Metrohm

Application Work AW NIR-US-073-092015

Real-time Analysis of Industrial Gases with Online Near-Infrared Spectroscopy

Branch 5 – Petrochemical, Biofuels

Keywords

Process, NIR, Gases, Gas Cell, Ethylene, Carbon Dioxide, Propane, Butane, Acetylene

Summary

Near-infrared (NIR) spectroscopy is a rapid, non-destructive method for analysis of products measured routinely that can eliminate lost time and product with real time quality control. In addition to gases, NIR can be also be used to monitor a variety of sample types including solids, pastes, slurries, and liquids. NIR spectroscopy is an excellent tool when high throughput or real-time analysis is desired. The real-time results makes NIR an ideal process analytical tool for process control. The main advantages of NIR are the high throughput, high precision, high accuracy, and the ability to monitor multiple chemical and physical properties in a matter of seconds.

NIR is used at various stages of production including feedstock qualification, online or inline analysis of various process streams, and final product qualification. This study focused on NIR spectroscopy as a tool for online, real-time analysis of industrial gases using a high pressure gas cell. Although the emphasis is on gases typically analyzed during ethylene production, the method may be suitable for a variety of industrial processes. The primary goal was to examine the feasibility of NIR spectroscopy for online analysis of industrial gases.

The results showed that NIR is well suited for monitoring the concentration of gases. The accuracy and detection limits for gas concentration determination was estimated to be ~ 1% at 1 atm. With higher pressures it may be possible to measure concentrations to a higher degree of accuracy within a narrow range.

Background: NIR in Ethylene Production

Approaching 150 million tonnes per year, ethylene is the largest volume industrially produced organic material. Feedstock, typically naptha or light gases (ethane, propane, etc.), is first heated to high temperatures to break down the feed into small hydrocarbon molecules. After being cooled, the products are then sent through a variety of separation processes with one product stream among many being high purity ethylene.

Process optimization focuses on maximizing the output of ethylene and other profitable products. Process analytics, such as NIR spectroscopy is a key component of process optimization because it provides the process control with real-time gas concentrations at various points in the process. The use of fiber optics allows for real-time sequential measurements from up to 9 positions (feed, recycle streams, product streams, etc.) with a single instrument. This allows for rapid adjustments to the process to account for changes such as changes in feed, temperature, etc. The net results of incorporating NIR into the process is increased capacity, improved process reproducibility, improved product quality, reduced in-process testing, and improved plant safety.

Analyzed Gases

The materials below were provided for the study.

Carbon Dioxide (CO_2), Ethylene (C_2H_4), Propane ($CH_3CH_2CH_3$), Butane ($CH_3CH_2CH_2CH_3$), Acetylene (HCCH)

Instrument Configuration

Metrohm NIRS XDS Process Analyzer with Single Fiber	6.928.0120
High Pressure Gas Cell	

The experimental setup is shown in Figure 1 (appendix). The Metrohm NIR Process Analyzer sends light to the gas cell via 50 m of fiber optic (single fiber). Gas concentrations were controlled by varying gas flow rates which were measured with flow meters. The light transmits through the 25 cm path length cell filled with ~ 1 atm of gas (the cell is rated up to 1000psi and -30-125C). Any light not absorbed is sent back to the NIR analyzer which records the NIR absorption spectrum (800-2300 nm).

In-line transmission cells are also available with path lengths up to 10 cm and are rated to 300 C and 5000 psi. For on-line analysis the gas may flow directly into the flow cell. Preconditioning such as adjustment of the flow rate, temperature, and/or pressure may be necessary in some cases.

NIR Data Collection Parameters

Data Collection Method

Reference Std.	Ref. Standardization
Collection Range	800-2300 nm
Scans per Spectrum (Sample/Reference)	32/32 (16 seconds per spectrum)

Experiment

The primary goal was to collect NIR spectra for the various gases listed in the *Analyzed Gases* section. The spectra will provide the wavelength positions where there is significant absorption for each gas. It would be possible to monitor the concentrations of each individual gas only if the absorption spectra of each gas is different.

The next goal was to determine the approximate accuracy of the NIR gas concentration prediction and probable limits of detection. The NIR absorbance value is directly proportional to the concentration of the gas. In this experiment, the concentration of select gases was varied at various increments and analyzed by NIR. The results helped to determine the lowest increment that would give a noticeable change in the absorption and therefore approximate the accuracy of the concentration prediction and probable detection limits.

