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REAL-TIME OPTICAL ABSORPTION ANALYZERS

APPLICATION NOTE

Hydrocarbon Gas Streams Using a NIR-O™ Spectrometer or ClearView® db Photometer

Our GUIDED WAVE™ product line includes a near-infrared (NIR) full spectrum spectrometer (NIR-O™) and a multi-wavelength photometer (ClearView® db) that are well suited for measuring many hydrocarbon gas streams. These instruments can make both qualitative and quantitative measurements in gas streams using long path gas cells coupled to our analyzer systems using fiber optics. This note will discuss the use of the hardware and software tools for the measurement of hydrocarbon gases under various conditions. NIR measurements can be used in real time directly in process monitoring to save both time and money when compared to traditional methods.

Measurement Background

The NIR region of the electromagnetic spectrum allows the use of the overtone and combination bands of the C-H, O-H, and N-H fundamentals. By measuring the NIR spectra of a series of polyol samples of known hydroxyl number, a quantitative model can be developed which will allow the measurement of hydroxyl number in future samples based only on their NIR spectrum. Our analyzer systems use fiber optics to allow the sample probe to be located in remote locations away from the spectrometer itself.

Most NIR spectroscopy is done on liquid samples where the hindered rotation blurs any rotational fine structure resulting in broad peaks. However, gases have well resolved rotational-vibrational fine structure which can be seen in high resolution. Most NIR process spectrometers and photometers are low resolution devices. As a result they do not resolve the fine structure, but instead record the spectrum as integrated P, Q, and R bands. When dealing with gases, one must always keep in mind that the real spectrum underneath is a complex series of narrow sharp peaks.

The molecular density of gases and vapors is significantly lower than that of liquids, hence much longer probe pathlengths are required. Good quality NIR spectra of gases can be obtained with probe pathlengths in the range of 25 to 100 cm. Not only is the density lower, but it varies with temperature and pressure according to the Ideal Gas Law. While the spectrometer measures the number of molecules in the beam, it may be necessary to measure temperature and pressure as well to exactly quantify the gas mixture.

Measurement Background (continued)

Another important aspect of gas phase spectroscopy is that the spectra are pressure and temperature dependent. Increasing pressure will broaden the rotational-vibrational lines due to pressure broadening. For first order effects, the integrated absorption observed with a low resolution spectrometer should remain the same as pressure is increased, however, there may be second order effects that have to be considered and added to the modeling efforts.

Temperature can pose a bigger problem. Many multi-atom molecules will have low lying bending mode bands whose Boltzmann thermal population will increase as the temperature is increased. These combination "hot" bands will appear in the spectra robbing intensity (population) from the fundamental ground state transition bands. It is best to calibrate a gas phase measurement at one temperature and maintain that temperature for the process measurement.

Finally, not all molecules exhibit an IR or NIR spectrum since a change in the dipole moment is required for a ro-vibrational IR spectrum to occur. Homonuclear molecules such as N_2, O_2, Cl_2, and H_2 do not have dipole moments hence do not have IR spectra. Fortunately, most hydrocarbons, and many other important gases such as NH_3, CO_2, H_2O, etc. do have strong IR spectra and as a result NIR spectra. Unfortunately many common sulfur compounds have weak IR spectra and correspondingly weaker NIR spectra.

Experimental

The vapor phase NIR spectra of a group of different hydrocarbons were measured between 1550 and 1900 nm using a GUIDED WAVE NIR-O process spectrometer. Figure 1 shows the absorbance spectra of several short chain alkanes collected using an on-line process probe with a 25 cm pathlength. Methane has the most unique spectrum, but this is to be expected as it is the simplest and has the smallest moment of inertia. This study concentrates on the first overtone region of the C-H stretching bands near 1700 nm. Figure 2 illustrates the differences between ethylene and propylene. Olefins typically have a strong band at 1625 nm. This is also seen in Figure 3 in the vapor phase spectra of several other olefins.

