



On-site Fuel and Lubricant Quality Control by Portable FTIR Analysers

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In today's quickly moving business there is an increased demand for rapid quality control and condition monitoring analysis of fuels and lubricants. This has sparked the development of portable analysers allowing on-site analysis with performances comparable to laboratory instruments. Their dedicated design also enables complex analysis to be carried out by non-experts, and the time from sampling to decision can be shortened significantly compared to testing at an off-site laboratory.

Quality control of gasoline, Diesel fuel and jet fuel includes fuel composition analysis as well as the determination of fuel properties, such as Octane numbers (RON, MON) or Cetane index. For condition monitoring of lubricant oils, the degradation of the base oil due to oxidation, concentrations of additives and contaminants like water and ethylene glycol as well as properties such as Total Acid Number (TAN) and Total Base Number (TBN) are key parameters.

For such applications infrared (IR) spectroscopy is the method of choice due to several reasons. The IR spectrum contains information about the sample on a molecular level. Because each molecular species has a unique signature, or fingerprint, in the IR part of the spectrum, it is possible to determine the concentration of multiple species from a single spectrum. The evaluation and interpretation of IR spectra can be fully automated, enabling non-experts to rapidly carry out complex chemical analysis. Additionally, no sample preparation steps are needed resulting in easy-to-operate analysers that only require a power connection for operation. The measurement device itself, called Fourier transform infrared (FTIR) spectrometer, can be made very compact, stable and robust so that it can be deployed in the field.

Principle of FTIR spectroscopy

Infrared radiation is an electromagnetic radiation with a wavelength between 0.7 μm and 100 μm . This range is further divided in the Near-IR (NIR) range (wavelengths 0.7 μm to roughly 4 μm), mid-IR (wavelengths 4 μm to roughly 20 μm), and far-IR (wavelengths 20 μm to 100 μm). For analytical applications, mostly NIR and mid-IR spectroscopy are used.

In IR spectroscopy, IR radiation is directed through the sample to be analysed and the intensity of the transmitted radiation is measured as a function of wavelength. When the wavelength of the light matches the energy difference between the ground and excited vibrational state of a molecule in the sample the light will be absorbed. The absorption of light is given by the Beer-Lambert law, stating that the absorbance A is given by

$$A = c \cdot l \cdot \alpha(\nu)$$

where c is the concentration, l is the sample path length and $\alpha(\nu)$ is a molecule specific constant. From this equation we can conclude that A increases linearly with both sample concentration and the sample path length. Generally, a molecule has multiple vibrational modes resulting in absorption of IR light. This implies that $\alpha(\nu)$ depends on wavelength. This is how concentrations of many different substances can be determined simultaneously by IR spectroscopy.

In mid-IR spectroscopy the fundamental molecular vibrations, which are typically narrow and substance specific signals, are excited. Moreover, a substance exhibits different vibrational modes at different frequencies helping to identify individual compounds even if partial overlap of bands occurs. Evaluating the whole spectrum enables the separation of chemically similar substances, such as ethanol and methanol and quantitative analysis of both substances at the same time.

Contrary to mid-IR spectroscopy, near-IR spectroscopy probes vibrational overtone and combination transitions. These bands are typically much broader than in the mid-IR and only characteristic for some groups, such as CH or OH groups. The near-IR spectrum shows only a few broad and highly overlapping bands. The lack of chemical selectivity in this spectral region makes it difficult to measure additives present at lower concentrations and the analysis of the spectra relies heavily on chemometric methods requiring extensive calibration and validation.

Due to the nature of near-IR signals all the information is present in the mid-IR spectrum as well. The mid-IR, however, has the advantage of more distinct features that exhibit higher signal intensities. Therefore mid-IR spectroscopy is better suited for quantitative analysis resulting in lower limits of detection due to the higher signal intensities observed.

The aforementioned mid-IR signals can be measured in different ways. A cheap but limited way is the use of optical filters selecting only one of the various bands in the mid-IR range specific for one substance. Such analysers do not obtain a whole spectrum, which highly limits their use for complex samples such as fuels. Nowadays the instrument of choice to measure complete spectra is the FTIR instrument which replaced the older technique of dispersive grating spectrometers.