Results & Discussion

The NIR spectrum of 1% and 10% CO_2 compared to the empty cell is shown in Figure 2. There is a noticeable change in the spectra near 1960 nm and 2010 nm. An expansion of this region in Figure 3 shows that the difference is apparent even at 1% CO_2.

Industry standard math treatments are often applied to NIR spectra to reduce scattering effect and help accentuate the absorption features of interest. The 2nd derivative math treatment was applied to these spectra and the 1900-2100 nm region is shown in Figure 4 for varied concentrations of CO_2. It is clear from the figure that there is a significant reproducible change in the spectra even with a change of 1% CO_2. A regression method could then be developed to correlate the 2nd derivative spectra value to CO_2 concentration. Predictions by NIR would be expected to have an accuracy and detection limit of less than 1% CO_2.

Absorption of additional gases were investigated. Figure 5 shows a similar change in absorption for varied concentrations of propane. The strongest absorption occurs at 1695 nm. The accuracy and detection limit is similar to CO_2 and expected to be about 1% at 1atm.

Acetylene had a strong absorption near 1528 nm. For this study, a wider range of concentrations were analyzed varying from 0% to 81.8%. The 2nd derivative spectra of various concentrations are shown in Figure 6. A linear regression model was developed to correlate the acetylene concentration to the changes in the spectra. The standard error of calibration (SEC) was 1.8%. Figure 7 shows the NIR values compared to the actual value for the calibration set.

Spectra were recorded for additional gases including ethylene and butane. Table 1 lists the wavelengths that showed strong absorption for each gas. Figure 8 shows the spectra of other common industrial gasses. Regression models could be developed for each gas and used to monitor the concentration of each gas. Careful wavelength selection and/or the use of partial least squares regression would allow accurate gas concentration determinations even for mixtures.

Factors Affecting Gas Measurements

There are several factors that must be considered when optimizing the NIR measurements of gases. First, the absorbance is directly proportional to the path length as expressed by beers law:

$$A = eLc$$

Where A is absorbance, e is the molar absorptivity which is constant for a given gas, L is the path length, and c is the concentration. So as the path length increases, so does the absorbance. Figure 9 shows the effect of path length on the absorbance of ethylene. For best results, the path length must be optimized at the appropriate temperature and pressure so that the absorbance of interest is below 2 AU.

Temperature and pressure are also critical parameters to consider. Variation in temperature and pressure can have significant effects on the measured absorbance. The ideal gas law states that the concentration of gas is related to temperature and pressure by:

$$c = \frac{n}{V} = \frac{RT}{P}$$

Where c is concentration, n/V is the number of moles per unit volume, R is the gas constant, T is temperature, and P is pressure. So as temperature increases/decreases so does the concentration and absorption. As pressure increases/decreases the concentration and absorption will decreases/increase. Figure 10 shows the effect of pressure on the NIR absorbance spectra of propylene. Additionally, variations in temperature and pressure may also slightly effect the peak position and band profile causing a bias in NIR predictions. So in an ideal situation the gas temperature and pressure will remain constant during analysis.

Comments and Recommendations

NIR spectra were collected for an assortment of industrial gases at varied concentrations. The results show that the NIR is well suited for monitoring the concentration of gases. The NIR spectra of gases have less overlap compared to spectra for liquids or solids and different spectra for each gas type. NIR models have better specificity and are less sensitive to matrix effects.

The accuracy and detection limits for gas concentration determination was estimated to be ~ 1% at 1 atm. With higher pressures it may be possible to determine concentrations to a higher degree of accuracy within a narrow range. The pressure in the gas cell must be stable and optimized in order to achieve the best results.

The use of NIR for industrial gas monitoring can reduce cycle time and improve process reproducibility. The main benefits of NIR are the accurate, real-time results which can be used for process control and optimization. This leads to improved product quality and plant safety.

Date

09/15/2015

Author

Keith Freel

Hari Narayanan

Ken VonBargen

APPENDIX

Figure 1. Metrohm NIRS XDS Process Analyzer (left) with high pressure gas cell right).

