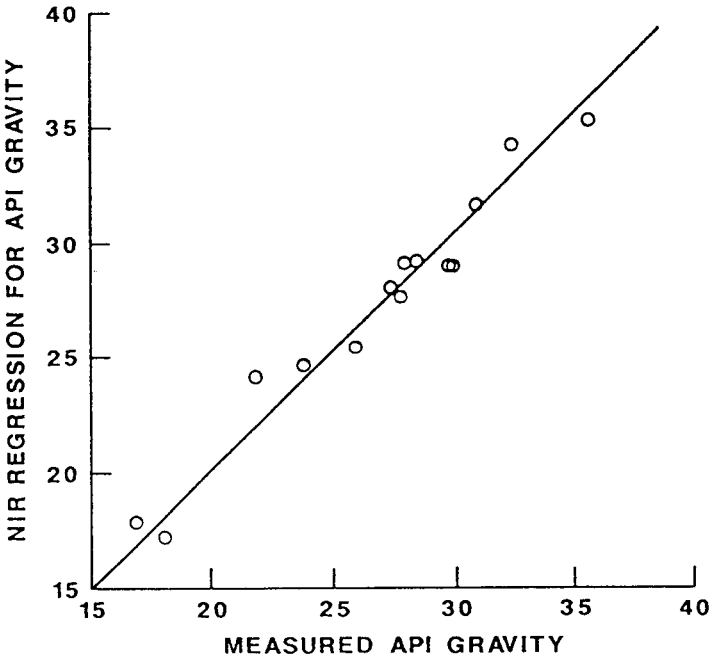

Figure 7 NIR Regression for API Gravity. A good correlation (R = .972) was found between API gravities (141.5/density - 131.5) of this training set of crudes and the corresponding near-infrared spectra. The regression equation was based on the absorbances at three wavelengths, 1842, 1898, and 1940 nm.

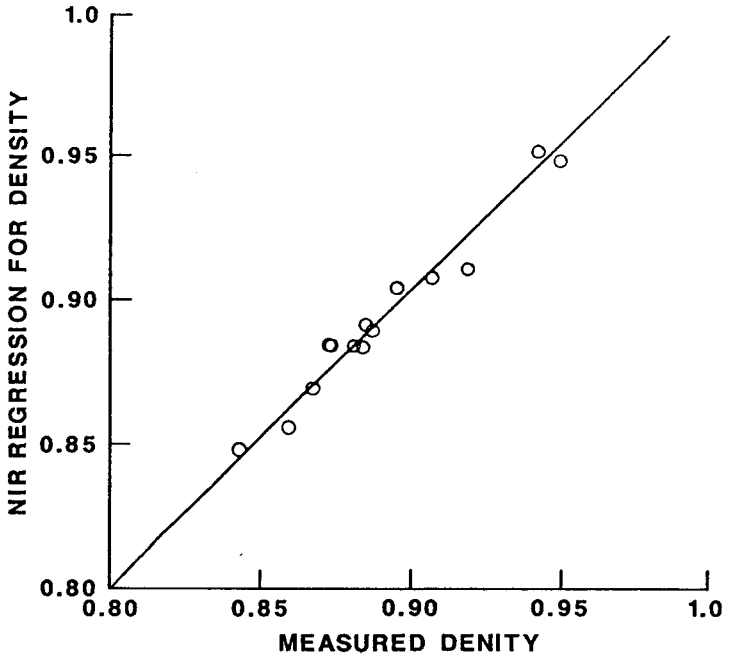

Figure 8 NIR Regression for Density. A good correlation (R=.972) was found between densities of this training set of crudes and the corresponding near-infrared spectra. Numerically, density and API gravity are inversely related. However, they both convey the same physical property information and the regression algorithm found the best correlation to the same three wavelengths, 1842, 1898, and 1940 nm as for API gravity.

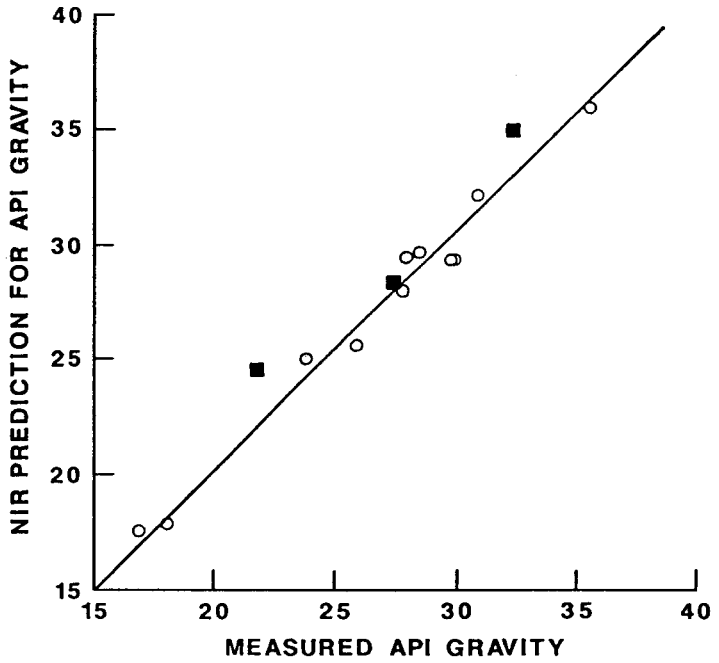

Figure 9 NIR Prediction of API Gravities. The API gravities of three crudes (shown as solid squares) were predicted using an equation developed from a training set of other crudes (open circles). The predictions lie near the equal value line.