

Physical Properties Analysis of Petroleum Products Using FT-NIR

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1. Introduction

Petroleum products have specifications based on their physical properties and chemical composition. These include such physical properties as octane, cloud point, and viscosity and chemical concentrations such as benzene, sulphur and nitrogen. Refiners in the past have turned either to the lab for analysis using ASTM methods or to on-line batch type analyzers that duplicate lab ASTM methods. Some even use gas chromatographs and infer the physical properties from the composition. These methods have many drawbacks associated with them. These include safety issues with handling flammable products, reliability issues due to the nature of the analyzer, and limitation in the usefulness for process control or optimization because of long sample lag times.

Recent advances in spectroscopy and increase in computing power have led to improvements in the spectroscopic methods to obtain physical properties and chemical composition of petroleum products. FT-NIR is one such method. It uses fiber optic technologies to bring the light to the sample versus bringing the sample to the light, requires little sample conditioning, and has minimal maintenance requirements. Couple that with capital costs 50 to 60% lower than traditional physical properties measurement, FT-NIR provides the lowest total cost of ownership and the highest net present value for your investment.

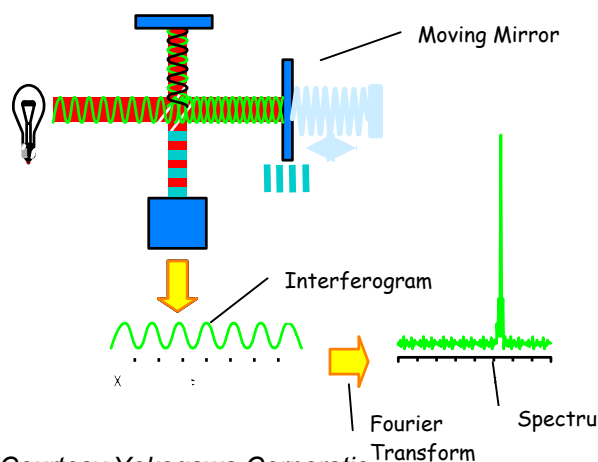
2. FT-NIR Spectroscopy

Near Infrared is the region of the spectrum that resides in the 700nm to the 2400nm.

Fourier Transform Near Infrared (FT-NIR) Spectrometer is a multiplex analytical instrument, a single channel device in which all wavelengths of the spectrum are observed simultaneously. This is accomplished by the use of a Michelson Interferometer. A beam of light is split into two via a 50% beam splitter. Half the light is reflected off a stationary mirror. The second half of light is reflected

off a moving mirror that is set 90° to the stationary mirror. The light is then recombined at the beam splitter where it produces an interference pattern. The result is that the longest wavelengths are modulated at low frequencies and short wavelengths are modulated at high frequencies.

The Michelson Interferometer



Courtesy Yokogawa Corporation.

Once the light passes through the sample and is integrated by the detector, the instrument's computer performs a Fourier Transform to convert the interferogram to a NIR transmission spectrum, which is then converted to an absorbance spectrum by taking its negative log. The absorbance spectrum, which follows the Beer's Law, is used to calculate concentrations or physical properties.

Advantages of FT-NIR Over NON-FT Instruments

Fourier Transform instruments have three distinct advantages over dispersion instruments.

Jaquinot Advantage

FT-NIR instruments use all the available light. Since the FT-NIR has few optical elements and no slits the power of the light energy reaching the detector is greater than dispersive type analyzers.

Connes Advantage

FT-NIR instruments pass laser light from a HeNe laser aligned with the NIR source through the interferometer. The laser light calibrates the spectrum on every scan and eliminates variations in the spectrum caused by vibration and changes in temperature (of the instrument hardware). Therefore, FT-NIR instruments have extremely high wavelength accuracy.

Fellgett Advantage

FT-NIR instruments detect the whole NIR spectrum simultaneously. A complete spectrum can be collected very rapidly and many scans can be averaged in the time taken for a single scan of a dispersive spectrometer.

These advantages result in an instrument that can produce spectrums with a signal to noise ratio an order of magnitude higher than dispersive instruments in a fraction of the time.