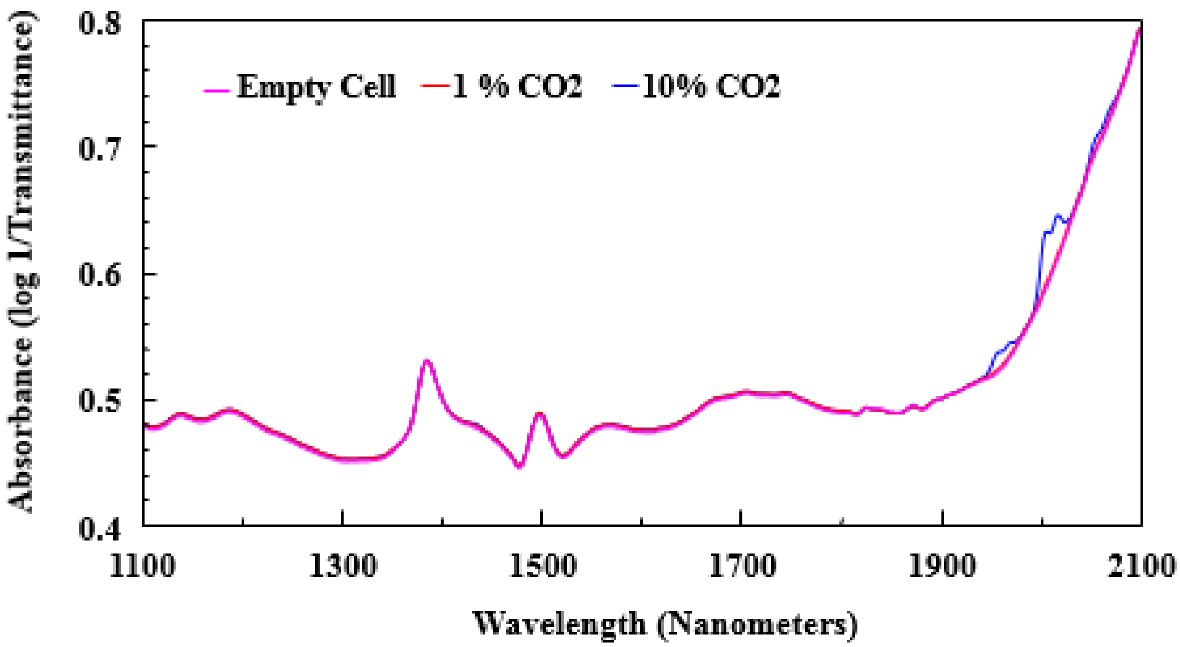

Figure 2. NIR spectra of empty gas cell, cell with 1% CO_2, and cell with 10% CO_2.

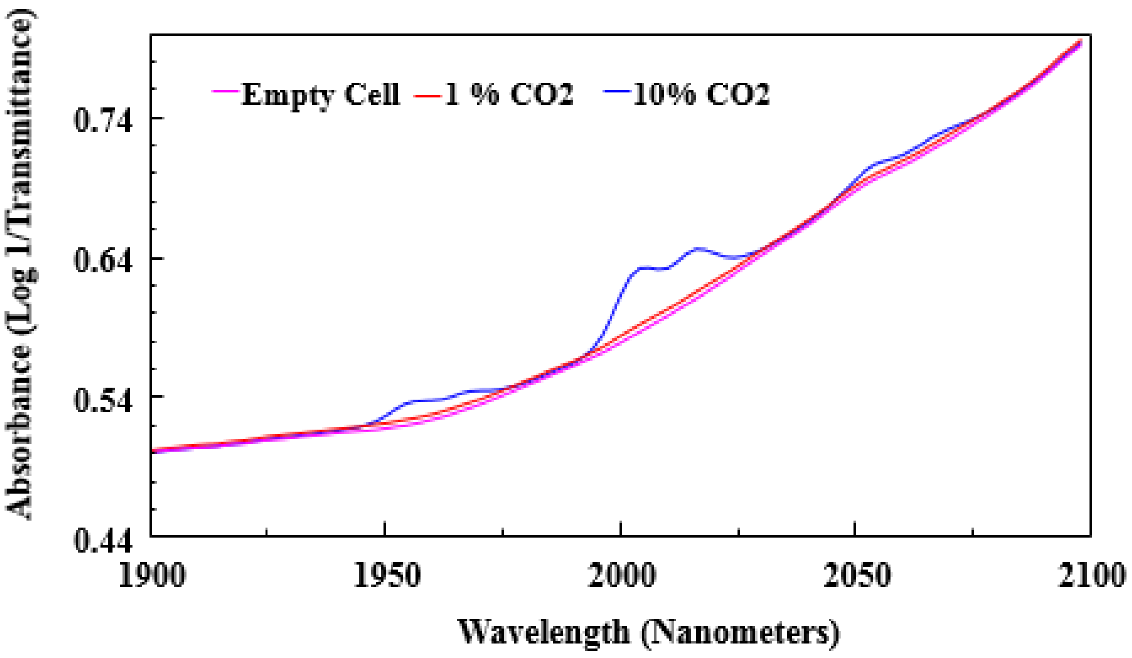

Figure 3. Expanded portion of Figure 2 showing absorbance of CO_2.

