



**Application study report for
Schlumberger-Doll Research**

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1. Study objective

The objective of the presented study is to demonstrate the near infrared signal strength and character of an LT-NIR analyzer through the Crude Oil Samples provided by Schlumberger-Doll Research.

2. Introduction

The near infrared spectroscopy (NIR) deals with the absorption bands, which can be detected in the spectral region from 900 nm to 2400 nm. These bands are due to overtone and combinations of fundamental vibrations. The overtone transitions occur between the ground state and the second (1st overtone) and third (2nd overtone) vibrational states. Higher energy transitions are less probable and give rise to weak signals, which can be ignored. Combination bands occur as a linear combination of fundamental vibrations and usually involve a stretch plus one or more bending or rocking modes.

Strong NIR absorbers include C-H, O-H, N-H, C=O, =C-H, and COOH groups. NIR techniques are typically successful for determination of organic compounds at concentrations of 100 ppm and higher.

LT's scanning spectrometer (Quantum1200 Plus, Quantum 1200I, and Quantum 2000) is capable of collecting data at 5 scans per second. The raw data are converted to absorbance units by dividing by a reference or background scan and taking the logarithm. To enhance the spectra, first and second derivatives are frequently used.

NIR is a correlation technique. According to the Beer's law, absorbance of a solution of a compound and its concentration are linearly dependent. To develop a prediction equation, single or multiple variable analysis routines are run on a calibration set of

spectra with known concentrations. After the calibration model is built, unknown samples can be predicted against the model. The accuracy of the NIR method cannot exceed the accuracy of the original method for the determination of concentrations of compounds.

Typical NIR calibration sets range from 20 to 400 samples. The number of samples required for robust calibration will vary with the nature of the calibration set, the number of variables in the sample matrix, and the precision desired.

The NIR quantitative analysis relies heavily on chemometrics, statistical tools for treatment of spectral data. Currently, the mathematical treatment of NIR data includes multiple-linear regression (MLR), principal component analysis (PCA), partial least squares (PLS), and discrimination analysis. Applicability of a calibration model is expressed in its Standard Error of Calibration, SEC; Standard Error of Prediction, SEP; and Mahalanobis distances, statistical measure of how distant are samples from the calibration set.

Another field of application of NIR spectroscopy is a qualitative type of measurements, which is frequently used in quality control, raw material identification, classification of post-consumer goods for recycling, etc. Instead of an absolute measure, the degree to which a sample belongs to one of many classes is reported.

To perform NIR qualitative analysis, discriminate analysis programs from the LT's standard software package can be used. The program provides discriminate analysis of unknown samples against a library of known samples. The library file is composed of pairs of spectra, the Mean and Standard Deviation, for each class of compounds. DISCR compares each of the unknown samples against the Mean and Standard deviation spectra and computes a cumulative probability of match. The discriminate analysis does not

require development of a calibration model with a set of samples with known ingredient concentrations.

3. Experimental Section

The Experimental results were achieved on an LT Industries Parafuel Petroleum analyzer. This analyzer is our standard analyzer for Blending and Refinery Projects with a standard wavelength range of 900 to 1800 nm, resolution of 1nm and a bandwidth of 7.5nm. It was equipped with a transmission fiber optic cable with the ends separated by 16 millimeters, viewing a sample cell of 2mm path length. The aperture was 5mm. In addition to the standard Parafuel Aqua range, a grating covering the NIR range from 1200nm to 2400nm and a bandwidth of 10nm was also used. All spectra were achieved in raw energy, then normalized, and finally absorbance was calculated.

4. Results and Discussion

The graph below shows the Aqua spectrum of 2 millimeters of API 35 Crude oil. The spectrum is shown in Absorbance units (Figure 1).

