

Monitoring oil degradation with infrared spectroscopy

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What is infrared ?

What is infrared? This thing that allows us to "see" in the dark, helps secure our homes, allows those couch potatoes amongst us to change the channel on the TV without leaving our seats and, in our case, monitor oil degradation. To answer this we need to take a look at the electromagnetic spectrum

(Fig. 1). To many, the electromagnetic spectrum is a formidable subject, yet to the analytical chemist it is a tool so useful it is without comparison. The electromagnetic spectrum is made up of electromagnetic waves. These are waves of energy that have both an electrical and magnetic component. These waves all travel at the same velocity - the speed of light (approximately 299 792 km per second) but their properties are determined by their frequency and wavelength. The electromagnetic spectrum ranges from gamma radiation and x-rays

The electromagnetic spectrum is a tool without comparison to the analytical chemist.

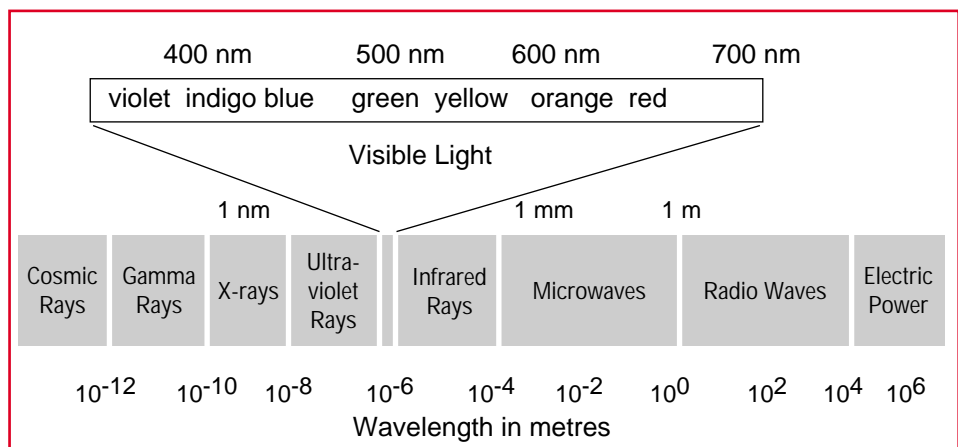


Figure 1.

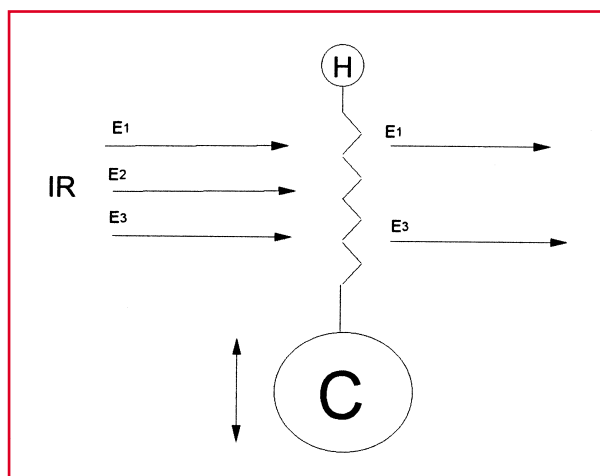


Figure 2.

Chemical bonds in a molecule exhibit "characteristic IR absorptions".

(molecular structure elucidation as in NMR spectroscopy) (Fig. 1).

The infrared region of the spectrum lies to the right of the red end of the visible spectrum. We are unable to see this "light" although certain animals such as the pit viper can, enabling them to hunt at night. Infrared radiation was first described by William Herschel in 1800. He produced a solar spectrum by placing a glass prism in the path of the sun's rays and observed the changes, which took place when light of different wavelengths (different colours) fell onto the bulb of a sensitive thermometer. He noticed that the temperature rose as the thermometer was moved from blue to red, but he also found that the thermometer registered even beyond the red end of the visible spectrum. Subsequent experiments showed that this portion beyond the red was composed of a similar type of radiation to visible light, in that it could be reflected, refracted and absorbed by materials, which would reflect, refract and absorb visible light.

How do we use it ?