FTIR instruments use an interferometer for the measurement of the sample spectrum. It splits the light emitted from a source into two equal parts by a beam splitter typically made of ZnSe. This allows the measurement of spectra in the range of 1.5-18 μm (6660-550 cm^{-1}) covering all relevant signals for fuel and lubricant analysis. The two light beams are directed onto a mirror reflecting the IR light back towards the beam splitter where they recombine and are directed towards the detector. If both mirrors are positioned at the same distance from the beam splitter no phase shift between the two parts is introduced. During a measurement one of the two mirrors moves away from the beam splitter at a constant speed. When the displacement of the mirror equals one quarter of the wavelength of the light, the combined beams are out of phase resulting in destructive interference. In this case no light hits the detector. As the mirror is scanned, the light intensity measured by the detector will show a modulation. The intensity measured by the detector as a function of the mirror displacement is called an interferogram. For a monochromatic source, the interferogram will be a sine wave. For polychromatic light, which is emitted by typical IR light sources exhibiting a broad wavelength distribution, the interferogram will be the sum of sine waves of all frequencies present in the source. A Fourier transform of the interferogram gives the spectrum. By referencing the spectrum of the sample to that of the source, the (sample) absorption spectrum is obtained. The absorption spectrum will show a set of bands corresponding to frequencies where the sample absorbed light.

The spectral resolution, a parameter influencing the separation of two nearby bands in the final spectrum, depends on how far the mirror is moved. For a spectral resolution of 4 wavenumbers (cm^{-1}) the mirror needs to be moved 0.25 cm whereas it has to be moved 0.5 cm for the higher spectral resolution of 2 cm^{-1} .

Considerations for building the ideal FTIR system

The goal for building an FTIR analyser is always to measure the desired samples with the best signal to noise ratio (SNR) for the most accurate quantitative analysis. Therefore the careful selection and attuning of the spectrometer's components, such as light source, detector, interferometer and electronics, are crucial for building high quality instruments.

Because absorption means attenuation of light, very high absorption means that little light reaches the detector. This implies that very high absorption cannot be measured accurately. On the other hand, if the absorption is too low, meaning that little light is absorbed by the sample, the signal might be smaller than the noise of the instrument. In both cases the SNR will limit the accuracy of the qualitative analysis. The best SNR ratio is obtained when approximately 70% of the light is absorbed by the sample. It is therefore obvious from the formula $A = c \cdot l \cdot \alpha(\nu)$ that for molecules with highly different $\alpha(\nu)$ or concentrations, the value of the path length (l) of the system has to be adopted so that the absorption falls within a range where it can be measured with high accuracy.

To be able to separate similar spectral features, it is necessary to measure the spectrum at a sufficient resolution. Figure 1 shows spectra from a methanol-ethanol mixture at different spectral resolutions (2, 4, 8 and 16 cm^{-1}). If the spectral resolution is too low the two signals (one for methanol and one for ethanol) cannot be separated anymore. It becomes impossible to distinguish between them at a spectral resolution of around 16 cm^{-1} . It can also be seen that the intensity of the signals decreases as the resolution is lowered. The spectral resolution not only affects the signal strength but also the noise level. Figure 2 shows how the noise of the baseline increases going from a spectral resolution of 4 to 2 cm^{-1} . For quantitative analysis the parameter that needs to be optimised is the repeatability i.e. the variation between consecutive measurements of the same sample. Figure 3 shows the repeatability as a function of resolution for MTBE (a gasoline additive). Higher spectral resolutions lead to an increased deviation of the measured absorbance deteriorating the repeatability of the measurement. These figures strikingly illustrate that a compromise has to be made between repeatability and spectral separation of overlapping features.

Inspecting figure 4, showing a spectrum of gasoline, it becomes clear that no spectral information is lost at a spectral resolution of 4 cm^{-1} . This is not surprising because the natural

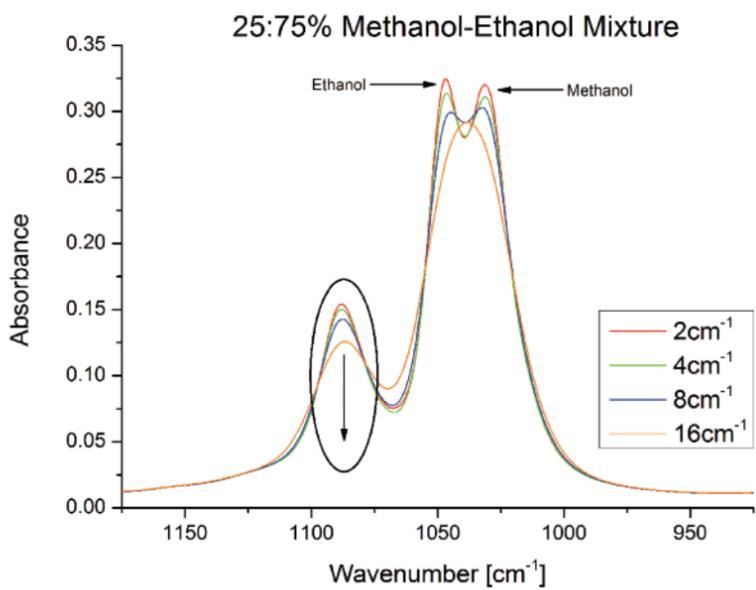


Figure 1: Spectra of a mixture of ethanol and methanol at different spectral resolutions