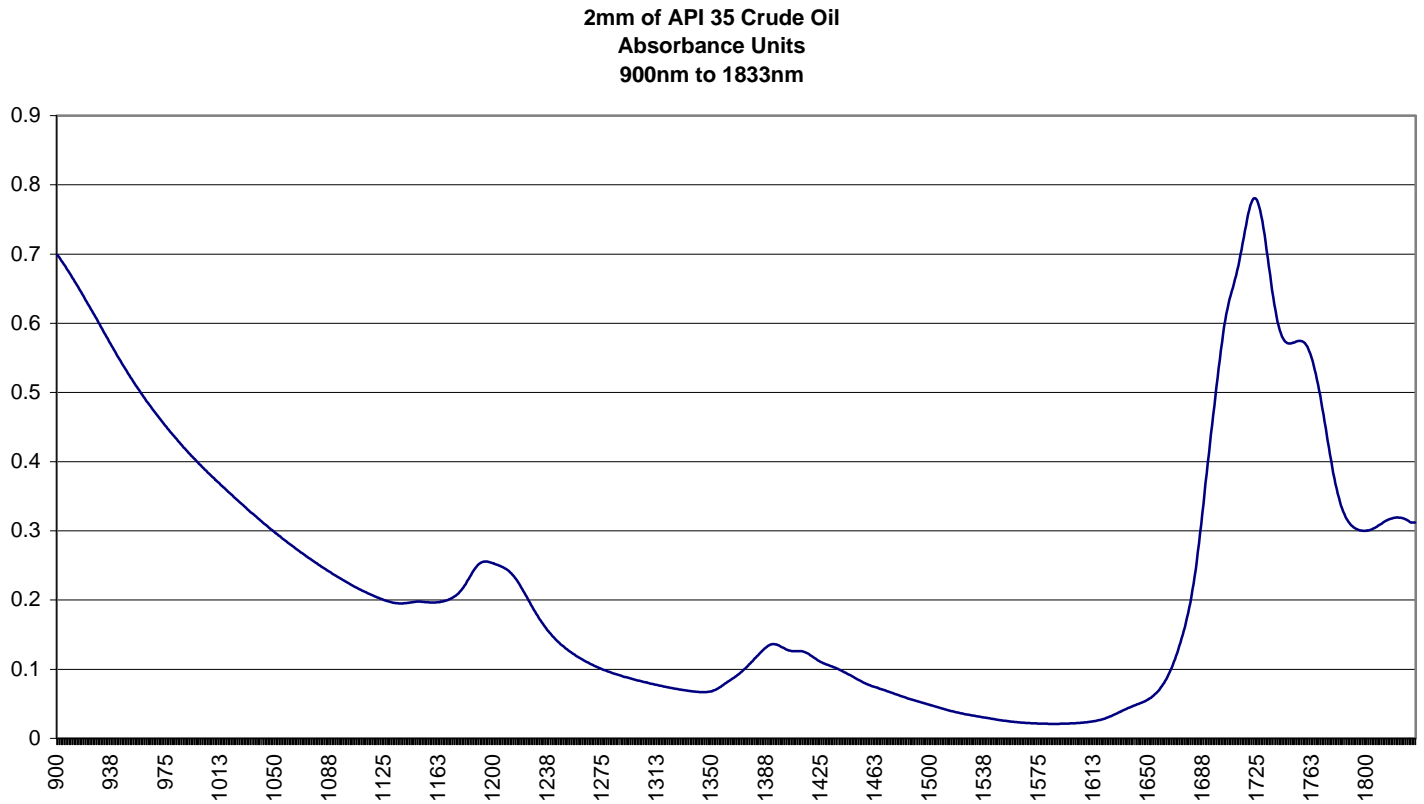


Figure 1

In the NIR range of 1200nm to 2400nm, the resulting spectrum was (Figure 2):