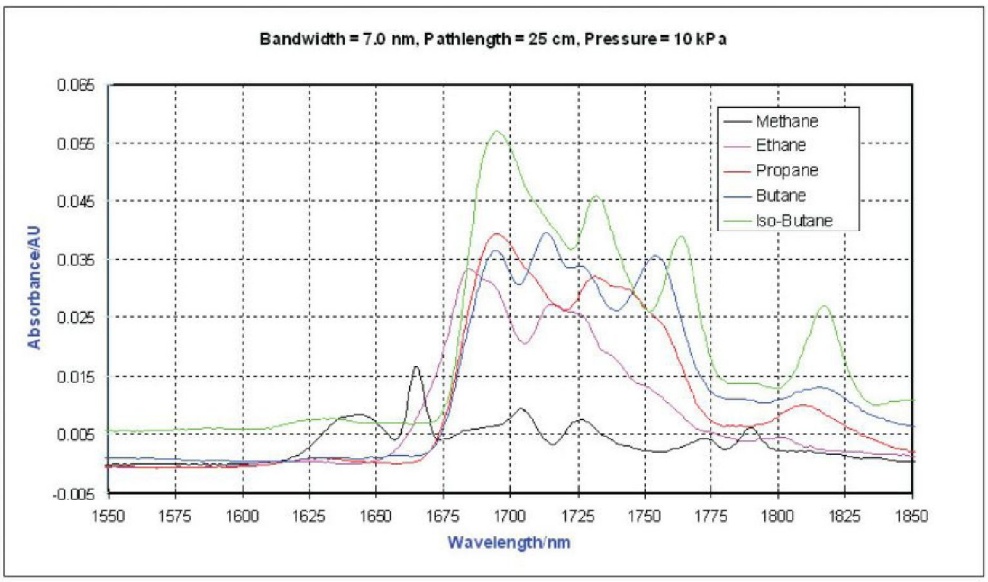

Figure 1: Vapor Phase NIR Spectra - Short Chain Alkanes

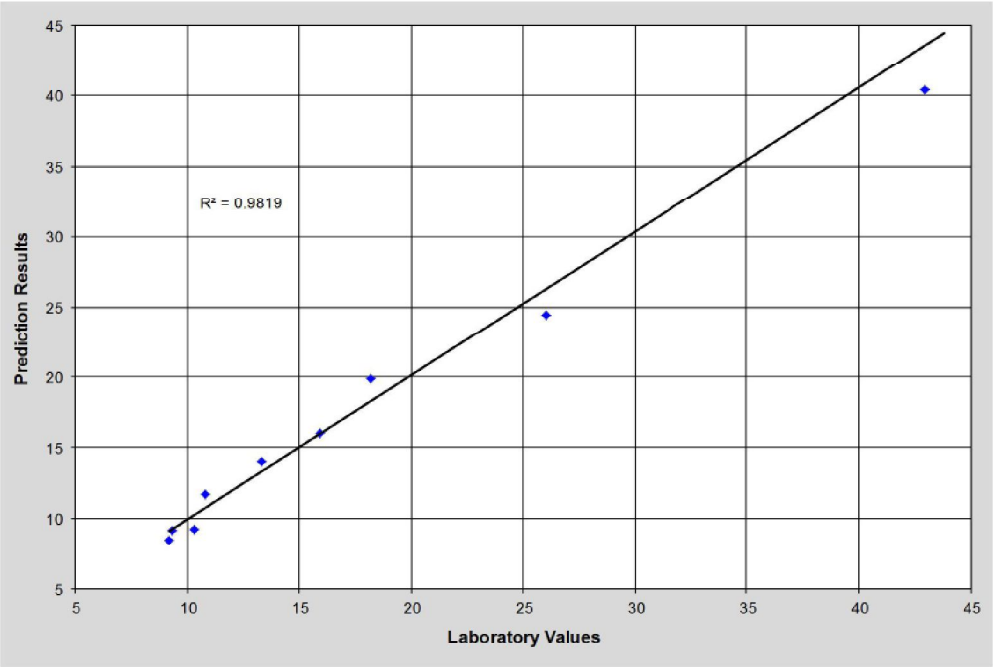

Figure 2: Vapor Phase NIR Spectra _ Ethylene, Propylene

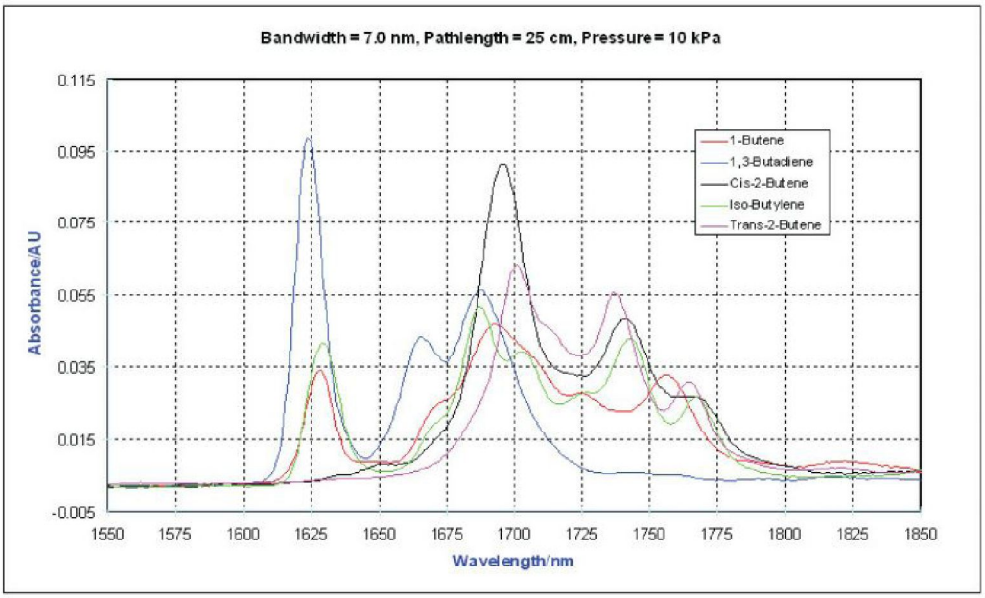

Figure 3: Vapor Phase NIR Spectra - Olefins

Experimental (continued)

