

**HYDROCARBON FUEL PROCESS ANALYSIS
BY ACOUSTO OPTIC TUNABLE FILTER
NEAR INFRA-RED SPECTROSCOPY**

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ABSTRACT

Octane and other properties of gasoline have been measured by near infra-red (NIR) spectroscopy since the laboratory trials at Technicon in the early 1980s. Over the past decade, systems have been developed for industrial process analysis. Acousto optic tunable filter (AOTF) is one of the NIR instrument technologies which has survived as appropriate for petrochemical process service. NIR spectroscopy is often the process analysis method of choice because of the speed of results and AOTF is one of the fastest NIR methods.

NIR spectroscopy is used for gasoline, diesel, and other hydrocarbon fuels as well as chemical and polymer process lines. One NIR sensor and instrument measures multiple properties -- octane, aromatics, vapor pressure, boiling points, and others of interest. The instrument is connected to sampling probes and cell at remote sites with fiber optics which can be used in the NIR. We have learned from experience which probes and sampling systems give good results. A double fiber optic and probe system provides the benefits of stable double beam spectroscopy.

Several chemometric systems have been used to develop the calibration equations required for NIR analysis. Those providing robust transferable calibrations will be presented.

INTRODUCTION

Because the ASTM research octane number (RON) and motor octane number (MON) knock engines (1,2) are lengthy procedures not usually done at-line and have poor precision, they are not the best for refinery process control. NIR spectroscopy is more appropriate for process monitoring and control measurements.

Whether in a laboratory, near a process line, at-line, or on-line; NIR is a process analysis and control technology. Calibration development from samples of known composition is required. Once the calibration equation(s) are established, spectroscopic answers are provided in seconds

Electronic transitions in the visible and ultraviolet spectral region and molecular vibrational transitions in the infra-red (IR) region absorb so much energy that dilutions or very thin samples are required. This means that sample preparation and handling are required as part of any spectroscopic procedure. The NIR transitions are overtones and combination bands of the fundamentals IR vibrational transitions. They are thus much weaker and reasonably convenient pathlengths can be used with no sample preparation.

NIR spectroscopy measures absorbance at more than one wavelength. One or more can be used as a constant reference signal. This provides the stability and precision for NIR which is either lacking or has to be achieved in some other way for other on-line instrumental technologies.

EXPERIMENTAL

Instrumentation

There are several different technologies for producing NIR spectra for instrumental analysis. The heart of an AOTF spectrometer is the tellurium dioxide crystal shown in

Figure 1. The incident beam is from a quartz halogen source lamp. The lithium niobate transducer converts a radio frequency (RF) signal into ultrasonic waves in the AOTF crystal. The frequency (wavelength) of the resultant tuned spectral beams depends on the wavelength of these ultrasonic waves (the acousto optic effect). Hence, as quickly and as accurately as the RF signal can be changed produces tuned beams of changed wavelength with no moving parts.

These tuned beams are sent through glass fiber optics to a sample probe up to hundreds of feet away and back to matched detectors in the instrument. One beam goes through the sample and the other is used as a reference beam. This provides the stable signal of double beam spectrophotometry. Flow through cells are provided on bypass lines or probes can be inserted into the main piping or vessel depending on the particular installation..

Calibration & Chemometrics

For calibration development, full spectra are taken as shown in Figure 2. For our example of MON, the knock engine reference measurements for the same samples are required. Software is used to drive the instrument for spectra collection and data regression to product calibration equations. Principle component regression (PCR) or partial least squares (PLS) calibrations use all or part of the full spectrum of usually several hundred data points. Multiple linear regression (MLR) selects the best few (usually 2 to 6) wavelengths from the spectra.

For almost all of the applications mentioned below, MLR provided the calibrations most robust for analyzing samples once the calibration has been established. This is because the selected wavelengths are the ones due to the components being measured. Interferences and variations due to other factors in other parts of the spectra do not influence the predicted answer.

