



Application Note AN # 57

Used Lubricating Oil Analysis by FT-IR

Infrared (IR) spectroscopy can be used for the routine monitoring of degradation by-products, contaminants and additive levels in used lubricating oils. Acceptance of this technique as a standard method for the analysis of used oils and lubricants has been slow in coming for several reasons. The most notable hindrance is the fact, that much of the data used in assessing engine and lubricant performance have been historically obtained using traditional physical and wet chemical methods.

The lower cost of modern Fourier transform (FT-IR) systems, along with the ability to obtain higher quality data rapidly has made this technique attractive for routine analysis applications. As the need for obtaining quicker analysis results for routine monitoring of in-service lubricants increases, spectroscopic techniques such as FT-IR will gradually replace various time-consuming and tedious traditional wet chemical and physical analysis methods. Recently, the ASTM has adopted a new standard practice E2412 entitled; "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.

Why are in-service lubricating oils tested?

In-service lubricating oils are tested to diagnose the lubricant's condition in order to determine when there needs to be an oil change to avoid engine damage and prolong

engine life. Engine oils provide lubrication of engines moving parts and protect them from wear and corrosion. In diesel engines, the oil must also suspend soot particles resulting from incomplete combustion of fuel. The composition of the lubricating oil can indicate whether there was improper combustion seal leakage or any changes in the base oil. The analysis of in-service oils also provides information about engine-related functions to identify component failures or harmful operating conditions.

Characteristics of degrading oil and classical analytical test methods for.

Fuel dilution

Residues of fuel normally gets into the oil due to improper fuel-to-air ratio, piston ring wear or fuel leaks. Fuel contamination coming as a result of a blow-by by way of the combustion chamber usually only results in the fuel heavy ends-entering the oil while fuel contamination as a result of a line leakage is much less frequent but also contains the lower boiling point fraction. In either case, to determine whether fuel is present or not is one of the most important parameters for used lubricant testing. High levels of fuel (typ. 2%) reduces the lubricant viscosity and decrease its efficiency. In addition the fire hazard potential of fuel leaks 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. Therefore it is very difficult to detect diesel fuel dilution in engine oils. GC is the method normally used for this kind of analysis but FT-IR based on serious datasets offer a more fast and simple way for this kind of analysis.

Water content and coolant contamination

Even though it is a by-product of combustion, water tends to be a rather infrequent contaminant because of the operating conditions in the average engine, but it could be indicative of coolant leakage. Water contamination can also be a result of condensation from the atmosphere, especially in cold engines, although water from this source is not generally a problem, since it will evaporate when the engine reaches its operating temperature. 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. Water is detected by its separation from a cooled oil sample at high levels, by Karl Fischer titration, or by using a hot plate (Crackle Test). Ethylene glycol coolant detection is done most with a colorimetric test using Schiff's reagent and quantitatively by help of gas chromatography.

Soot

In diesel engines, anytime a rich fuel/air mixture is burned, the incomplete combustion of fuel leads to the formation of soot. The increase of soot content of 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, but when the levels of soot increases beyond the oils capacity to hold them, the viscosity of the oil increases and carbon sludge can build and accumulate plugging filters and passageways. Abnormal soot contamination levels normally occur in engines with excessive ring wear or a high fuel to- air ratios. Common methods used to access the level of soot are, membrane filtration and thermogravimetric analysis (TGA). The first two methods indicate all particulates present and are not specific for soot. Total insolubles can be done by the pentane insolubles method or by using the ASTM coagulant approach before centrifugation. TGA is a very good method that is specific for soot.

Oil quality

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

Reaction with oxygen – In all lubricants, organic compounds exposed to high temperatures and pressures in the presence of oxygen leads to the formation of carbon oxygen bonds which then leads to the formation of carboxylic acids. A wide variety of by-products such as esters, ketones, aldehydes and carbonates or carbonic acids are produced during the combustion. The distribution and composition of all these compounds are very complex. Some compounds are dissolved in the oil others are adsorbed by the oil additives. The carbonic acids contribute to the acidity of the oil and its formation can be measured using total acid number (TAN) or indirectly by total base number (TBN), which assesses the consumption of basic reserve additive in the oil. in the oil.

Reaction with nitrogen – The reaction of the organic compounds with nitrogen and oxygen in the at high temperatures and pressure produce leads to the formation of nitrogen oxides (NOX). These products can cause thickening, increased acidity, varnishes and sludge due to the formation of higher molecular weight compounds, varnishes, sludge and acids. The acids present in the oil can again can be detected by TAN or, TBN levels and the high molecular weight products can be detected by measuring changes in viscosity.

