Chemical changes that can readily be monitored using IR spectroscopy contain contaminations, degradation of the oil and the depletion of additives being consumed during operation. During its combustion fuel is oxidized forming water and carbon dioxide at high temperatures. Incomplete combustion, especially during the warm-up of the engine, however, can lead to a series of by-products. Partly oxidation of fuel may lead to esters, ketones, carboxylic acids and other substances dissolving in the lube oil. Especially the carboxylic acids decrease the pH of the oil and are typically neutralized by the base reserve of the oil to counteract acidification. Reactions with nitrogen stemming from the combustion air can lead to nitration forming mainly nitrogen oxides. Sulfur contained in some heavy fuels may lead to the formation of SO2 and SO3 resulting in sulfation of the lubricating oil. All these chemical processes change the properties of the lube oil. If for example the base reserve or phosphate antiwear additives as well as a base reserve. These additives are used up during the operation and the oil should be changed on time before they are depleted completely.

Physical Background of IR Spectroscopy

Infrared radiation is 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

To meet this demand for on-site testing eralytics developed the portable, rugged FTIR spectrometer ERASPEC OIL. It offers automatic sample introduction and automatically calculates results from the measured IR spectrum in seconds. Its operation was simplified so that anyone can be trained within minutes making it the ideal tool for on-site testing.
applications, mostly NIR and mid-IR spectroscopy are used. In IR spectroscopy, IR radiation is directed through the sample to be analyzed 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

$$A = -\log \left( \frac{I_0}{I} \right) \propto c \cdot l \cdot \alpha(v)$$

where $c$ is the concentration, $l$ is the sample path length and $\alpha(v)$ 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 $\alpha(v)$ depends on wavelength. By measuring the absorption at a constant path length over a broad spectral range in the IR region the concentrations of many different substances can be determined simultaneously.

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.

**FTIR Spectrometer**

Nowadays the instrument of choice to measure complete IR spectra is the Fourier Transform InfraRed (FTIR) spectrometer. 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 modulation 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 $I_v$ to that of the source $I_0(v)$, the (sample) absorption spectrum is obtained according to formula 1. The absorption spectrum will show a set of bands corresponding to frequencies where the sample absorbed light.

**IR Spectroscopy of Lubricating Oils**

As already mentioned earlier IR spectroscopy is a widely accepted technique for in-use oil analysis. The all-embracing standard is the ASTM E2412 method which sums contamination and degradation analysis but also distinguishes different methods to analyze three kinds of lube oils: Petroleum lubricants, extreme pressure fluids and synthetic polyol ester lubricants. Each of these three groups needs to be treated differently due to their completely different chemical nature. In the following paragraphs the focus lies on the evaluation of petroleum lubricants. The standards describe how the IR spectrum recorded from in-service oils has to be evaluated. They define areas in the spectrum that correlate with one property of interest of the in-service oil such as nitration or oxidation. For contaminants such as water, Diesel fuel or glycol specific absorption signals of these contaminants are evaluated. Soil as a contaminant is treated differently due to the fact that it doesn’t exhibit a specific IR absorption. Soot particles disperse the IR light and therefore cause a loss of light over the whole spectral region seen as a shift and/or tilt of the baseline. Therefore soot is evaluated in a spectral region where no other substances cause absorptions in the mid IR region. Figure 1 shows two typical spectra of in-service oil highlighting different signals correlating with chemicals exhibited by the oil during operation.

As seen from figure 1 oil spectra exhibit various overlapping features reflecting the complex mixture of modern lube oils. For an oil condition monitoring program, however, only the changes of the oil during operation are relevant. If the spectrum of the fresh oil was measured before use, these changes can be visualized easily by subtracting the fresh oil spectrum from the used-oil spectrum. Such a so-called difference spectrum is shown in figure 2. Positive signals in the difference spectrum stem from degradation products or contaminants whereas negative signals result from the depletion of additives. Figure 2 highlights the evaluation of phosphate anti-wear additives according to ASTM D7412 in red using spectral subtraction analysis.

The applicability of IR spectroscopy doesn’t stop at the evaluation of chemical compounds whether they are contaminants or caused by degradation. IR spectroscopy generates a fingerprint of the current state of a sample also including intrinsic properties such as the total acid and total base number. Such properties can be calculated from the recorded spectrum together with a database containing spectra of oil samples with known properties by using chemometric algorithms such as multi linear regression (MLR). It is self-evident that the database will have a big influence on the quality of the results. A correlation technique like MLR also depends on the quality of the reference data and therefore will always be limited in terms of accuracy by the reference method itself. The prediction of TAN, TBN and viscosity works well in oil-condition-monitoring as long as the database of oil samples from corresponding engines, Figure 3a shows TBN predictions of oil samples taken from a gas engine (red) and a Diesel engine running on Biodiesel (blue). In both cases the library for the Diesel engine was used for predicting the TBN value. Figure 3b shows the same measurements as figure 3a with the only difference that for the prediction of the gas engine values a specific gas engine library was used. The increase in accuracy for the gas engine is striking, underlining the importance of choosing the correct library.

Predicting viscosity class, change in viscosity as well as the viscosity itself can also be achieved using appropriate libraries. Especially fuel dilution effects are decreasing the viscosity of the sample and can be readily monitored with IR spectroscopy. Summarizing one can state that IR spectroscopy is a highly valuable tool to assess the condition of an in-service oil due to the comprehensive parameter list accessible.
Comparison of ERASPEC OIL with Laboratory Systems

Developing ERASPEC OIL, eralytics’ goal was to reduce the footprint of typical laboratory systems while making it a ruggedized analyzer that is robust enough to be used in the field. The complex evaluation of the spectra itself should be fully automated to ensure easiest operation for the operator. The analyzer is controlled via the intuitive touchscreen and alerts the user automatically after a completed measurement if predefined limits are exceeded or underrun. This gives the user immediate feedback on the condition of the oil facilitating decisions regarding exchange intervals or necessary downtimes.

The centerpiece of any IR spectrometer is the interferometer. Whereas typical laboratory instruments are designed for air-conditioned, vibration-free environments a portable field analyzer has extended requirements regarding its robustness. ERASPEC OIL therefore uses an interferometer design with self-aligning optics which can’t get misaligned due to vibrations for example. The second important difference to laboratory systems is that a field instrument can’t be purged with dry air removing moisture from the system. Moisture must be kept out of the instrument because it potentially interferes with the measurement of the oil-condition. To eliminate any ingress of moisture the interferometer of ERASPEC OIL is completely capsuled and equipped with an automatic drying system.

The target of an on-site analyzer must be to deliver indistinguishable results from laboratory systems. Only then operators will trust the field system to directly base decisions on the obtained results and they will no longer have to wait for confirmation from centralized testing facilities. To meet this requirement the sampling procedure, data evaluation and the spectral quality of the field instrument must be equivalent to laboratory systems. To evaluate the performance of ERASPEC OIL we ran a comparison study using Bruker and Perkin Elmer spectrometers on real world used-oil samples. Figure 4 exemplarily shows the result for nitrations measurements with a Bruker spectrometer. The obtained correlations for various parameters including nitrations, oxidation, sulfation and fuel contamination showed that ERASPEC OIL is perfectly in line with results from laboratory grade instruments.

Using ERASPEC OIL an operator will no longer be required consulting off-site oil condition monitoring experts because reliable, high quality results are generated directly on site.

Read, Print, Share or Comment on this Article at: Petro-Online.com/Articles