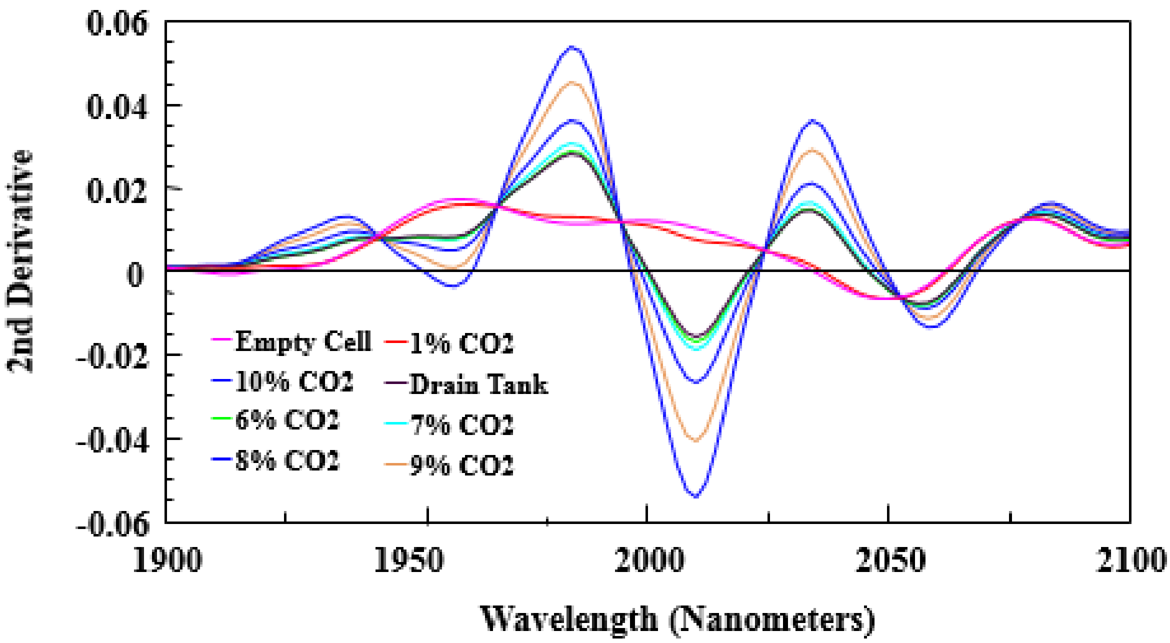

Figure 4. 2nd derivative of NIR spectra for varied amounts of CO_2 in gas cell.