Applications

The Bran+Luebbe InfraPrime was designed as an industrial environment system for liquid measurement in the refining and petrochemical industry. The most common installations are to measure those properties used to control motor fuel refineries: RON, MON, RVP, density, and characteristic distillation points. NIR nicely provides all these analyses from one spectrum. One calibration equation is used for each property measured. Several sites have added aromatics and PONA as measured properties.

Cetane number, boiling points, cloud point, freezing point, flash point, and CFPP are being measured for diesel fuel and kerosene production. Some of the calibration statistics are not as good for some of these properties because of the less precise nature of the reference analysis methods.

Sulfur, viscosity, and heat content are being measured at heavy fuel operations.

A wide range of applications are being used in polymer and chemical industries. Less than 0.1 % additives are measured and controlled in high pressure and temperature extruders. Major components in polymerization reactors are being controlled. Physical properties such as viscosity are regularly being measured.

RESULTS AND DISCUSSION

The prediction plot (Figure 3) shows how well the resulting NIR calibration and instrument agree with the reference knock engine for measuring MON. For this particular example, the standard error of the calibration samples was 0.18 MON and a standard error on predicting samples not in the calibration set of 0.22 MON. These are well within the variability of the MON knock engine method. NIR is often more precise than the reference method which generated the calibration set data.

The installation has been monitoring MON with on-line answers at this accuracy every 1.25 seconds continuously since August 1993. Several systems have been functioning for over 30,000 hours. With years of on-line design, installation, and evaluation experience; AOTF NIR spectroscopic systems have lived to their exciting promise as a technology for the on-line quality and process control of hydrocarbon fuels.

REFERENCES

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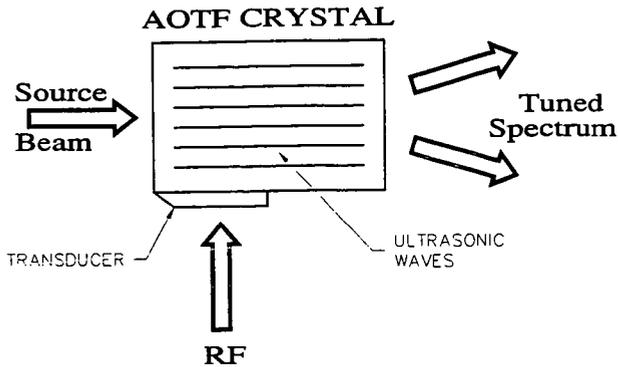


Figure 1. AOTF: acousto optic tunable filter crystal spectroscopy

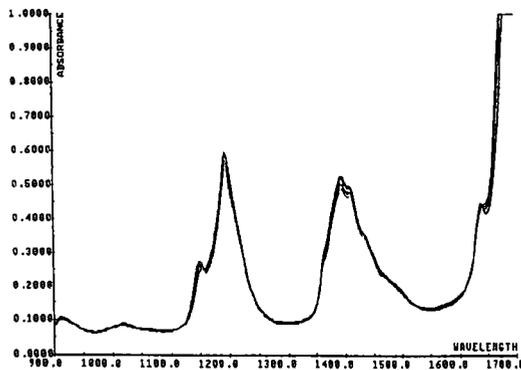


Figure 2. AOTF spectra of gasoline after the "naphtha cracker" in a European refinery

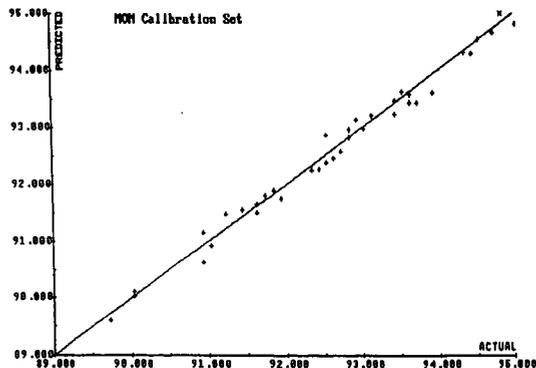


Figure 3. Prediction plot of MON predicted by the NIR calibration model versus actual knock engine measured MON