Intelligent FTIR System for Efficient Fuel Analysis

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From the very beginnings of fuel characterisation, infrared spectroscopy was widely applied in the field of fuel analysis. Fuel, be it gasoline, diesel or jet fuel, consists of a complex mixture of hydrocarbons of which many have no characteristic absorption in the IR. They constitute the "matrix" or "background".
In contrast, aromatics, olefins and the many additives which are used to compose a fuel show absorption bands and are used to characterise it. The content of aromatics like benzene is strictly monitored by authorities and IR standard procedures exist to assess their concentrations, for example ASTM D6277 or ISO EN238.

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The amount of additives used to enhance fuel properties also requires regulation, firstly for optimised blending and secondly for environmental reasons. Various components that enhance the oxygen content and foster a better combustion have been designed and since the chemical bond between oxygen and carbon atoms is nicely accessible with IR radiation, IR spectroscopy became the method of choice to detect such substances (for example ASTM D5845). Currently the US Environmental Protection Agency (EPA) lists close to 7,400 different substances of different brands from different vendors used as fuel additives.

Usually a well defined number of specific additives are used to tune important fuel characteristics, such as the octane number (or cetane number in diesel fuel). Over time it became evident that the spectrum of a fuel must have a correlation with typical additives determining its properties. As the standardised methods to obtain information about fuel properties are time consuming and expensive (for example CFR Knock Engines), chemometric methods linking the IR method with such fuel properties became popular.

In the nineties, Dr. Werner Grabner, founder of Grabner Instruments in Vienna, Austria developed the IROX, the first portable FTIR spectrometer to measure the concentration of Oxygenates in gasoline by mid-IR. Another instrument specialised on Diesel followed in the year 2000. Both instruments are used to measure concentrations of different fuel components as well as predicting classical fuel properties by developing a robust prediction model for various regions around the world.

Towards the middle of the last decade, the classical benchtop IR producers identified the fuel market as a new business area and developed similar specific applications for fuel analysis, and also applied Raman IR spectroscopy as complement to classical IR. Other technologies like the attenuated total reflection (ATR) IR spectroscopy were introduced. FTIR, Raman and ATR technologies however are essentially different ways to look at the same thing from slightly different angels. There is no method better or worse that the other and each technology brings its own merits and drawbacks for the particular purpose it is applied for. ATR can be easily applied in process for online applications, FTIR instruments are typically designed very compact and robust and can be used in mobile fuel labs. The actual differentiators come from: the ease of use, the available support, the flexibility and application range, the quality of the design, the robustness and finally also from the precision and accuracy of the device, which is a direct function of the spectrometer design, its resolution, stability, the spectral range and intensity of the IR light source.

Concentration Measurement and Property Prediction

With modern IR equipment specialised on fuel analysis, taking a measurement and obtaining the concentration of several fuel components as well as properties like octane number, distillation properties or vapour pressure take only a few minutes in comparison to potentially expensive, and often difficult methods defined in the fuel standards. Measuring the concentration of substances, like additives, with infrared spectroscopy is defined in standards, such as ASTM D5845, D6277, EN 238 or EN 14078. In contrast, a correlation for fuel properties is a method very difficult to standardise. The issue is that fuel is such a complex mixture and so different throughout different countries so that establishing a standardised one-fits-all fuel model is not feasible. As a consequence, certain questions arise.

Is the Property Prediction a Measurement in the Scientific Sense?

No, it is not; spectroscopy uses electromagnetic waves that induce electronic transitions in matter, allowing in many cases to identify the matter and assess its concentration within an object composed of different substances. The octane number is not a concentration.

Is Property Prediction Precise?

It depends on the quality of the collected spectra and on the accuracy to which the actual properties where measured. For that reason, various numbers of fuel spectra are collected, analysed, sorted and stored in a database along with their known properties. Through principal component analysis (PCA) those components in the wavelength range can be identified that correlate most with a certain property allowing to establish a prediction model for those properties. If an unknown fuel is then measured the IR spectrometer can use the prediction model to assess RON or distillation properties among others.