Components of an FT-NIR Analyzer System

In addition to the analyzer itself, there are two other components that make up the system: Fiber Optics and Sample Cells.

Fiber Optics transports the NIR light from the interferometer to the sample cell and back to the detector. The fiber optics can be either single beam (single fiber) or dual beam (dual fiber). Dual Beam fiber optics has the advantage that they compensate for changes in the fibers refractive index, which changes with temperature. This is accomplished by taking one fiber directly to a reference detector and the other fiber through the sample cell and then to the detector. Since both fibers are subject to the same temperature any changes in the refractive index is negated.

Sample cells allow the light to interact with the sample in a controlled fashion. There are two types of cells: In-situ and flow cells. In-situ cells are placed into the process piping. No sample is extracted and no sample conditioning is required. In-situ probes are best used on clean samples that have a constant

temperature and pressure. Flow cells are ex-situ and provide a path for the sample and light to interact. Flow cells can be used on all sample conditions, but care must be taken to ensure a clean sample is delivered to the cell with a controlled temperature and pressure.

There are many important considerations when designing a sample conditioning system for FTNIR applications. First and foremost is temperature where a minor change in temperature can result in a significant error in the measurement. The effects of temperature can be minimized by coarsely controlling the temperature of the sample and then fine-tuning using the calibration model or a correction factor.

Course calibration control can be accomplished by either using heat tracing to keep the sample at its elevated process temperature or by use a sample cooler to cool the sample down to a set temperature. Which method to use will depend on the nature of the sample and at what temperature it is most feasible to scan the standards.

After coarsely controlling the temperature, the next step is to fine-tune the calibration model to correct for some minor variance in temperature. This is accomplished during the modeling when the samples are analyzed at various temperatures. This model is called a Robust Model, as it is robust to temperature changes. An RTD placed in the sample handling system and input into the analyzer allows the instrument to correct the analysis back to the calibration temperature.

FT-NIR and Physical Properties

Physical properties measurement is a lucrative measurement in a refinery, however, until recently the analysis of these characteristics has been difficult and expensive to achieve. Traditional physical properties analyzers analyze for a single physical property. A typical gasoline blender required 5 to 10 analyzers, elaborate sample systems, and a large analyzer shelter. A total cost of ownership well over \$1 million dollars before factoring in maintenance and operating costs.

Today, however, a refiner can install one single FT-NIR analyzer and analyze a number of streams for those 5 to 10 physical properties simultaneously. Therefore, a typical gasoline blender can install one single FT-NIR and utilize the fiber optics to eliminate more than 50% of the cost traditionally encountered.

Below is a table that outlines a capital cost comparison between a traditional analyzer and a FT-NIR measuring the same components. Dollar values include engineering, materials and construction labor and are +/-30%.

Gasoline Blender Comparison

	Traditional	FT-NIR	Notes
Analyzers	\$ 750,000	\$ 350,000	(3 knock, RVP, Density, Oxygenates, Distillation)
Shelter	\$ 250,000	\$ 25,000	Traditional would require a 10 x 30 rated class 1, div 1, grp c, d). FT-NIR would require a 8x8 GP.
Sample Systems	\$ 100,000	\$ 15,000	Includes probes, transport systems, conditioning
Sample Disposal	\$ 50,000	\$ -	
Total	\$ 1,150,000	\$ 390,000	

The FT-NIR not only provides a lower total cost of ownership, it allows the refinery operations to operate closer to the set point. Operating a 21,000 bbl/day gasoline blender 0.03 Octane units closer to the set point can result in savings of \$150,000/month. Payback of an FT-NIR analyzer system is mere months.

3. Building a Model

Though FT-NIR has tremendous advantages over traditional ASTM on-line analyzers many facilities choose not to apply this technology. The main reason is that building a model is a time consuming and complex task. However, with an understanding of the fundamentals of FT-NIR and a well thought out plan this task does not need to be overly difficult.