Now we know what infrared radiation is, how is this utilised by the analytical chemist? All covalent chemical bonds such as those in organic molecules (i.e. CH_4 or

(used to determine crystal structure) through the visible radiation (used in all emission spectroscopy such as ICP) right down to radio waves

methane) as opposed to ionic bonds, those found in inorganic molecules (i.e. NaCl or common salt), absorb infrared radiation, causing them to vibrate by stretching and contracting. Which part of the infrared spectrum the molecules absorb, depends on the strength of the chemical bond between the atoms, which in turn is influenced by their atomic structure. An analogous way of visualising this phenomenon is demonstrated by Hooke's law of springs, where the amount of energy to start the spring oscillating is related to the strength of the spring and the mass on the end. In our case this is the energy of the absorbed IR and the nature of the bond between the C and H atoms (Fig. 2). The amount of energy in the IR beam is related to its wavelength; the smaller the wavelength the more energy. Although in this case only the exact energy, E_2 , required to cause vibration, is absorbed. All others, both smaller and greater, have no effect, i.e. E_1 and E_3 .

Therefore for a molecule with several different kinds of bonds (e.g. a C-H and a C=O), we would expect to see at least two different absorption bands. Chemical bonds within a molecule are therefore said to exhibit "characteristic IR absorptions". It is this property that is utilised by the analytical chemist. Chemists refer to these absorbencies as "wavenumbers". This is just a more convenient way of discussing the frequency of the absorbed radiation, and is simply the number of waves in one centimetre. The final piece to the equation is how much of this radiation is absorbed. This is given by a simple law called the Beer-Lambert law that says the amount of infrared absorbed is proportional to the concentration of the absorbing species and the distance the IR light has to travel through it.

What is FTIR ?

IR spectroscopy uses an electrically heated glowbar as the infrared radiation source, and this radiation is passed through the sample to the detector. The chemical constituents of the sample absorb some of the infrared at reproducible and specific wavenumbers.

The original method involved using a prism or diffraction grating to separate out the individual wavenumbers and then detect them portions at a time as they were passed through the sample, and plot the absorbance against the wavenumber. This process was incredibly slow and depending on the accuracy required could take as long as 10 minutes per sample.

The modern FTIR or Fourier Transform infrared uses something called the Michelson interferometer. This nifty device utilises a moving mirror, whose speed is monitored by a laser, which also acts as a wavelength reference. The detector then measures the summation of all the frequencies over time resulting in a time-dependent interference pattern called an interferogram. A computer algorithm called a Fast Fourier Transform is then used to convert this signal to an absorbance spectrum. This is then ratioed to a

background spectrum of the empty cell to remove the contribution of atmospheric contaminants such as CO₂ and water vapour (Fig. 3). This whole process takes as little as 1,5 seconds per scan which allows for multiple scans on the same sample and for amplifying signal differences so that minute variations can be detected, giving greater accuracy.

Several years ago, Wearcheck purchased a new Biorad FTIR. This represented two major changes in the methodology for determining oil degradation and combustion by-products.

- Spectral subtraction was replaced with computational interrogation of the IR spectrum and the resultant data "trended".

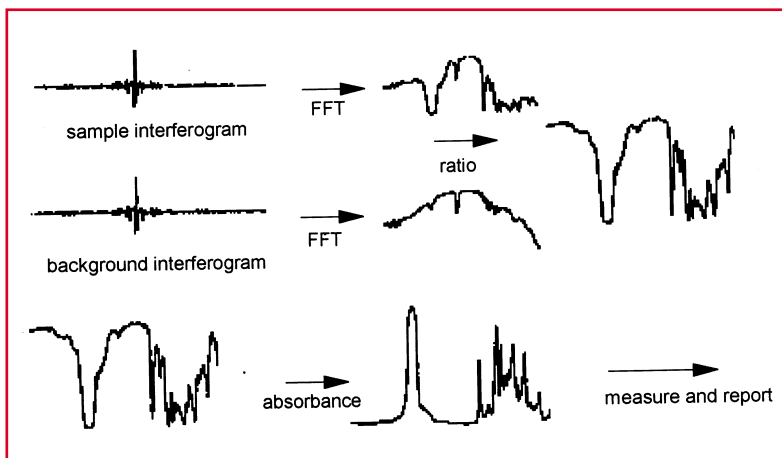
- The HATR or horizontal attenuated total reflectance cell was replaced with a 100-micron transmission cell.