A common concern of hydrocarbon vapors, especially in ambient air mixtures, is the concentration relative to the Lower Explosion Limit (LEL). Table 1 shows the detection limits for several light hydrocarbons under the following conditions: Instrumental Signal-to-Noise Ratio of 40 µAU, a minimum concentration equal to 10 x the SNR or 400 µAU, a pathlength of 1 m, and a neat sample condition at 20 °C. Note that the detection limits are all significantly below the respective LEL.

A further series of tests were conducted with butane in nitrogen to study the self and foreign gas broadening issues. Collisional energy transfer also contributes to changes in absorption coefficients. Neat butane to 1 atm was measured as well as various fixed levels buffered with N_2 to 1 atm. The concentration matrix studied is shown in Figure 4.

	Wavelength of Max Abs.	Absorption Coefficient	Detection Limit	Detection Limit	LEL
	nm	AU/kPa/cm	kPa	ppm-V	ppm-V
Methane	1665	0.000064	0.063	618	50000
Ethane	1680	0.000129	0.031	307	30000
Propane	1690	0.000159	0.025	248	21000
Butane	1714	0.000154	0.026	257	18000
Ethylene	1619	0.000171	0.023	231	31000
Propylene	1695	0.000208	0.019	190	20000
1-Butene	1693	0.000180	0.022	220	16000
1,3-Butadiene	1625	0.000376	0.011	105	20000
Cis-2-Butene	1696	0.000353	0.011	112	18000
Iso-Butane	1695	0.000192	0.021	206	14000
Iso-Butylene	1687	0.000197	0.020	200	16000
Trans-2-Butene	1701	0.000241	0.017	164	18000