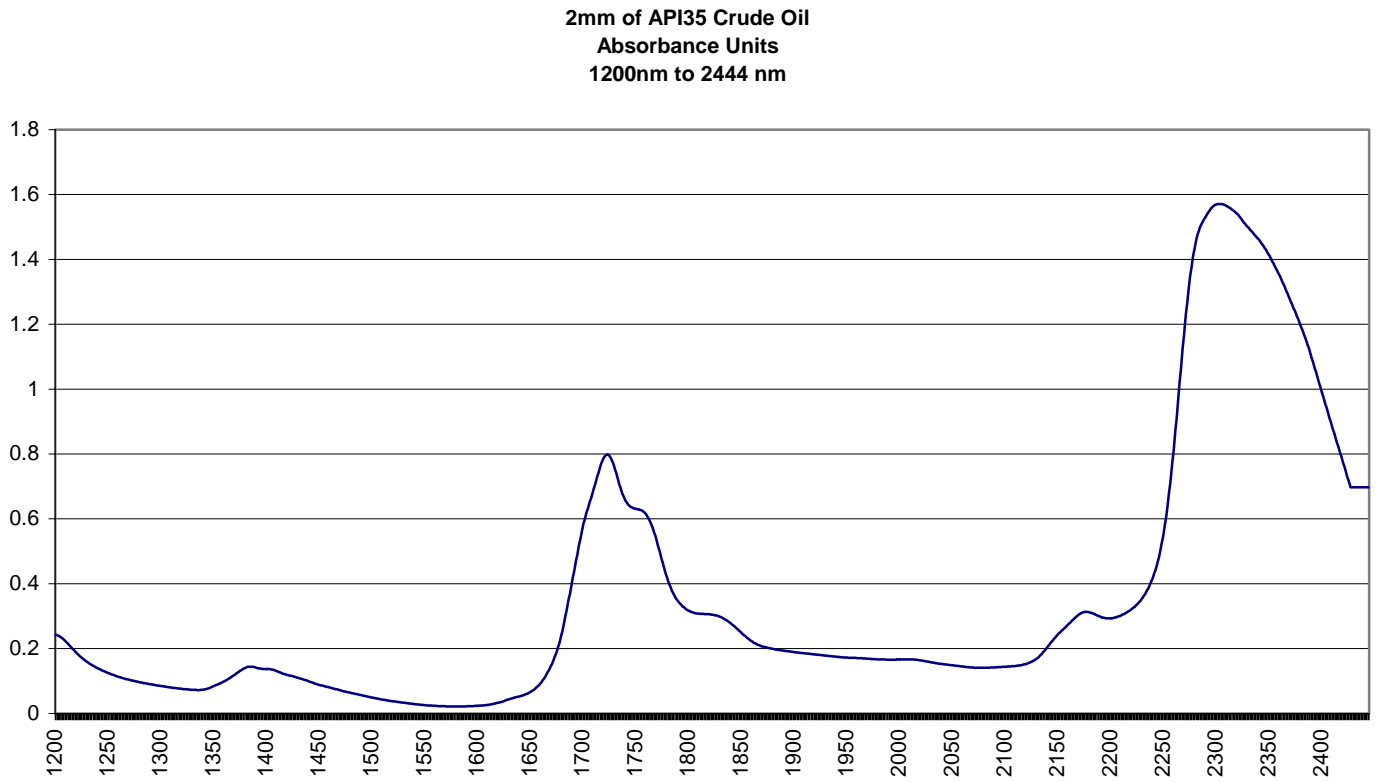


Figure 2

Next are spectra of the API 20 gravity Crude. These were also taken with a 2mm path length. First is shown the Aqua range of 900nm to 1800nm (Figure 3) and following is the NIR range of 1200nm to 2400nm (Figure 4).