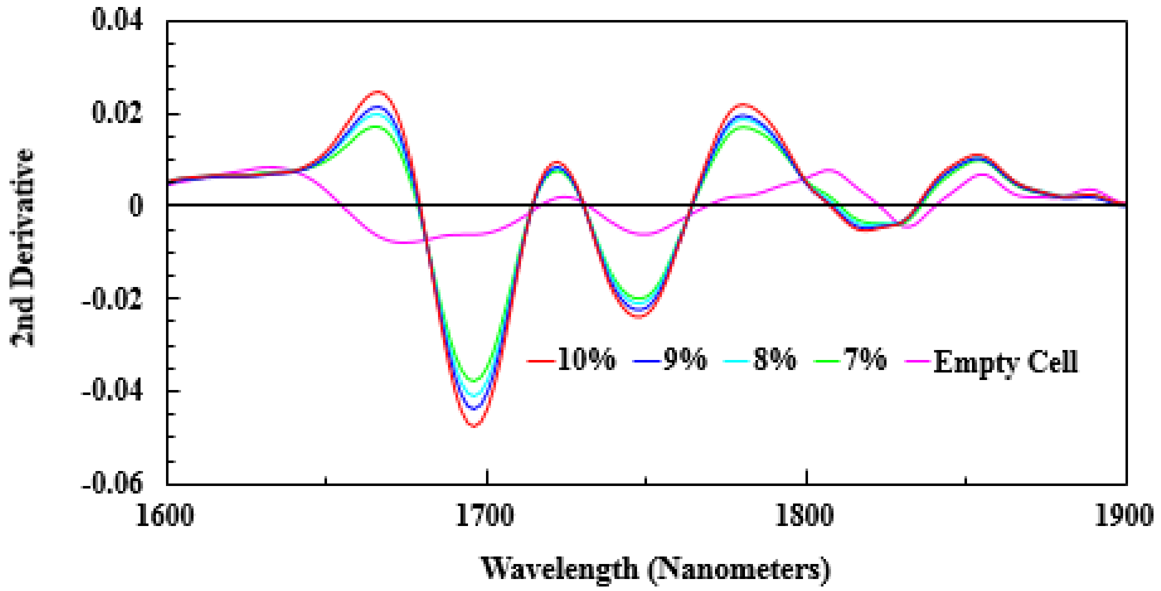

Figure 5. Select region of 2nd derivative of NIR spectra of varied amounts of propane in gas cell.

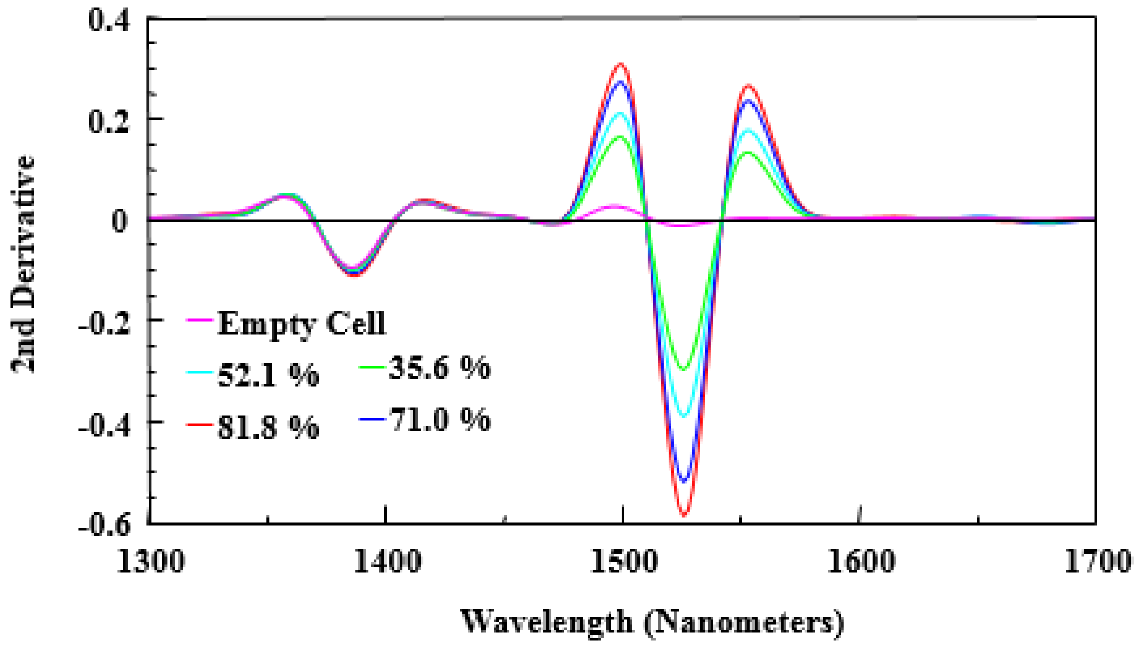

Figure 6. Select region of 2nd derivative of NIR spectra of varied amounts of acetylene in gas cell.