Spectral subtraction vs trending

Spectral subtraction is essentially the subtraction of all the IR spectra data from a sample of the new oil from the IR spectra of the used oil, essentially resulting in the difference between them. This difference data is then used by software routines to calculate numbers representative of the degree and type of degradation or contamination which has occurred.

There are various computer algorithms, which can automate this process thus removing any operator interpretation or bias. However, these algorithms cannot address the strict requirement for using the correct new oil in the subtraction process.

Figure 3.



Wearcheck uses trending to eliminate spectral subtraction problems.

Such a requirement complicates the overall laboratory procedure as the exact new fluid placed in the machine must be submitted, tracked, stored and correctly recalled and re-measured with all later samples from the same machine. Additionally, oil in machines is topped up periodically to compensate for oil consumption which further complicates the subtraction process. Although the top-up oil may be the correct type, it may not be the same manufacturer, lot number or even the same blend. These complications will inevitably produce misleading or incorrect results.

Wearcheck has therefore adopted a simple trending methodology to eliminate the problems associated with spectral subtraction. In this method, areas under the infrared curve are measured and reported. The key to successful implementation is the careful selection of appropriate areas to be measured. (This work was carried out by Biorad and is embedded in the FTIR control software.) These measurements can then be compared to either the expected infrared response from similar or identical machine components, or as in Wearcheck's case, to the set of previous infrared measurements from the same machine. If a particular parameter is maintaining a constant value and no adverse wear or performance degradation is apparent, then there is no reason why that parameter should be unacceptable. However, what is acceptable in one component doing a particular type of operation may not be acceptable in another component doing a different type of operation. As long as the overall analysis with respect to trend remains constant, a state of normality is assumed. This trending methodology is already utilised in wear metal analysis by ICP. Using

this method and the conversion of spectral data into numerical condition indicator data, simplifies tracking and documentation and greatly reduces storage requirements as neither the new oil sample or its spectrum need be saved.

Initially FTIR work was performed using an HATR or horizontal attenuated total reflectance cell. This was a horizontally mounted zinc selenide (ZnSe) crystal. The oil sample was placed on the cell and an IR beam bounced off the bottom of the crystal, penetrating slightly into the oil on each bounce. The sampling depth was effectively about 2 microns per reflection. This however had several major disadvantages.

- The cell could be easily scratched by metal particles found in the used oil.
- Low sensitivity was experienced due to the small beam penetration.
- It was manually intensive, with potential exposure to cleaning solvents.

A more recent addition to sampling techniques is the transmission cell (Fig. 4). This consists of two ZnSe crystals separated by a 100-micron spacer. The oil sample occupies the space between the two crystals and the IR beam passes directly through the cell and sample to the detector. This has the following benefits.

- A 20-fold increase in sensitivity.
- The filling and cleaning of the cell can be automated.
- Cell damage is eliminated by an in-line filter designed to remove particles big enough to scratch the crystals.

