IN-SITU, REAL TIME ANALYSIS OF LIQUID AND GAS HYDROCARBON STREAMS USING A BROADLY TUNABLE SPECTROMETER

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ABSTRACT
Near infrared (NIR) spectroscopy is a powerful tool for process measurement of chemical composition and estimation of the physical properties of materials. Various spectroscopic designs have been employed, including both dispersive and interferometric devices. Recently, a novel analyzer using a broadly tunable laser spectrometer has been developed and deployed into process monitoring applications in the hydrocarbon processing industry. The system has been designed for field applications and uses advanced chemometric models to convert high resolution, high signal-to-noise spectral data into actionable results. The device performs in-line multicomponent and physical property analysis at line temperatures and pressures, and the type of spectrometer used provides the system with significant performance advantages over other methodologies.

INTRODUCTION
Near infrared (NIR) spectroscopy has been applied to on-line analysis for decades in the petrochemical, food and chemical industries. Vibrational spectroscopy in the near infrared region of the spectrum is dominated by overtones and combination bands. Like other spectroscopic measurements, NIR is used for both qualitative and quantitative assessment of the chemical composition of samples. It may also be employed to predict physical properties of the sample.

The near infrared region lies between 700 and 2500 nm and is information rich. The functional groups almost exclusively involved in NIR spectroscopy are those involving the hydrogen atom [1]: C-H, N-H, and O-H (Figure 1). These groups are observed at the overtones and combinations of their fundamental frequencies in the mid-IR and produce absorption bands of useful intensity in the NIR. The molar absorption of vibrational overtone and combination bands are weaker in this region than their counterparts in the mid-infrared, and thus the spectra of
condensed phase, physically thick samples can be measured without sample dilution or the need to resort to difficult short-path length sampling techniques.

<table>
<thead>
<tr>
<th>Third Overtone Region</th>
<th>Second Combination Overtone</th>
<th>First Combination Overtone</th>
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<tbody>
<tr>
<td>λ (nm)</td>
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<td>800</td>
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<tr>
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<tr>
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<td>R-NH-R'</td>
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<td>CH3</td>
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**FIGURE 1. ABSORPTION BANDS AND REGIONS IN THE NEAR INFRARED**

Various types of spectrometers have been employed to make measurements in this region of the spectrum. These include filter photometers, scanning spectrometers, diode array spectrometers and Fourier Transform Near Infrared (FT-NIR) devices. Each of these exhibit some strengths and some deficiencies when applied for process applications [2]. Recently, a new class of spectrometer technology has been developed and deployed for the measurement of chemical composition and physical properties of hydrocarbon steams. The technologies represent advancements in the fields of near infrared spectroscopy and process monitoring and overcome some of the deficiencies of older spectrometer designs.

This class of spectrometer employs a broadly tunable laser source covering the second and first combination overtone regions of the spectrum. The type of device enables superior signal to noise ratios, higher spectral resolution and greater wavelength accuracy than other readily available methodologies. This in turn enables sophisticated and robust chemo metric analysis and model transfer from device to device. The spectrometer of choice has been integrated into a package which may be fiber optically coupled to an in-line sample cell to make reliable measurements of stream composition and physical properties at line temperatures and pressures of up to 1500 psi. The entire system has been designed with process applications in mind and can be installed without requirements for an analyzer shelter.
THE SPECTROMETER

The VERAX™ analyzer utilizes a type of unique high-resolution NIR spectrometer that targets the first overtone regions of the carbon-hydrogen stretching and the oxygen-hydrogen stretching modes. This region is key for the qualitative and quantitative analyses of virtually all organic compounds (aliphatic and aromatic), in all phases (gas, liquid, and solid).

Near infrared spectrometer design has been hugely influenced by the telecommunications industry, which has spurred the development of an assortment of spectrometers based on micro-opto-electro-mechanical systems (MOEMS) [3]. Many of these developments are applicable to process analysis, and the devices developed for the telecommunications industry are typically rugged, reliable, long lived and able to withstand a broad range of environmental conditions.

A common telecommunications application is Wavelength Division Multiplexing (WDM), where fiber optics are used to carry more data by having different data streams available at different wavelengths. Given that the fiber and detectors are optimized for a narrow wavelength range, the multiple carriers must be close to each other in wavelength. As a result, the industry has developed technologies capable of accurate measurement while resolving very nearby wavelengths. All of these devices operate in the near infrared region of the spectrum.