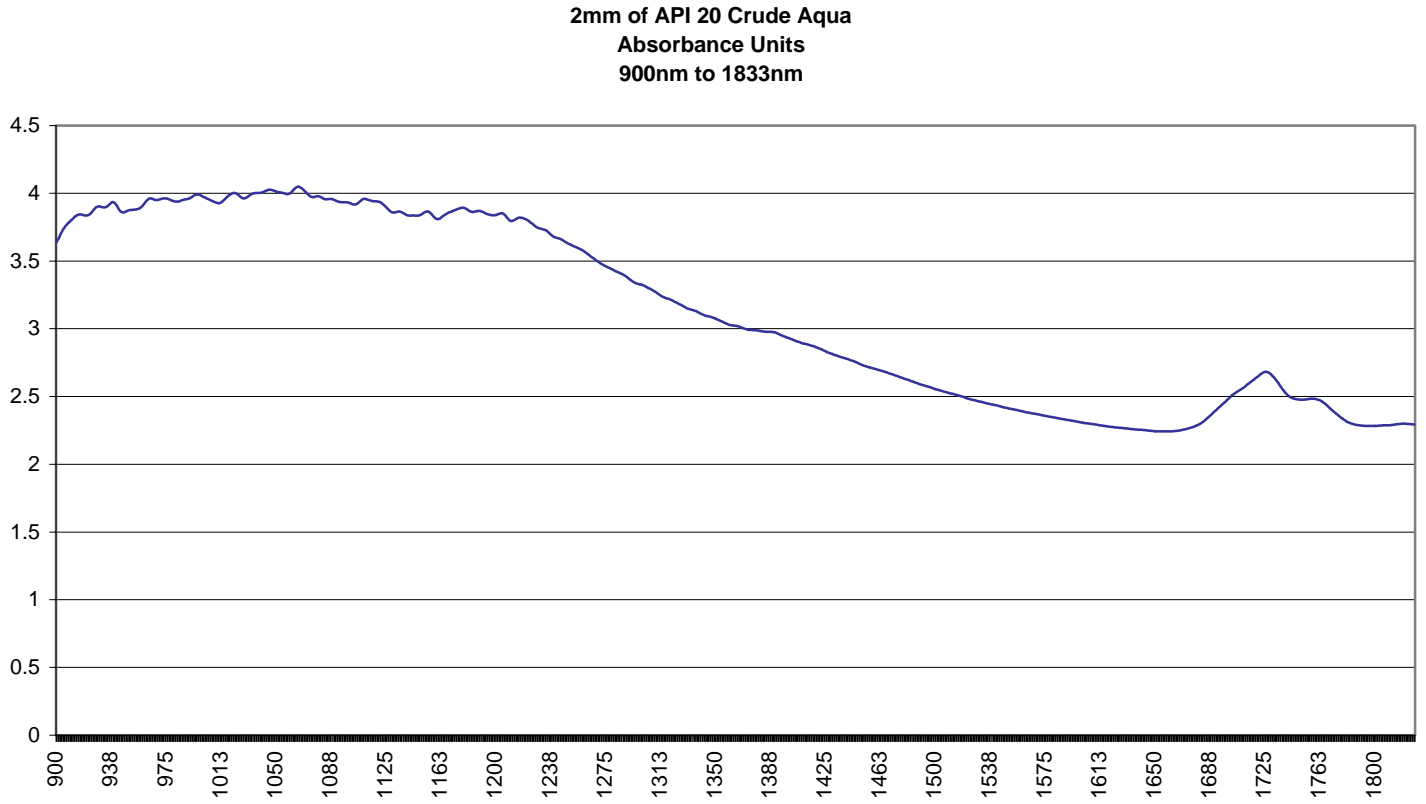


Figure 3

2mm API 20 Crude Oil
Absorbance Spectra
1200nm to 2444nm

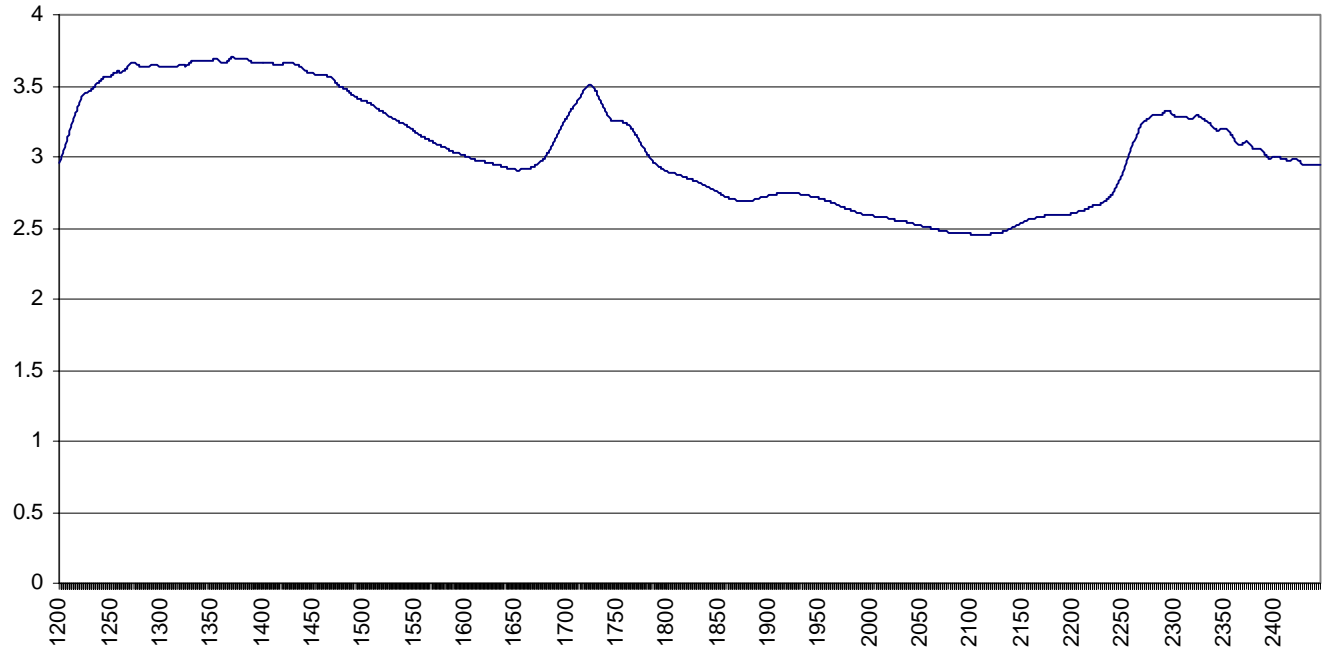


Figure 4

5. Conclusions

The results of this study indicate that the LT-NIR spectrum are of adequate signal strength and character to enable the creation of strong calibration models. These tests were all ran at low detector gain to keep the background from clipping. A 4 to 5 times increase in gain could easily be achieved if needed.

The test utilized the standard Parafuel bandwidth of 7.5nm and an NIR grating with a bandwidth of 10nm. For an application such as this we would offer the IsoChem analyzer, which includes a higher energy throughput and combine it with a detector configured for higher detectivity. We believe that this bandwidth smoothed out some of the spectral signature. Reducing the bandwidth would increase our ability to resolve the spectral character if required and is another standard option available if the application warrants it. The signal strength and character seen in this study are adequate to create excellent calibration results.