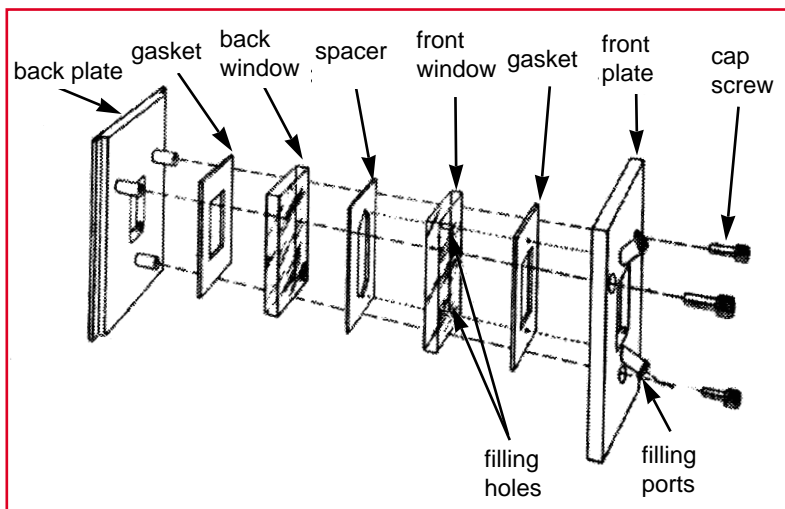


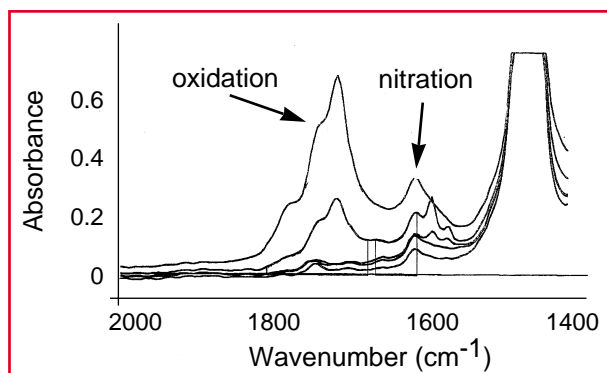
Figure 4. Construction of an FTIR transmission cell.

Combustion by-products

Oxidation products

In all lubricating systems, organic compounds exposed to high temperatures and pressures in the presence of oxygen will partially oxidise (react chemically with the oxygen). There are a wide variety of by-products produced during the combustion process such as ketones, esters, aldehydes, carbonates and carboxylic acids, and the exact distribution and composition of these products is complex. Some of these compounds are dissolved by the oil or remain suspended owing to the dispersive additives in the oil. Carboxylic acids contribute to the acidity of the oil and deplete its basic reserve as neutralisation takes place. The net effect of prolonged oxidation is that chemically the oil becomes acidic causing corrosion while physically an increase in viscosity occurs.

Figure 5.



Superimposed spectra of successive samples showing the increase in the oxidation and nitration peaks.

FTIR determines the level of oxidation by a general response in the carbonyl (C=O) region of between 1800 to 1670 cm^{-1} . In this region, infrared energy is absorbed due to the carbon oxygen bonds in the oxidised oil. Very few compounds found in new petroleum lubricants have significant absorbencies in this area. Monitoring this region is thus a direct measurement of the oxidation level, as compared to a secondary technique such as the TAN (Total Acid Number), which takes into account all the acidic species in the oil.

Nitration products

In addition to oxidation products, nitration products are also formed when organic compounds are exposed to high temperatures and pressures in the presence of nitrogen and oxygen. These are generally in the form of nitrogen oxides such as NO, NO₂ and N₂O₄. In addition to causing oil thickening and some of these products being acidic, nitration products are the major cause of the build-up of varnish or lacquer. A rise of the nitration index of an oil can indicate mistuning (i.e. incorrect fuel/air ratios) or improper spark timing. It can also reflect operating conditions, i.e. high loads, and low operating temperature and such things as piston ring blow-by.

Nitration products can be monitored by FTIR as they have a characteristic absorbance of between 1650 to 1600 cm^{-1} , the region immediately below that of the oxidation products (Fig. 5).

Sulphation products

Sulphur compounds are typically found in crude oils and may also be used as additives in lubricating oils to achieve certain desired properties. Sulphate by-products such as