The micro-spectrometer employs a broadly tunable laser source. Unlike conventional tunable diode lasers typically used for single component monitoring, these types of devices may be tuned over large wavelength ranges [4]. Additionally, the devices may be fabricated with dynamic power control for excellent stability, very narrow line widths and internal wavelength meters for active wavelength control [5]. There are a number of methods by which the wavelength may be swept, such as the use of an external grating; the most compact and reliable devices are fabricated using MEMS-based Fabry Perot filters for automated wavelength tuning and selection [6]. Such tunable laser sources are thousands of times brighter than the conventional sources used for NIR spectroscopy, and yet operate at very low power. They are an ideal source for a miniature spectrometer, in that they are intense, have high signal to noise ratios, highly resolved and the beam is small, coherent and easily coupled to a fiber optic.

FIGURE 2. FRINGE PATTERN FROM A FABRY PEROT INTERFEROMETER
The optical bench is designed with both internal amplitude referencing and an internal wavelength reference. Every point of every scan must be referenced in order to provide long-term stability. Part of the beam from the tunable source module is typically split off via a beam splitter and directed through an interferometer and onto a detector. As the spectrometer scans, the signal from the detector is a fringe pattern (see Figure 2), analogous to the He-Ne reference signal in an FT-IR. This provides real-time wavelength referencing. The optical bench in the module must also be thermostat-controlled, ensuring both short- and long-term dimensional stability for the etalon, and thus both short- and long-term wavelength reproducibility. A second beam splitter may be used to direct another portion of the light, directly to a detector. This provides real-time source amplitude referencing.

**SPECTROMETER PERFORMANCE**

The type of broadly tunable laser spectrometer used in this system differs greatly from a tunable diode laser, in that it has a much wider spectral range. In tunable diode laser absorption spectroscopy (TDLAS) the laser is typically swept across a single finely resolved peak that is characteristic of one and only one chemical species. The spectral range may be only a nanometer. By sharp contrast, this class of broadly tunable laser source has a spectral range covering the region from 1300 nm to 1850 nm or greater. This wide spectral range enables the analyzer to measure multiple components simultaneously and equally important, correct for the background caused by interfering components. Other spectrometer configurations, such as diode arrays and FT-NIR, have even larger spectral ranges, but may have other deficiencies when compared to the broadly tunable laser spectrometer.

In the broadly tunable laser spectrometer, the internal Fabry Perot interferometer performs the same role as the helium neon laser in an FT-NIR. The monochromatic beam from the tunable laser source is split and part of the beam is directed to the Fabry Perot interferometer. The transmission of the interferometer is a strong function of wavelength with strong resonances at characteristic and repeatable wavelengths. In this case, the resonator is an integrated part of the temperature controlled and hermetically sealed laser package, and not subject to drift. The use of a resonator of this type provides wavelength accuracy on the order of 0.025 nm for calibration transfer and wavelength repeatability of 0.01 nm.

Wavelength accuracy and precision is critical to calibration transfer in NIR spectrometers. While precision can be designed into an FT-NIR, wavelength accuracy requires calibration against a wavelength standard [7,8,9]. The class of broadly tunable laser system employed in the analyzer described does not use a broadband source but rather is calibrated against a precision wave meter. To successfully transfer the calibration from one unit to the next, it is imperative that the units are capable of producing spectra for the same analyte that are as close to identical as possible. This may only be achieved with a precise and accurate wavelength axis, in addition to other criteria like reproducible linearity curves and high signal to noise ratios [10,11,12]. The combination of accurate wavelength axis calibration via the wavemeter and the use of the internal Fabry Perot interferometer ensure that reliable calibration transfer between units can be achieved.
The maximum achievable resolution varies greatly between different types of near infrared spectrometers, with TDLAS devices having picometer (pm) resolution and filter photometers have resolutions on the order of 20 nm or greater. In spectroscopic applications, it is also desirable to have as high a resolution as possible while not impacting signal to noise ratio. Of the broad spectrum NIR analytical techniques, only FT-NIR compares to the broadly tunable laser in terms of achievable resolution. The broadly tunable laser source can operate with resolutions as low as 100 picometers (pm), while a typical FT-NIR will operate can be operated as high as 0.5 wavenumber or 300 picometer resolution at 2 microns. The ability to operate at high resolution allows the spectrometer employed in this system to clearly discern sharp peaks in the spectra and equally important, to quantify subtle changes in peak shoulders if the signal to noise is high enough [13].

