Used Lubricating Oil Analysis by FT-IR: An Overview

Application Note M57

Oil analysis by FT-IR is a simple method to detect dilution, degredation or illegal additives in all types of oils.

Fourier-Transform Infrared spectroscopy utilizes the interaction of invisible infrared radiation and matter. This yields valuable molecular information and allows the identification of chemicals in a few seconds without consumables or additional chemicals.
Generally, this can be used on solids, liquids and gases and of course industrial oils. This method has been widely accepted and is used by automotive industries, drilling companies, legal authorities and even at F1-racing events.

Why are in-service lubricating oils tested?

To readily assess the lubricant's performance, testing and diagnosis of oils in-service is necessary. This is especially important to prolong engine life and avoid sudden and unforeseen damages to the engine. Lubricating oils reduce friction and protect the engine's moving parts from wear and corrosion. In diesel engines, the oil must also suspend soot particle resulting from incomplete fuel combustion to avoid depositions.

If the lubricant is saturated, performance decreases significantly. The analysis of in-service oils also provides information about engine-related functions to identify component failures or harmful operating conditions.

Advantages of FT-IR in oil analysis

For one, the low cost of modern Fourier transform (FT-IR) systems, along with the ability to obtain high-quality data rapidly has made this technique very attractive.
Especially in routine analysis, there is a strong demand for for quick results in routine monitoring of in-service lubricant. FT-IR has already started to gradually replace replace various time-consuming and tedious traditional wet chemical and physical analysis methods.

Therefore, the ASTM adopted a standard practice E2412 titled; "Standard Practice for Condition Monitoring of Used Lubricants by Trend Analysis Using Fourier-Transform Infrared (FT-IR) Spectrometry" illustrating the increased application of FT-IR spectroscopy in this field.

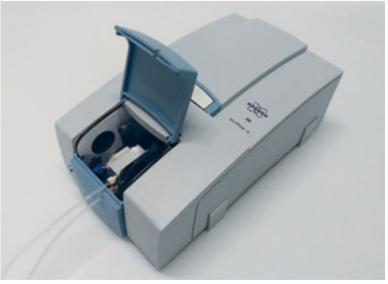

Fig. 1
ALPHA II FT-IR spectrometer equipped for oil analysis.

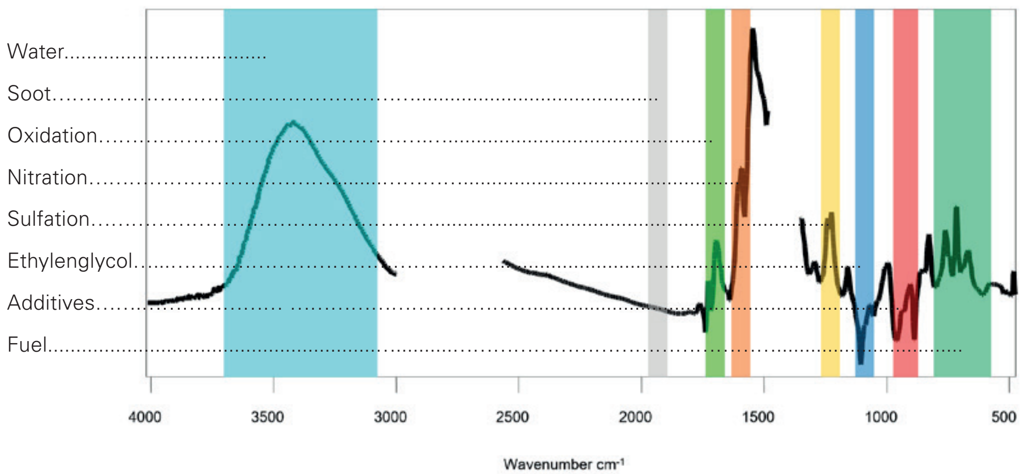

Fig. 2
The spectrum above shows the difference spectrum of a used-oil versus a new-oil reference. The areas (as marked) are used for the determination of the compounds.

The Possibilities of FT-IR Spectroscopy

Figure 2 is an overview of where exactly you can find the information you are looking for in an FT-IR spectrum of used oil. The colors are indicating the spectral region of e.g. water bands (around 3500 cm^{-1}) or oxidation products (around 1700 cm^{-1}).

It is obvious that the chemical information can be distinguished even in mixtures since the spectral features are also clearly distinct from each other.

Why FT-IR is so simple to apply

As discussed, used lubricating oil is a complex mixture of a large amount of different components and include compounds derived from the original formulation of the base oil as well as its additives, oil degradation by-products and contaminants.
The challenge of the analysis is to determine the low concentrations of these contents in the presence of the base oil and additives.

In FT-IR spectroscopy (see Fig. 2), you can subtract the spectrum of the base oil and additives from the used oil sample spectrum to obtain a differential spectrum that **only displays changes in the oil**.

In that way, the changes in the oil due to accumulation of degradation by-products, additive depletion and contamination levels can be more readily visualized.
Thanks to the digital data handling of FT-IR spectrometers, the spectra of many reference oils simply samples can simply be stored to the hard disk and compared to their respective used oil sample analysis results at a later time.
This allows for the condition of the lubricant to be trended **at different sampling time points** while it is in-service.