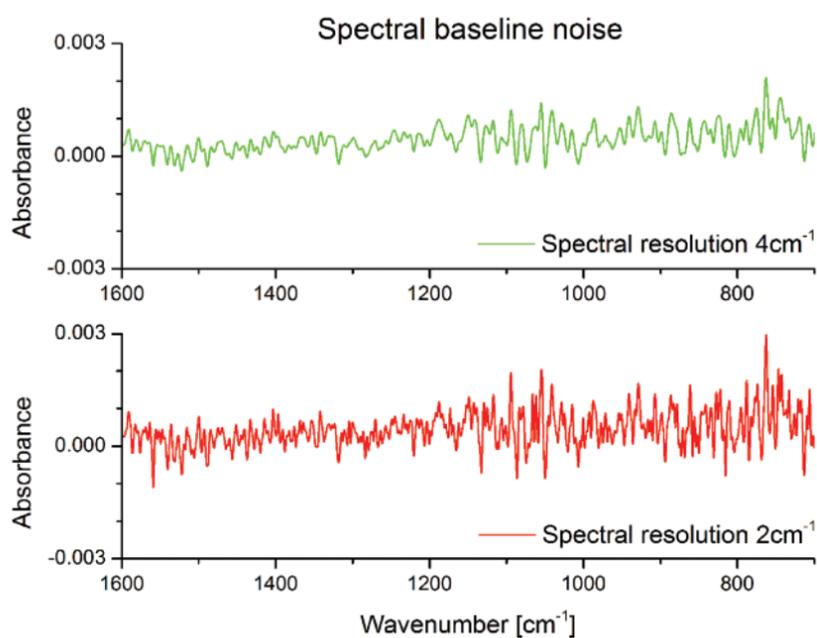


Figure 2: Noise increase of the spectral baseline with higher spectral resolution

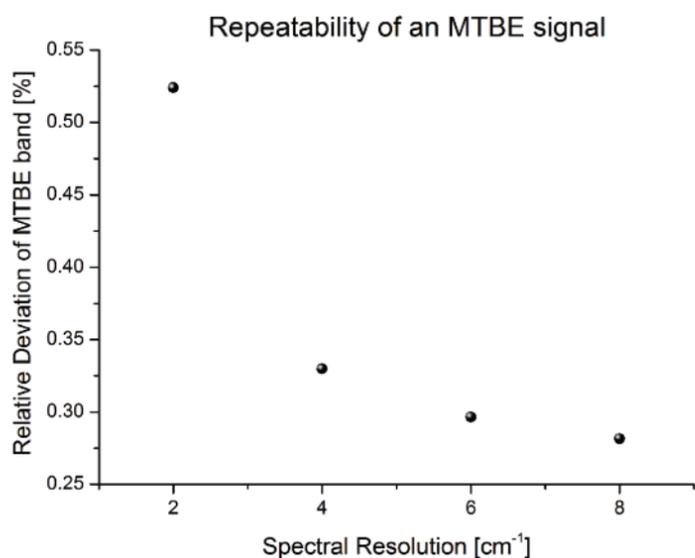


Figure 3: Influence of spectral resolution on the repeatability of the measurement