Generally, FT-NIR devices are not operated at resolutions higher than 4 wavenumbers (or even 16 wavenumbers). While the argument is often made that this resolution is sufficient for the task at hand, in reality, the factor which drives this decision is signal to noise ratios. Under optimal conditions, increasing the resolution of an FT-NIR by a factor of two will reduce the signal to noise ratio by a factor of two [14]. This variation in signal to noise ratios requires that the resolution of the FT-NIR be optimized for the task at hand. The maximum analytical sensitivity is achieved is found for measurements made at the lowest resolution that adequately separates the lines of interest from interfering lines [15]. As depicted in Figure 3, changing the resolution affects both the band shape and the signal to noise ratio on FTIR devices [16].

FIGURE 3. THE EFFECT OF RESOLUTION ON BANDSHAPE AND NOISE IN FTIR

In the class of broadly tunable laser spectrometer used in this system, the resolution is selectable and may be varied during a scan, selecting a high resolution of 0.1 nm in regions where very fine structures exist and lower resolution (1-10 nm) where the extra resolution is not required. These types of devices operate at comparable signal to noise to that of an FT-NIR at low resolution, and exceed the signal to noise ratios achieved by FT-NIR at higher resolutions.

The combination of a very bright source, cooled, targeted cut-off detectors and a wide dynamic range (24 bit) data acquisition system enable linear absorbance measurements as high as 4
absorbance units (A.U.) with noise levels as low as $10^{-5}$ A.U. This has been verified experimentally using NIST traceable neutral density filters, and a Lambert Law plot using a pure substance with varying path lengths. The tests showed the current instrument was linear to an absorbance of almost 4, and above that the response curve becomes concave down. Also tested was a commercial FT-NIR which shows an opposite deviation at much lower absorbance levels, most likely due to limited dynamic range in the centerburst region coupled with phase correction and apodization effects.

In summary, the new class of spectrometer presents significant potential advantages for applications in near infrared process spectroscopy, if appropriately integrated with modeling software and system hardware for specific applications. The spectroscopic method exhibits exceptionally high linearity coupled with excellent signal to noise ratios, as well as high spectral resolution and wavelength precision. This combination of performance characteristics makes the system powered by this class of spectrometers uniquely capable of performing sophisticated analysis of hydrocarbon products in applications where other NIR techniques may have failed.

**IMPLEMENTATION**

Despite the technological benefits of this type of high resolution, linear and precise NIR spectrometer, those features alone are insufficient to meet the demanding needs of on-line, at-line and real-time process analysis. To achieve these goals, this type of spectrometer has been integrated within a suitable system for use in industrial applications that does not require an analyzer building or analyzer shelter. The unit is environmentally stable and has been used in remote facilities with limited utilities available. It has low power consumption and may be run from solar panels. A typical installation of the analyzer enclosure is shown in Figure 4.
FIGURE 4. ANALYZER INSTALLATION AT NGL STABILIZATION TOWER

The analyzer enclosure houses the spectrometer, which is coupled to the process via fiber optic connections. The enclosure also houses a PLC which can be used for various control functions in the analyzer as well as at the process (such as isolation of process valve when out of specification conditions are met). It may also include a wireless communication system, as evidenced by the antenna in the above picture, to allow secure, remote access to the unit by facilities personnel and/or the design engineers. One application of the wireless connection is to allow for seamless and remote monitoring of the analyzer and model updates as necessary. A second allows for a producer to remotely check performance of all installations directly from a cell phone or tablet.

The spectrometer is fiber-optically coupled to the process via a custom designed flow cell. The flow cell has been specifically designed for process applications, in that the window surfaces are optimized to reject particulate and fouling, and the sapphire windows are welded into stainless steel housings, such that there is no need for elastomeric seals. Since the system is designed for at-line process measurements, and the spectral features in the NIR are both temperature and pressure sensitive, a typical installation (Figure 5) will incorporate appropriately rated pressure and temperature sensors. Note in this application at a natural gas liquids extraction facility, the process pressure is over 1100 psig and the spectroscopy is being performed in situ.
FIGURE 5. SAMPLE CELL MOUNTED ON PROCESS LINE

An important aspect of the system implementation is the powerful chemometric features built into the analytical platform. Multicomponent analysis in the NIR requires that the complex spectrum generated by the spectrometer be subjected to a mathematical analysis to identify the components which make up the spectrum, or to estimate physical properties of the absorbing medium based on the spectrum measured. Since such models involve identifying specific spectral features at the same position in the spectrum every time, the precision and repeatability of the wavelength axis is extremely important. The exceptional wavelength stability and resolution of the spectrometer class utilized, along with the linearity and signal to noise ratio, facilitates the use of advanced chemometric processing algorithms and allow the unit to routinely extract important information from small variations in the data.