Traditional Analysis Methods

Conventionally, lubricants where tested with sometimes even archaic methods like testing for water content with a ‘sizzling’ test, where the lubricant is placed on a hot plate.
Of course methods like TAN and TBN anaysis (ASTM D2896 and D4739) , viscosity tests or even gas chromatography yield better and more reliable results, but require additional chemicals, preparative effort or just take a lot of time.

Degradation Processes

All lubricants will undergo degradation while in use. Three classes of reactions are dominant in the oil degradation process:

Reaction with Oxygen

Organic lubricants are exposed to high temperatures and pressures in the presence of oxygen. This inevitably leads to the formation of carbon oxygen bonds which will later form carboxylic acids. A wide variety of by-products such as esters, ketones, aldehydes and carbonates or carbonic acids are also produced during the combustion.

Reaction with Nitrogen

Nitrogen and oxygen react at high temperatures and pressure to form nitrogen oxides (NOX). These products can cause thickening, increased acidity and form sludges due to the formation of higher molecular weight compounds.

Reaction with Sulfur

Sulfate by-products are a result of the reaction of sulfur-containing compounds in fuels and oxygen present during combustion. Although high quality fuels show very low sulfur content, depending on country and regional supply this degradation increases.

Application #1: Oil Quality Testing

All lubricants will undergo degradation while in use. The most common signs of base oil degradation are increased oxidation and shear thinning.

Oxidative degradation occurs as a result of reactions with oxygen in the environment in which a lubricant resides.

Shear thinning is a physical breakdown of the oil due to pressure and temperature conditions to which the lubricant is exposed.

These and other degradation processes of the lubricant make it unable to provide adequate lubrication for mechanical moving engine parts. Therefore test methods to assess the levels of degradation by-products are paramount to determining the condition of the oil.

Application #2: Oil Dilution by Fuel

Due to improper fuel-to-air ratio, piston ring wear, fuel leaks or residual fuel get into the oil. Combustion residues mainly consist of long chain hydrocarbons with high combustion and boiling points, while fuel leakage also brings in lighter material.

Thus, in either case, the increasing fire hazard potential makes determining the presence of fuels in diesel engine oils of prime importance.

Since both diesel fuel and lubricating base oil stocks are derived from crude oil distillation cuts, they are very similar in chemical composition and physical nature. Despite that, FT-IR offers special datasets for a reliable, fast and simple analysis (Fig. 3).

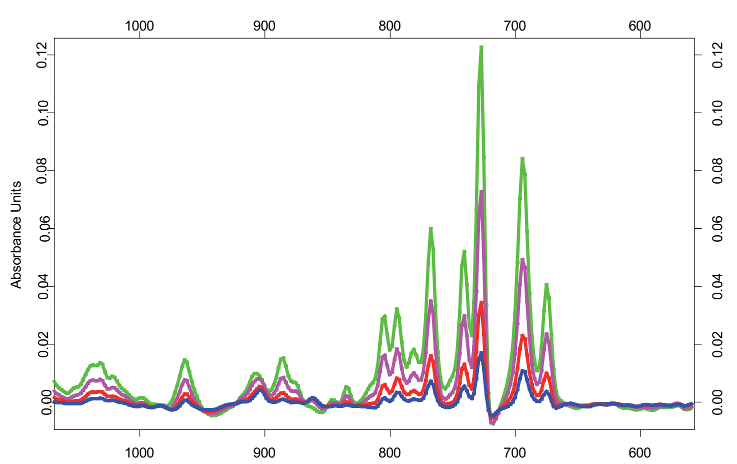

Fig. 3
The quantitative determination of gasoline fuel in oil is shown in the upper spectra. 1% (blue), 2% (red), 4% (pink), and 6% (green) of gasoline are added to an oil sample for calibration.

Application #3: Water content

Depending on fuel and lubricant quality, water tends to be a rather infrequent contaminant because of the operating conditions in the average engine. However, if present, it can indicate coolant (water) leakage.

Water contamination promotes base oil oxidation and hydrolysis of additives resulting acidity build-up and in increased wear and corrosion. The presence of water can also cause gelling of the oil and formation of emulsions affecting the viscosity of the oil leading to engine failure.

Application #4: Checking for Soot

In diesel engines, whenever a rich fuel/air mixture is burned, the incomplete combustion of fuel leads to the formation of soot. Soot buildup in the oil can be indicative of combustion problems or the excitation of the oils drain period.

Diesel engine lubricants have dispersants designed to suspend and control the size and growth of soot particles. If the levels of soot exceed the oils' capacity to hold them, the viscosity of the oil increases and carbon sludge can accumulate which starts clogging filters and passageways.

Fig. 4
INVENIO FT-IR plattform offers higher sensitivity and many productivity tools to enhance routine analysis tasks. A special feature is the transit channel, a second sample compartement.

Conclusion

FT-IR is a reliable and valid approach to oil analysis, that not only allows you to access a lot of information with a single measurement, but also simplifies the procedure.
Infrared spectrometers come in various shapes and configurations and Bruker even offers a dedicated used oil analysis kit.

Bruker Optics GmbH & Co. KG

info.bopt.de@bruker.com