Table 1: Vapor Detection Limits

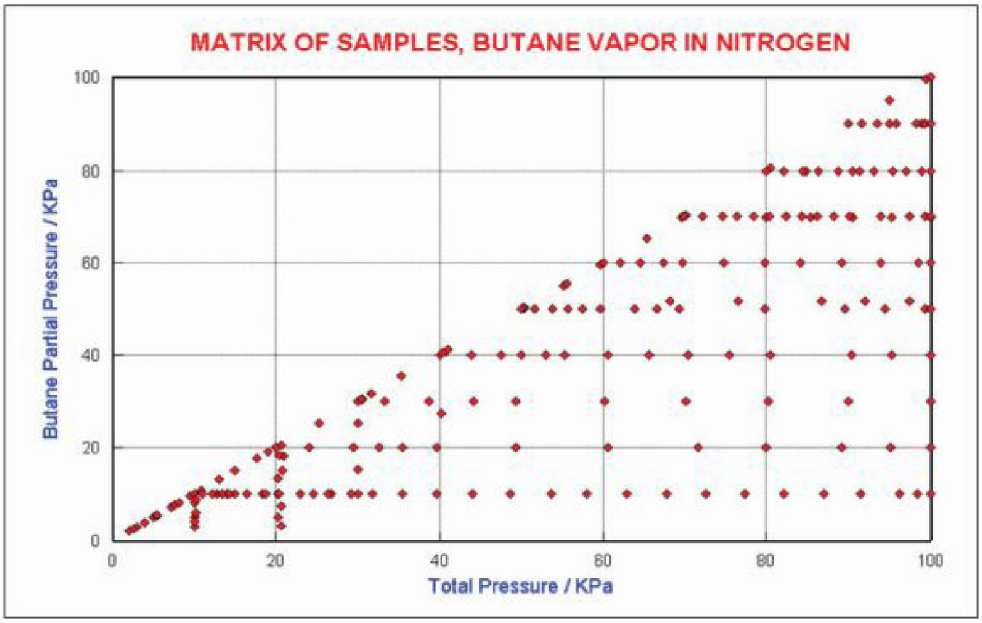

Figure 4: Butane Concentration Matrix

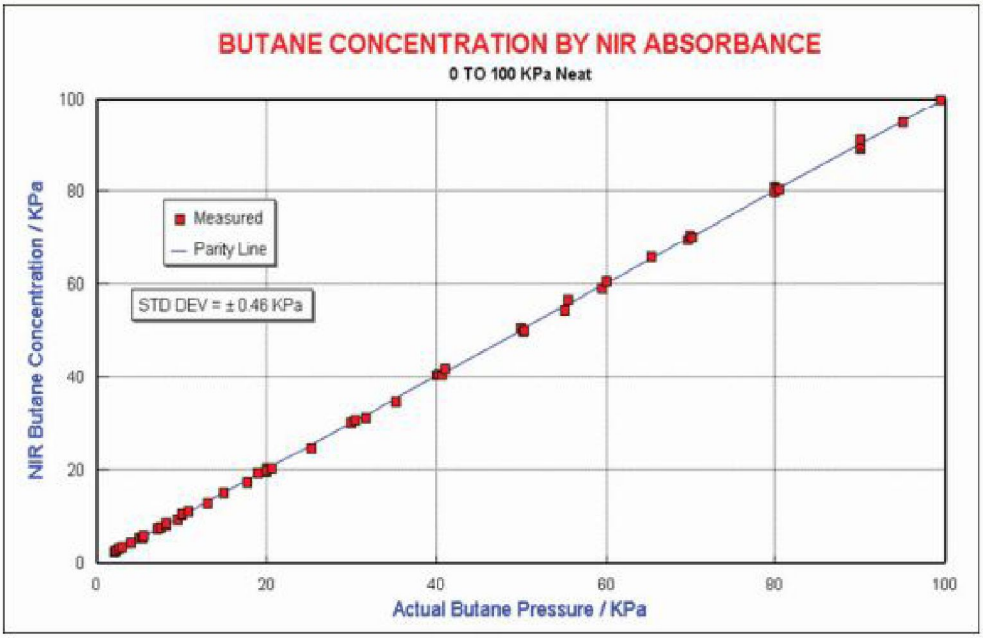

Figure 5: Butane Results

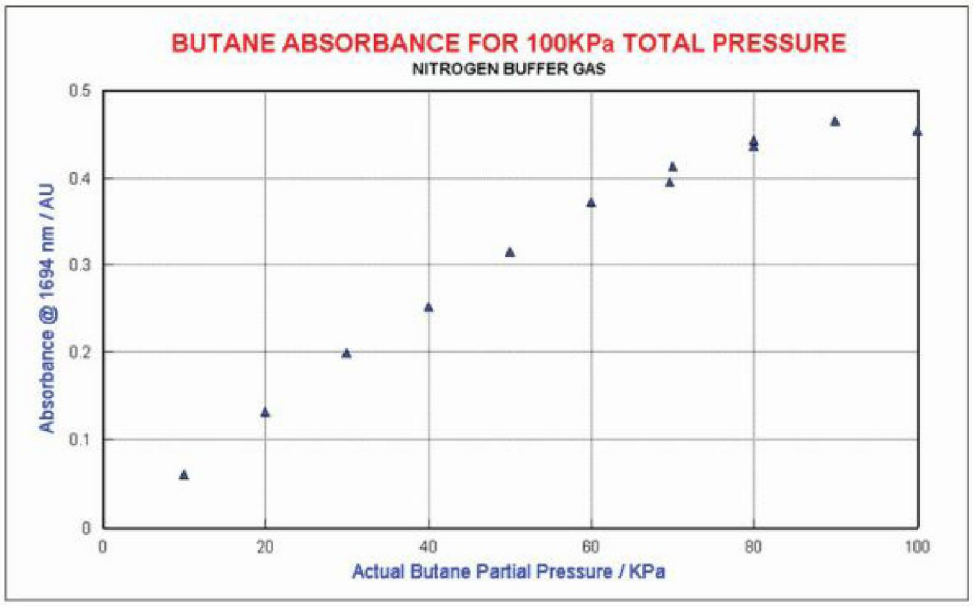

Figure 6: Butane at Constant Total Pressure

Analysis

Simple data analysis was used to prepare a model for butane in N_2. Prediction of neat butane concentrations up to100 kPa is straight forward. A four wavelength model produced the regression results shown in Figure 5. Quantification is to about ±0.46 kPa.

Looking at butane concentration at constant total pressure, again in an N2 matrix, butane shows reasonably linear relationship to absorbance for dilute mixtures. This is shown in Figure 6 where mixtures that are more than 80% butane deviate significantly as the broadening and energy transfer mechanisms transition from foreign gas to self-broadening. This non-linearity was modeled with a quadratic equation. Regressing all of the non-neat butane data using a two wavelength model plus linear and quadratic terms in total pressure produces the regression results seen in Figure 6. Concentrations were predicted to ±3 kPa.

Conclusion

The data presented demonstrates that neat vapors and gases can be measured by NIR spectroscopy to better than 500 ppm. The data also shows that foreign gas collisional energy transfer significantly alters the absorption coefficients. The foreign gas induces small measurable spectral shape changes. For more information on chooseing the right anazlyzer for your application contact a Process Insights sales or technical representative.

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