APPLICATIONS AND FIELD DATA

The analyzer is suitable for a multitude of applications in the hydrocarbon processing industry. The spectral range enables measurement of almost any hydrocarbon, of many organic sulfur compounds, amines, carbon dioxide and water. Sophisticated chemical models may also be
developed to correlate the acquired spectra and predict the physical properties of mixtures. Both types of analysis (compositional and physical properties) have been performed with the device in gas processing facilities.

In one case in particular, a fiber optic multiplexor is used to allow a single analyzer installation monitor five streams in a gas processing facility. The five streams are the low pressure inlet gas, a liquid C2-C4 hydrocarbon stream from the top of a cryoseperator, the liquid C5-C6+ stream, and the high pressure gas stream on the outlet of the facility both before ethane re-injection and after ethane re-injection. Ethane is re-injected to make sure the final product gas meets the BTU specification. Typical spectra from within the facility are shown in Figure 6. At each of the points, complete stream composition is analyzed and reported in real time, including water and CO2 content as well as C1-C6+ hydrocarbons. The model also predicts BTU for gas phase and API gravity for liquid phase materials and shows excellent correlation to the gas chromatograph at site. The information from the gas and liquid phase streams has enabled superior ‘Plant Balancing’ reporting for the operator.

![FIGURE 6. SPECTRA FROM VARIOUS SAMPLE POINTS AT GAS PROCESSOR](image)

In another installation, a physical properties application measuring REID Vapor Pressure (RVP) was undertaken to optimize the performance of a condensate stabilization process. With the industry focus on liquids rich resource plays, some industry analysts are estimating that as much as 70% of the “crude oil” production in areas like the Eagle Ford shale should actually be classified as condensate, based on API gravity[17]. Condensate is lighter than crude oil, but heavier than natural gas liquids. The issue with condensate in its natural form is that the lighter hydrocarbons can make it dangerous to store and transport.

The stabilization tower is used to control the content of light hydrocarbons present in the produced condensate stream. It does this by essentially boiling off some of the lighter species, and thereby reducing the vapor pressure of the condensate. Oftentimes, the specification for condensate transport and storage requires that the RVP of the condensate be less than 10 psi. This reduction of the vapor pressure also reduces the production volume from the facility and thereby has a direct impact on lowering revenues if the process is taken too far. As well, the
produced vapors can potentially contribute to increased volatile organic carbon (VOC) emissions from the facility.

The ideal method to control the stabilization towers is to monitor the RVP of the product stream and use that to optimize temperatures and contact times. In the ASTM test methods, the RVP is determined at 100°F, and this criterion is also applied in many automated RVP analyzers. In this particular facility, an automated RVP analyzer based on non-spectroscopic techniques was put in place to provide control of the process. However, that analyzer would suffer from significant downtime from waxy buildups in the sample system and analyzer assembly, and the plant was unable to trust the analyzer for continuous control. As a result, they controlled the stabilization tower by a manual means that had been optimized against laboratory RVP methods, in which they cycle the temperature of the stabilization tower at a given frequency. Lab analysis was used to ensure that they maintained a large safety margin compared to their pipeline specification. However, it was recognized that this was costing the facility on the order of $5,000 to $10,000 a day in reduced production volumes.

The plant agreed to a trial installation of the new spectrometer, and to acquire spectrometer data as well as laboratory data such that a model could be built to predict the RVP from the infrared data. Until the model could be built, the analyzer was used to monitor the system but was not used for control purposes. A chemometric model was built, which showed excellent correlation to the laboratory results (see Figure 7). The excellent correlation in the model was noted and the analyzer results began to be used for process control.

Without the analyzer for monitoring and control purposes, the RVP measurement varied through large swings on a cyclic basis as the facility attempted to manually control the RVP. As can be seen from the upper trace (Figure 8), the typical RVP was far below the pipeline specification of 10 psi, which resulted in substantially less production volumes. With the analyzer in place and the model fully developed, the facility now runs at a standard RVP of 9 psi, is well controlled.
and is generating substantial additional revenue. Four additional units have been purchased by
the same client to perform RVP measurements at other plants.

Figure 8. RVP of Condensate Without and With Analyzer Control

Summary and Conclusions

A novel NIR spectrometry-based platform has been developed which exhibits exceptional
characteristics for process applications. These include:
1) Small and mechanically robust,
2) High resolution and wavelength precision,
3) High linearity and signal to noise ratio, and
4) Reproducible from unit to unit simplifying calibration transfer.

One class of this spectrometer platform has been built into a rugged and field worthy analyzer
system capable of performing sophisticated chemometric analysis on a real time basis through at-
line and inline measurements. The unit has been proven in a number of hydrocarbon processing
applications.

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