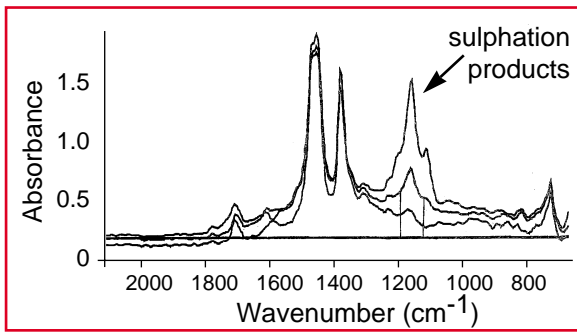


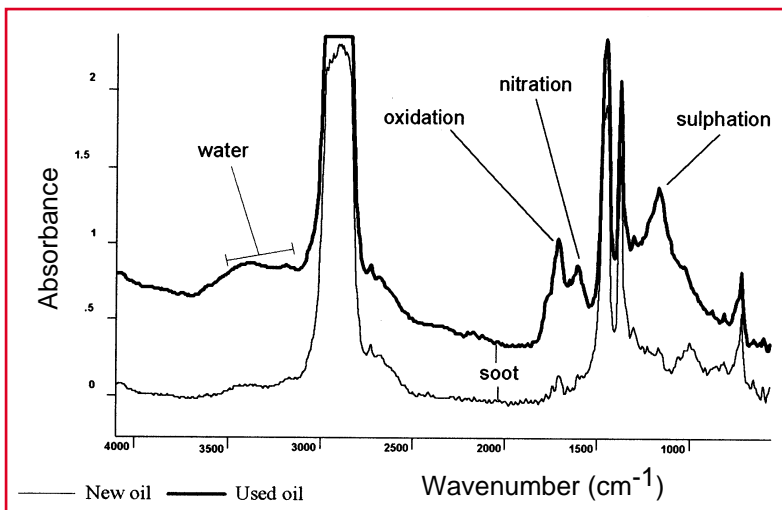
Figure 6.

SO₂ and SO₃ are formed by the oxidation of these sulphur containing compounds. They subsequently escape into the lubrication system around the piston rings and seals and build up over a period of time. These compounds increase the production of varnish and sludges and generally degrade the oil. They also react with the water formed during combustion to produce powerful inorganic acids such as sulphuric acid (H₂SO₄). These acids are neutralised by, and therefore deplete, the basic reserve in the additive package of the oil. Measurement of these compounds gives additional information on mistuned engines and ring failures. Sulphates are measured by FTIR in the same way as oxidation and nitration, by monitoring the increase in their characteristic infrared absorbances, found between 1180 and 1120 cm⁻¹ (Fig. 6).

Soot

Anytime a too rich fuel/air mixture is burned, soot particulates are formed. An increase in the soot content of the oil is therefore usually indicative of combustion problems,

Figure 7.



or that the drain period may have been extended. Soot build-up is a problem in lubrication oils as it changes the viscosity and prematurely clogs the filters and oil galleries.

The FTIR analysis of soot is an exception to the general area-under-the-curve technique used for other contaminant parameters, since a characteristic feature of soot is the lack of any specific infrared absorption bands. Rather the soot particles cause a general scattering of the infrared radiation, which is more severe at higher wavenumbers. Soot loading is therefore simply measured by taking the absorbance intensity at 2000 cm⁻¹. Figure 7 shows the overall spectrums of a used and new engine lubricating oil.

Fuel dilution

Automotive fuels can consist of a wide variety of branched aliphatic compounds such as octane, aromatic compounds such as benzene, and many other compounds blended to produce a desired set of physical properties. This is especially so in countries such as South Africa where the fuel comes from either coal-derived or petroleum-derived sources. In addition, the conditions in an engine will cause the overall composition of the fuel to change, partly due to incomplete combustion and partly due to the distillation of the lighter fractions.

In an ideal situation the choice of the fuel remains constant and FTIR becomes a powerful tool in detecting fuel dilution, by measuring the absorption bands of the specific components of the fuel and the drop in the absorption bands of the oil as it is diluted (Fig. 8).

In light of the real and non-ideal situation, fuel dilution is usually

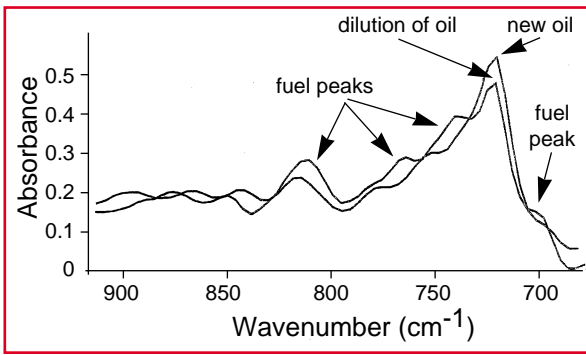


Figure 8.