The first fundamental is, FT-NIR analyzes a number of wavelengths in a spectrum and the absorption at each wavelength is a contribution from a number of components. Simple linear calibration curves ($y=mx+b$) will not suffice. Instead, Chemometrics must be applied to solve for the components of interest. Chemometrics can be defined as the application of statistics and mathematical models to chemistry problems.

The second fundamental is it can be difficult to transfer models from one instrument to another and is virtually impossible to transfer a “global” calibration

model from one location to another. Calibration models are unique to a set of sample characteristics and instrument responses. Though it is possible to transfer a model from one instrument to another, some additional modeling will have to be performed to take into account variances from instrument to instrument.

Models from one location will most likely not transfer from one site to another because the samples will vary too greatly from one site to another. For instance, gasoline refined from West Texas Intermediate will be much different than Alberta Synthetic Crude because of varying concentrations of aromatics and other constituents.

The third fundamental is the FT-NIR analyzer will only be as accurate as the calibration data. The accuracy of NIR systems is limited by the accuracy and precision of the lab data used to calibrate NIR analyzers. An on-line NIR system measures only the spectrum of the sample. The variations in the spectrum at several wavelengths are correlated to laboratory measurements made on the same sample and any error in the lab data ultimately affects the accuracy of the NIR calibration.

The precision of FT-NIR analyzers is typically much better than the ASTM analyzers as the instrument is always measuring a spectrum of the sample and comparing it to the calibration curve. As mentioned earlier, the FT-NIR’s optics are internally calibrated with a HeNe laser, and therefore has a high degree of repeatability.

The simplest approach to developing a model is:

- Select a series of standards
- Keep everything else constant
- Measure the response
- Produce a model

However, under each step in the model is a number of details that must be considered and sources of error that must be addressed

Selection of Standards

The selection of the standards to use in the modeling process is the most crucial step.

- 30 to 100 samples will be required
- Should span the whole range of analysis
- Should be taken over a long period of time
- Should be stored in a sealed container and cooled (minimize volatile loss)

Keeping Variables Constant

There are several variables that must be kept constant during the calibration process. These include:

- Lab analysis method and equipment
- Analyst
- Sampling technique and sample handling
- Time from sampling to analysis
- Temperature at analysis. (Except when building a Robust Method where temperature is varied during analysis)

Creating the Calibration

There are a number of Chemometric methods of analysis, but the most commonly one used for FT-NIR is Partial Least Squares Regression. Partial Least Squares is a method to find the linear relationship in complex data. As mentioned previously, the absorbption at a certain wavelength is a contribution of a number of components. Therefore the absorbption can be broken down to its constituents and related to the predicted variable by the offset and the coefficients.

$$Y = A + Bx_1 + Cx_2 + Dx_3 + Ex_4$$

Where,

- Y is the predicted variable
- X_n is the measured variable
- A is the offset
- B, C, D, E are the regression coefficients

Fortunately, FT-NIR instruments have software available to perform the mathematical functions required to generate a valid calibration. However, there are some methods of validating data that should be understood:

- Root Mean Square Error of Calibration is used to evaluate the performance of a quantitative measurement. The closer the RMSEC value is to zero, the better the method will perform.
- Correlation measures the how two sets of data relate to one another. Correlation (r) has a direction (+ or -) and a numerical value. An r value approaching 1 or -1 means the data shows a strong relationship between each other. An r

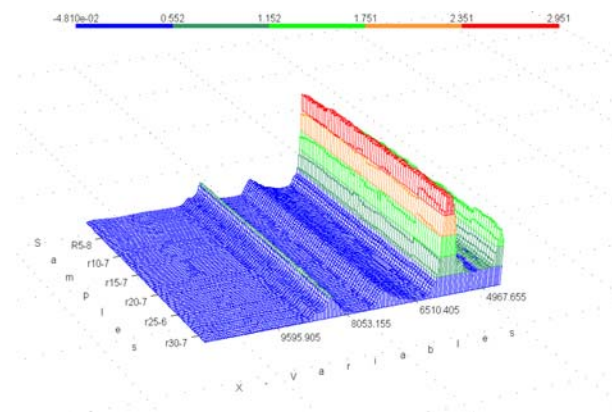
value approaching 0 means there is no relationship between each other

- Dixon Test for Outliers is a statistical method of determining if a data point is valid or not. This provides the justification to throw out data based on statistics versus the "it doesn't look right rule".