Reaction with sulphur – Sulfate by-products are a result of the reaction of sulfur-containing compounds in fuels with oxygen during combustion as well as oxidation of sulfur containing additives in the oil. Often the measurement of the oil's viscosity is used to get information on the oil's lubrication abilities. The viscosity however is not specific to oxidation processes but also to other factors, such as dilution or shear thinning. Therefore, TAN and TBN measurements are used in addition to viscosity measurements to monitor oil degradation, due to the normally acidic species formed during oxidation.

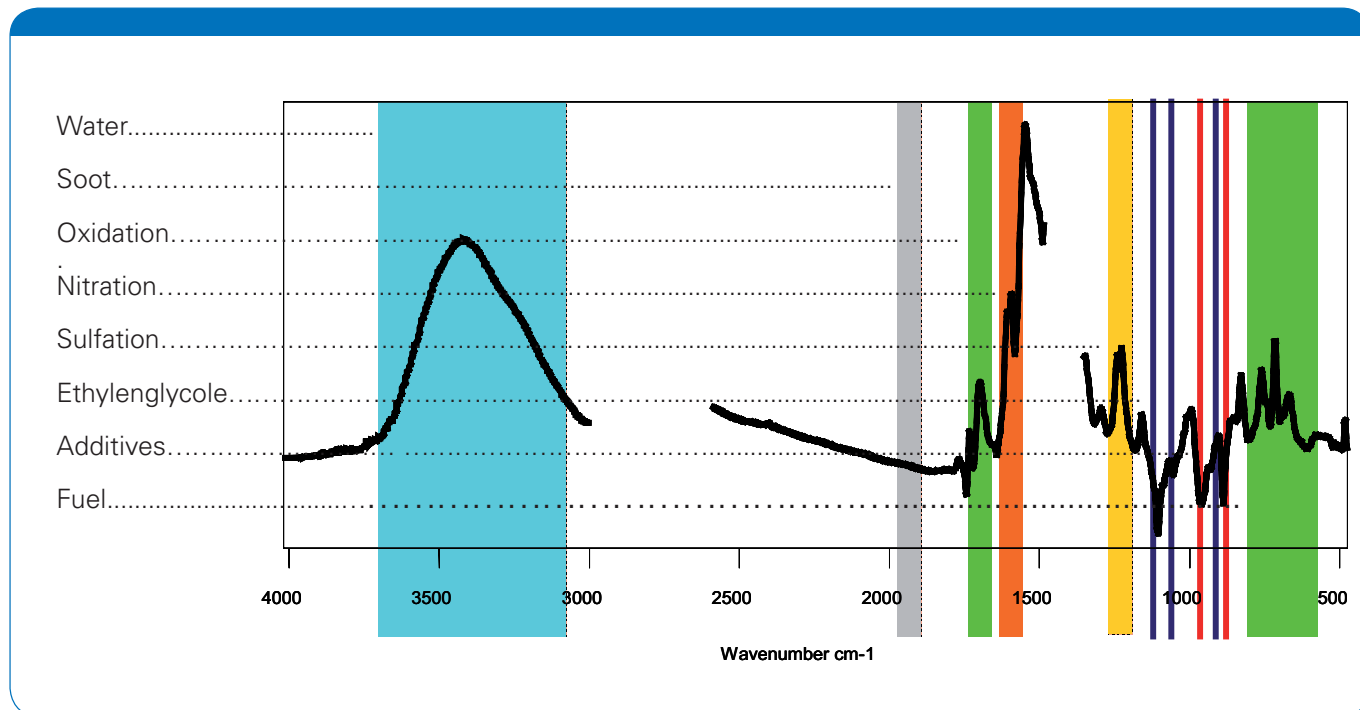
Wear metals in the oil

Metals are detected by elemental analysis, as well as other elements originating from coolant contamination or infiltration such as silicon, boron and sodium are detected. For the infrared analysis. These compound may influence the soot value during infrared analysis.

Oil analysis by Fourier transform infrared spectroscopy

Used oil samples are complex mixtures of a large number of different compounds and include compounds derived from the original formulation of the base oil and its additives, oil degradation by-products and contaminants. The challenge of the analysis is to determine the small concentrations of degradation by-products and contaminants in the presence of the base oil and additives. In FT-IR spectroscopy, you can subtract out the spectrum of the base oil and additives from the used oil sample spectrum to obtain a differential spectrum and which represents only the 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. Due 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.



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.

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