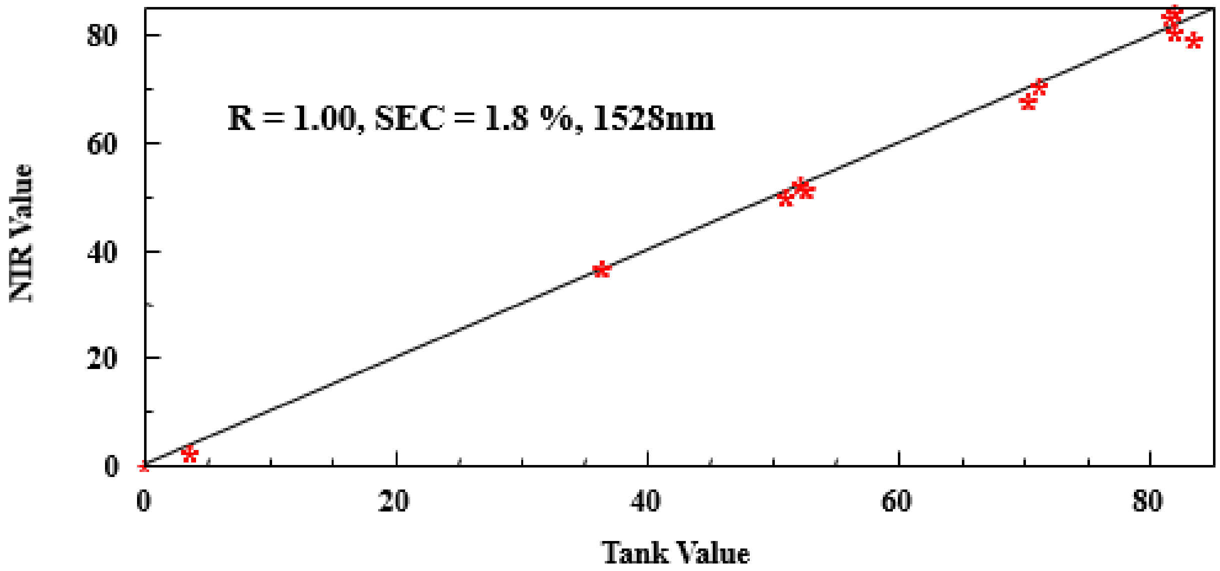

Figure 7. NIR value (y-axis) compared to tank value (x-axis)

Table 1. Wavelengths showing spectral absorption features in NIR region for various industrial gases.

Gas	1600-1650nm	1650-1700nm	1700-1750nm
Ethylene	1624	1680	1748
Propane		1696	1748
Butane		1698	1752
Acetylene		1678	1732

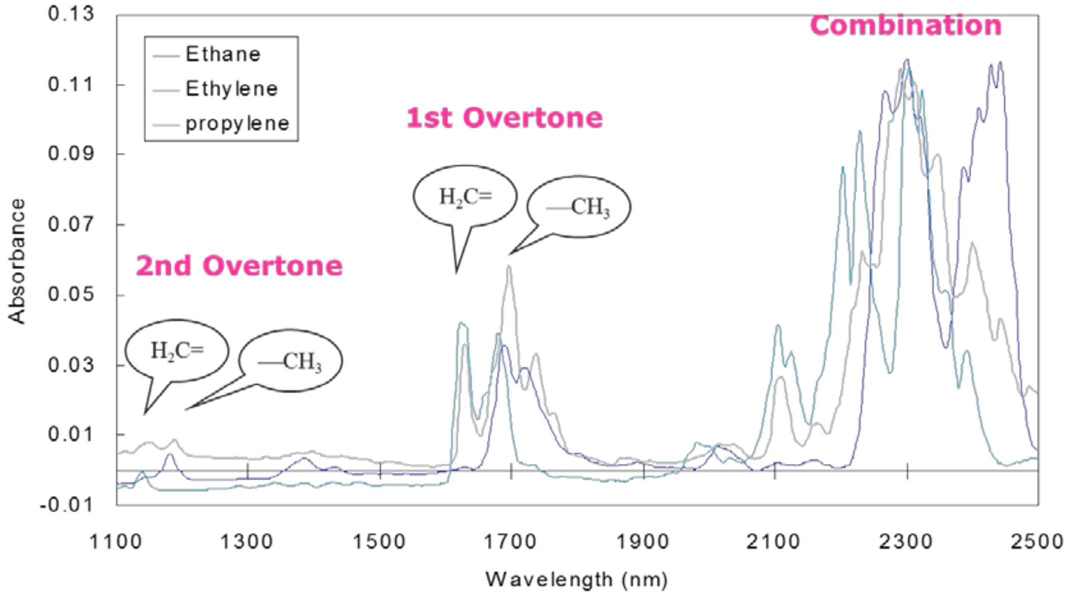

Figure 8. NIR spectrum of ethane, ethylene, and propylene.