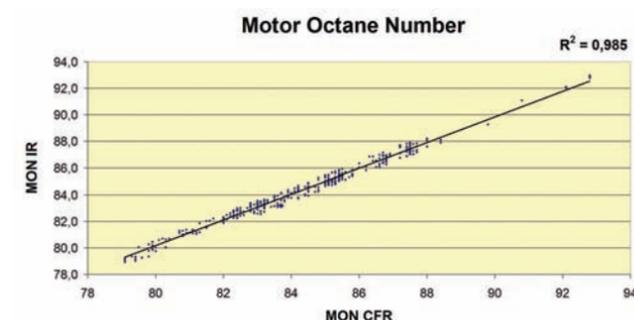### Can Property Prediction Beat Standardised Methods in Accuracy?

Figure 1: Motor Octane Number - Predicted vs. CFR

Yes and no. If the reproducibility (R) of a certain property measured by the conventional standard is not better than ±1, the R of the prediction cannot be better than ±1. In contrast, the repeatability (r) which corresponds to the standard deviation of the results of the same sample measured over and again at the same instrument can be better than for the original standard. The precision of the property prediction also depends on the prediction model that was derived from the database. The better the identified areas of certain components of the full spectra correlate with a property the better the prediction. The robustness of the property prediction is also linked to the chemometric methods applied. Nowadays, cluster analysis, multi linear regression and partial least square methods are applied simultaneously to get the best results derived from the existing data.

How Can a Prediction Achieve Robustness?

For the robustness of prediction but also owing to the simpler design of the instrument, NIR devices have been introduced to the market over the past 15 years. Those devices can be made small and portable and can use a longer absorption path. Since the spectra of a fuel in this range shows mainly the overtones of molecule vibrations (especially C-H, O-H and N-H bonds) and different combinations of molecule rotation and vibration modes, distinct bands are difficult to measure, but within the overall feature of the spectrum a robust correlation to fuel properties can be established. Owing to be less informative, NIR devices usually do not measure the concentration of individual substances and for establishing a prediction model, a larger number of different fuels is required.

The mid-IR range is also known as the fingerprint region of the IR spectra. Here individual substances show most of the time, nicely separated bands, which help to identify the substance due to the location of the bands and to assess their concentration. Looking at only a limited number of substances or even just one specific substance like ethanol in gasoline or biodiesel (FAME) in diesel, filter instruments are widely used in the market. Their costs are low and their application limited but they are usually easy to handle, small and compact. They can also develop a prediction model using the correlation found between the spectral ranges their selected filters and typical fuel properties.

Again the limited number of ranges (corresponding to the number of filters) requires a larger amount of collected data to establish a reliable prediction model. Inherent to all filter based IR instruments is that they cannot measure the baseline of a spectral band. In determining the concentration of a substance the background coming from the fuel matrix, the optical components used in the instrument can influence the accuracy. As a consequence, IR spectrometers following this design use dual beam systems to measure at the same time the intensity of incoming (Iin) and transmitted (Iout) IR radiation.

You Cannot Fool Physics

Some physical facts dictate the spectral range of infrared spectrometers. The optical components and the heat of the IR source are essential components of the interferometer design and limit the achievable wavelength range and resolution of a spectrometer design.

Firstly, the material of the beam splitter (and cell windows) must allow for the IR light to pass without itself absorbing any IR components. This becomes more difficult in spectrometers with extended wavelength ranges. Most standard FTIR spectrometers for the mid-IR range use the same design. As material for the beam splitter a salt of ZnSe (Zinc selenide) is used. This material allows to pass IR radiation between 2.5μm (4000cm^{-1}) and 15.5μm (645cm^{-1}). It basically works like a broad pass filter for IR waves. To extend the wavelength range, either the range of this "filter" or the "filter" has to be changed depending on the wavelength currently measured. The latter option is costly and tedious and not practical for routine measurements. Better is the

Figure 2: Interferogram Retardation and Maximum Resolution

use of special material which is both, inert over degradation and allows passing IR radiation from 1.25μm (8000cm^{-1}) to 25μm (400cm^{-1}).

Secondly, the best resolution of the spectrum is related to the maximum retardation (δ in cm) of the interferogram. The intensity of the beam will be at its maximum where both reflecting mirrors are the same distance from the beam splitter and there is no phase shift between the two parts of the IR light (zero retardation or zero path difference, ZPD). For a defined wavelength it will have its minimum where the moving mirror has passed a distance (δ) of exactly half the wavelength (ν) as then the IR wave maximum of one beam meets the wave minimum of its counterpart and they eliminate each other. In fact, the IR sources used to produce polychromatic IR radiation with a wide wavelength distribution.