4. Example Analysis of Gasoline

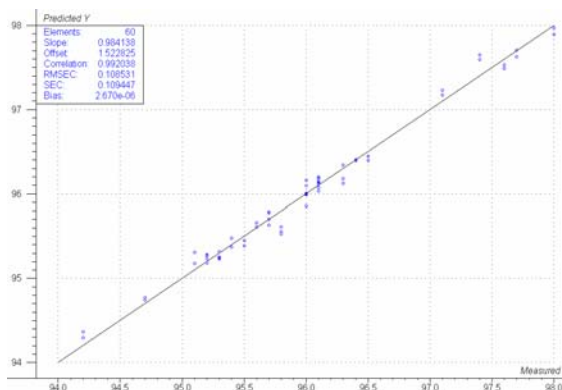
This section contains an analysis of gasoline for a number of physical properties and chemical constituents. The scatter graphs show excellent correlation between the known samples and the predicted results as well as low RMSEC. This shows the validity of the technique as compared to the standard or comparison method.

Spectra of Regular Gasoline



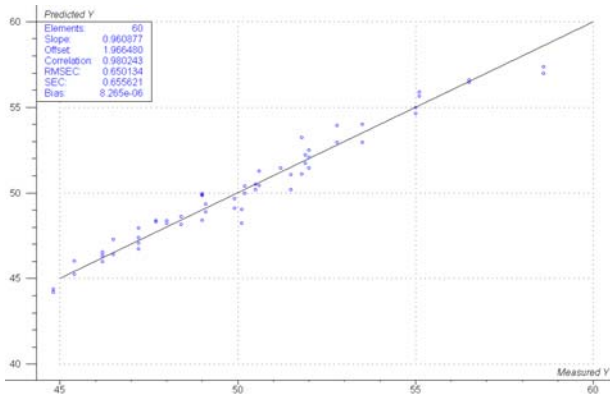
Courtesy Yokogawa Corporation

RON – Actual vs. Predicted

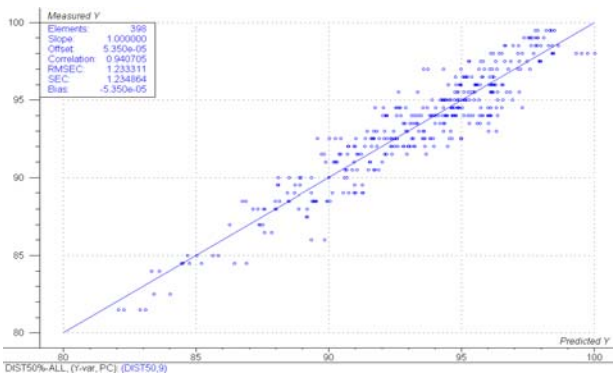


Courtesy Yokogawa Corporation

RVP – Actual vs. Predicted

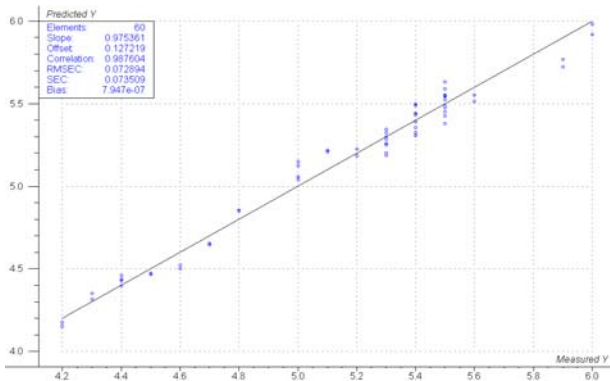


Temperature at 50% Off – Actual vs. Predicted



Courtesy Yokogawa Corporation

Benzene – Actual vs. Predicted



Courtesy Yokogawa Corporation

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