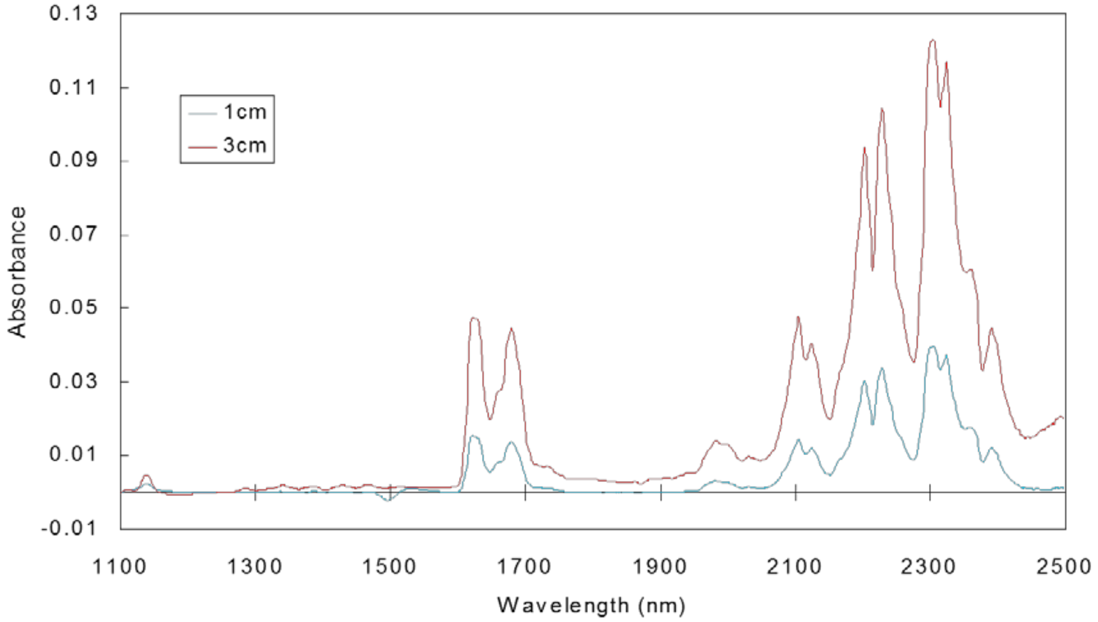

Figure 9. NIR spectrum of ethylene with 0, 1, and 3 cm path length.

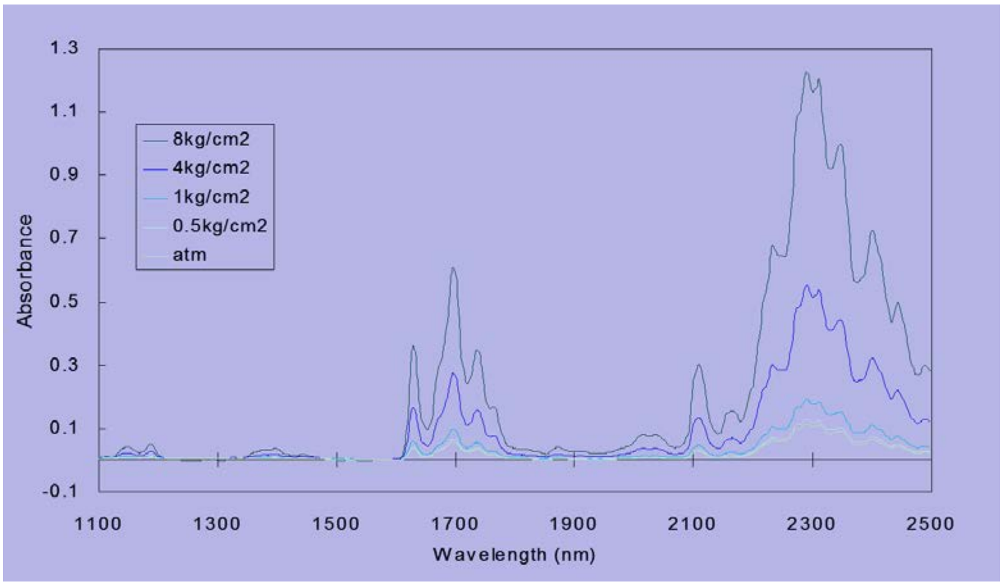

Figure 10. NIR spectra of propylene at various pressures.