The interferogram consequently has its maximum at the position of δ=0 and then the envelope over the graph decays rapidly. The distance δ in cm of the interferogram where the envelope reaches its signal over noise limit gives the best resolution by inverting δ (1/δ) in cm^{-1}. If the data of the interferogram reaches up to 0.5cm; the resolution is 2cm^{-1}.

Thirdly, as a consequence of Max Planck's laws about irradiation of bodies, the wavelength distribution produced from an IR source is wider the hotter the IR source is. One can observe a similar effect when dimming the light of a light bulb. Under full voltage the light appears white (and also bright) and the lower the dimmer regulates the voltage the more the light colour shifts towards red, a colour, on the lower end of the energy spectrum.
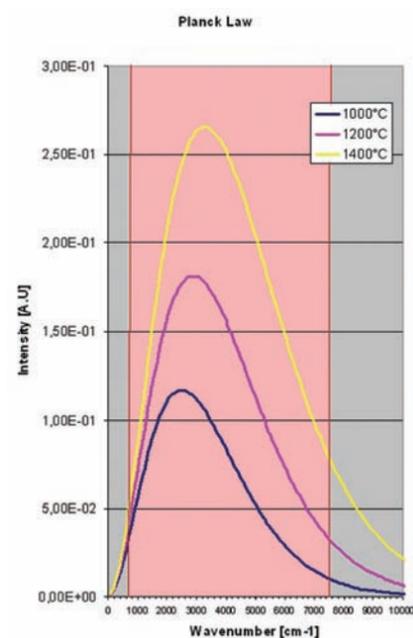

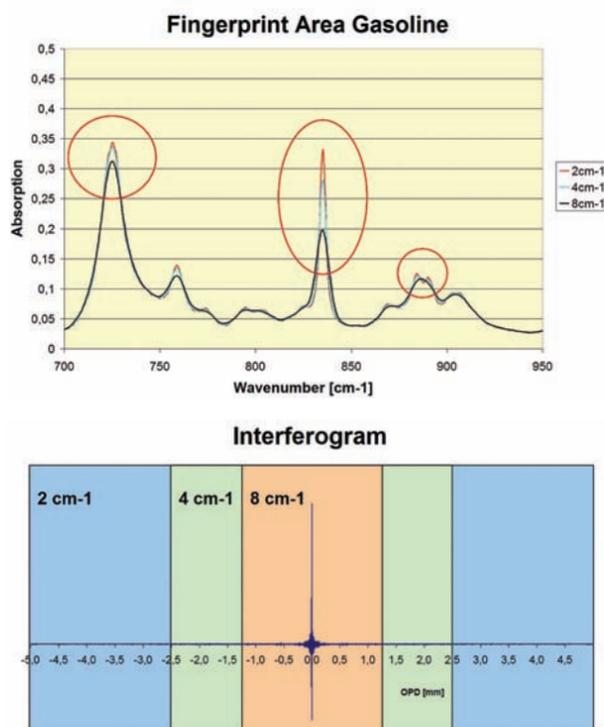Figure 3: Spectral Range of IR Sources according to Planck's Law

For applications in IR spectrometers glowing Kantal wires have widely been used. Their temperature is limited by the melting point and usually regulated to 1050°C. Better IR systems are using special ceramic IR sources that are reaching temperatures between 1200°C to 1400°C and can cover a wider spectral range. Also their peak intensity is higher up to a factor of two and the more light we have in spectroscopy the better this will be the counting statistics of the spectrometer or the signal over noise ratio.

Need for More

The market shows that fuel compositions are very versatile. On one side fuel technology strives for ever more efficient fuels with better combustion and higher energy efficiency and on the other side our environment demands low emission fuels with a minimum of environmentally controversial substances in the exhaust. In addition, with fuel prices on a global rise, the problem of fuel adulteration is no longer limited to certain regions, but is on the brink of becoming a worldwide phenomenon. The demand for fuel analysers nowadays is to allow accommodation for all this versatility with intelligent, flexible analysers that can automatically adapt to progressing changes of different fuel components. In reference again to the list of 7,400 fuel additives it is evident that the implementation of all those substances in order to reflect every possible fuel type is not practical.