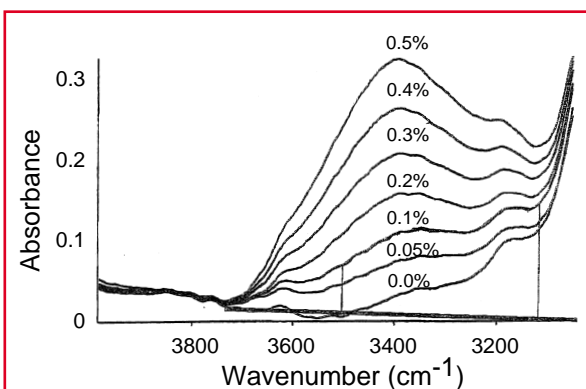
Predictive technology

Additionally, the Wearcheck FTIR is used as a screening tool for water and TBN (Total Base Number) measurement of engine oils.

Water

Even though it is a by-product of combustion, water tends to be a rather infrequent contaminant (approximately 1% of samples) because of the operating conditions in the average engine, but it could be indicative of a coolant leak. When there, however, it "readily" dissolves or disperses in the oil. Water is a very strong IR absorber and as such is very easy to detect (Fig. 9). It also appears in a region of the IR spectrum where few other compounds that appear in petroleum oils will have significant absorbencies. Due to the increased difficulty of doing crackle tests on engine oils where the "boil" of any fuel present might mask the crackle of any water, and since all these samples

Figure 9.



determined by flashpoint measurements or, as is the case at Wearcheck, by gas chromatography (GC).

samples submitted only 5% are trapped for an actual water test and of these only 20% contain actual water.

TBN

Due to the potential health hazards and environmental considerations, it is not possible to carry out actual TBNs on all engine samples that come into the laboratory, so infrared is used as a screen and only those that are predicted to be below 6.0 will have an actual TBN measurement done.

The TBN of an oil sample cannot be easily defined by infrared analysis as can oxidation or sulphation which have very characteristic absorbencies. TBN is dependent on a wide range of factors each having varying degrees of influence. PCR/PLS or principle component regression and partial least squares analysis are mathematical routines which have allowed Wearcheck to develop a system which enables the laboratory to predict the apparent TBN of a sample. This method uses the whole spectrum instead of an individual peak or discrete area to derive a value for an unknown.

A series of 80 oils with duplicate TBN values were used to create a "training" set, to establish the measurement criteria. These oils came from various engines, various lubricant manufacturers, differing grades and were not limited to any particular application. The software was used to break down the training set to a smaller set of principle components or factors. These factors were then integrated to predict the unknown.

A correlation graph of the actual and predicted TBN values is shown overleaf (Fig. 10). This process avoids unnecessary wastage and consequently only 7 % of samples

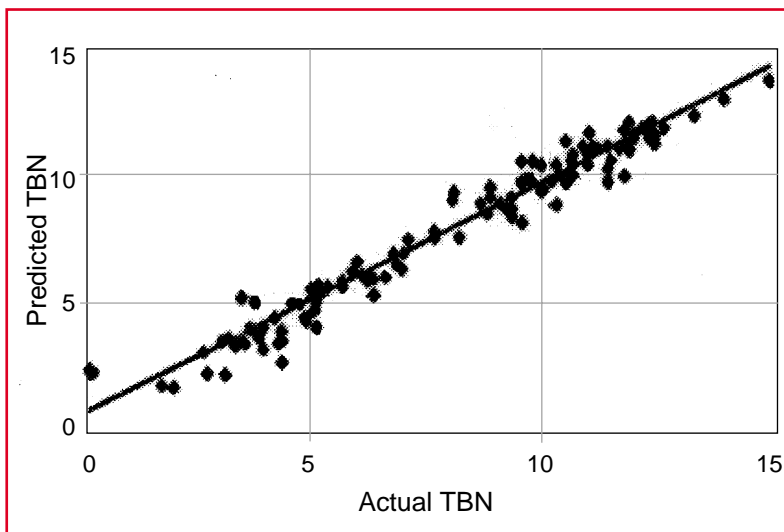


Figure 10.

have an actual TBN carried out. Of these over 70% fall in the 3 to 7 range.

Although FTIR provides a wealth of information about the condition of used lubricating oil, this information is complementary to that obtained by the various other spectroscopic and physical property tests used by Wearcheck to give an overall picture as to the condition of the oil and machinery in which it is used. ✓

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