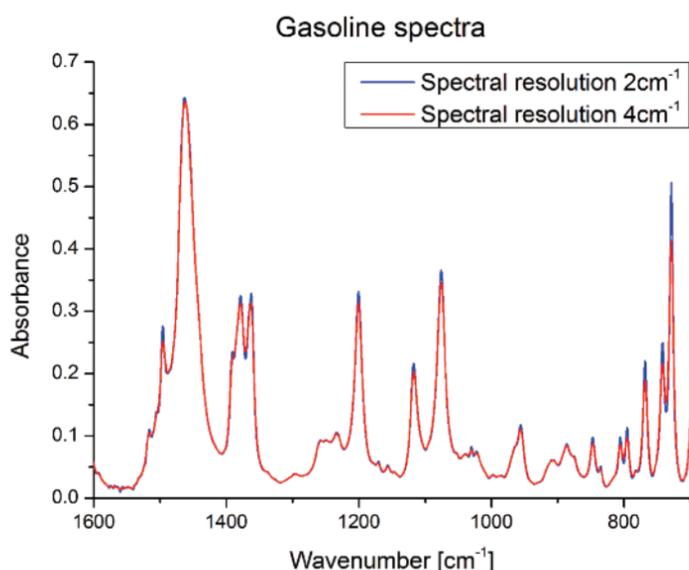


Figure 4: Gasoline spectra at different spectral resolutions

linewidth of vibrations for molecules found in gasoline is larger than 10 cm^{-1} . To resolve these bands a resolution of 4 cm^{-1} as described in ASTM standards is sufficient. Increasing the spectral resolution further only leads to a decrease of the signal to noise ratio as illustrated in figure 3. Additionally spectra at a spectral resolution of 4 cm^{-1} are measured in half the time as at a resolution of 2 cm^{-1} because the moving mirror has to move a shorter distance. This helps to shorten analysis time and to increase sample throughput.

Fuel and lubricant analysis using FTIR spectroscopy

Fuels are complex mixtures of alkanes (paraffins), alkenes (olefins) and aromatics. Moreover, they are blended with a wide range of additives to enhance combustion and exhaust emission parameters. Therefore typically oxygenates are used such as MTBE, ethanol or methanol, which can be readily monitored by IR spectroscopy according to ASTM D5845. Other components have to be monitored because they are strictly regulated by authorities due to environmental and health concerns. Benzene for example can be monitored according to ASTM D6277 and EN 238 using IR spectroscopy.

In recent years the increasing desire to use renewable fuel sources led to blending of bio-ethanol to gasoline. FAME, an ester produced from vegetable oil, is often added as a CO_2 -neutral component to Diesel fuel (ASTM D7806, EN 14078). All these components are present in modern fuels in typically high concentrations. However, there are fuel additives such as MMT or 2-EHN which have a significant effect on fuel properties already at very low concentrations. 50 mg/l MMT for example boosts the RON by typically 2.5 and 250 mg/l of 2-EHN the Cetane number by 1.7. It is therefore of high importance to measure these parameters as accurately as possible alongside other additives that are present at much higher concentrations.

As described earlier, longer path lengths of the transmission cell lead to higher signals allowing lower limits of detections. Components of high concentrations will lead to strong or even total absorption of light if the path length is too long. To be able to measure additives present in both high and low concentrations accurately, ERASPEC, an FTIR fuel analyser by eralytics, offers a dual cell system. Typically, additives present in high concentrations like ethanol (up to 25 Vol%) are measured in a 20 μm cell while additives present at low concentration like MMT (added in the ppm range) are measured in a 100 μm cell.

Component concentrations, however, are not the only interesting values of fuels. There are various parameters such as RON, MON, distillation properties, evaporation points and vapour pressure, which are of high interest as well. Such fuel parameters cannot be pinned to specific signals in a spectrum because they do not correlate with single fuel components. Using various different signals and applying advanced statistical methods such parameters can be calculated from a spectrum. For most accurate results it is not enough to measure the spectrum as accurately as possible but the analyser has to use a spectral database for the correlation of the parameters. Therefore the result also highly depends on the quality of the reference data, for example the knock engine results for the octane numbers or the vapour pressure measured using one of the available mini methods. To obtain reliable predictions using such a model the predicted value also has to fall within the calibrated range of the model. If only samples with octane numbers between 90 and 92 have been used for calibration, the analyser will not be capable to calculate accurate results for gasoline with an octane number of 95. Additionally, due to the complexity of fuels and their regional variations no overall database can be created. ERASPEC, with several hundred installations worldwide, therefore offers comprehensive databases for different regions in order to achieve most accurate results.

Another field of application of IR spectroscopy is the condition monitoring of lubricants. In contrast to fuel analysis the main interest is to monitor chemical changes of the oil during use affecting its performance. Parameters such as oxidation (ASTM D7414), nitration (ASTM D7624), sulphation (ASTM D7415) and phosphate antiwear additive depletion (ASTM D7412) as well as antioxidant depletion (ASTM D2668) can be readily monitored in the mid-IR spectrum. In addition, IR offers a quick screening for various contaminants like water, glycol, fuels or soot according to ASTM E2412. ERASPEC OIL also calculates total acid and base numbers using a database spanning all relevant values of the sample range.

IR spectroscopy is a versatile tool for various analytical questions concerning fuels and lubricants. Thorough design regarding the spectrometer itself combined with intelligent spectral analysis using extensive databases is the key element for reliable fuel or lubricant analysis. ERASPEC and ERASPEC OIL by eralytics are portable and rugged analysers offering tailor-made solutions for fuel and lubricant analysis. They deliver precise analysis results in the lab as well as in the field.



Figure 5: Portable ERASPEC analyser by eralytics (www.eralytics.com)