Grabner Instruments new FTIR analyser MINISCAN IRXpert is preconfigured for the measurement of the most important fuel parameters. The instrument can learn to analyse more from a simple concentration series of a given substance. The system assesses automatically the limits for the detection and intelligent statistical algorithms avoid errors in the calibration of a new substance. This addresses the need for more substances to be analysed. This method also allows defining typical contaminants.

The need to add new and different substances bears the risk that the absorption of the new substance lies outside the classical mid-IR range or shows too strong or too low absorption. The extension of the mid-IR range on the low and on the high energy end and especially the addition of the NIR range allows the MINISCAN IRXpert to overcome such restrictions.

More substances with similar molecular functions like alcohols will also show overlapping bands that are difficult to separate if the resolution of the spectrum is not sufficient. At a resolution of 4cm^{-1}, typical for classical FTIR instruments, bands from methanol and ethanol can hardly be separated. With a resolution of less than 2cm^{-1}, the MINISCAN IRXpert solves this problem. Bands of a better resolved spectrum are not only sharper, but also higher; this helps in reducing the detection limits for substances like benzene.

There is also a need for higher precision and more stability in the results. Although the IR spectrum of solids or liquids is not strongly influenced by temperature, higher temperatures are a result of stronger molecule vibrations and movements that blur the bands of an IR spectrum. This means the absorption bands become wider the higher the temperature of the sample. At a resolution of 4cm^{-1} this broadening cannot easily be observed, but in order not to lose the gain of an improved resolution, it makes sense to temperature control the sample in the IR measuring cell when going to better resolution and higher precisions.

The MINISCAN IRXpert has a unique temperature controlled double cell spectrometer for maintaining highest precision independent from the environmental conditions the instrument is used in. To avoid CO_2 or water from the atmosphere interfering with the measurement, we have totally enclosed the spectrometer in a sealed and air tight housing filled with specially dried gas.

With the need for more fuels to be analysed in a shorter given time period and as fuel adulteration becomes an increasing global problem, FTIR systems are getting more attention for general screening of fuels outside traditional laboratories. The FTIR systems are often the only instrument for fuel screening in remote fuel terminals, by small custom labs at borders, at pipeline terminals or in mobile laboratories. Hence there is a need for ever more classical fuel parameters to be predicted. Not only octane number or volatility properties also certain cold properties, the viscosity or the flash point could be worth to be predicted.

A modern and very flexible fuel analyser like the MINISCAN IRXpert takes the development of new fuel models into account. As additional feature, the instrument also implements a temperature controlled density meter because density is an important fuel parameter and straight forward to be directly measured and secondly, because it allows conversion of concentrations from mass percent to volume percent.

With the application of the instruments in remote areas or mobile laboratories there is also the need for more physical robustness. The spectrometer of the IRXpert is therefore enclosed in a hermetically sealed aluminum housing which is mounted on special suspensions inside the instrument housing. The need for robustness, however, also extends to the results. The stability of the measurement itself has been described and the reliability of predictions is improved through using the NIR region. Not only is noise reduced; the property prediction calculations also benefit from the stretched spectral range.
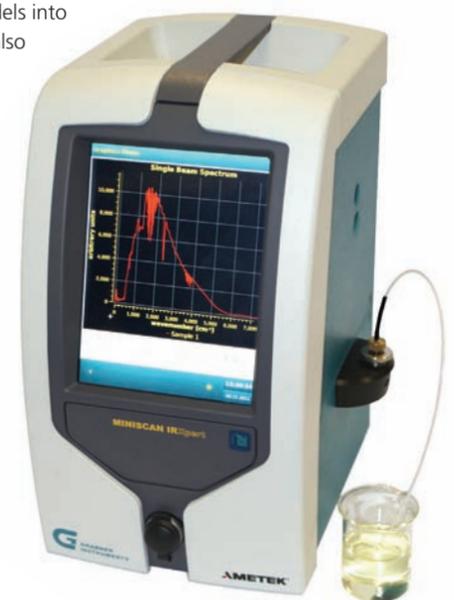

Figure 4: New MINISCAN IRXpert from Grabner Instruments