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Infrared Analysis as a Tool for Assessing Degradation in Used Engine Lubricants

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Introduction

The use of infrared spectroscopy for routine monitoring of oil-lubricated components, breakdown products and contaminants has not been widely used in the past, although infrared studies of lubrication oils themselves have been performed for a number of years. The reason for this is that older dispersive infrared spectrometers would take several minutes to generate a spectrum of the used oil and then considerable additional time would be needed to reduce and interpret spectral data.

Infrared analysis has become a powerful, practical, analytical tool.

New technology has yielded the Fourier Transform Infrared (FTIR) Spectrometer and the micro computer. This combination in modern equipment produces infrared spectra in seconds and sub one minute data reductions. Infrared analysis has become a powerful, practical analytical tool for used oil analysis. Wearcheck purchased an FTIR Spectrometer and Oil Analysis software from Perkin Elmer in September 1990.

Oil degradation processes

To extract information from infrared spectra of used oils, a basic knowledge of the processes involved in oil degradation is required.

The lubricant in a combustion engine is operating in a very hostile environment, temperatures are high, and the lubricant is dispersed over a large surface area where it is exposed to chemically reactive by-products of the combustion process. In addition to this, the oil is exposed to sources of internal and external contamination.

Oil degradation by chemical change

The chemical degradation of an engine lubricant may be defined by a number of processes:

OXIDATION - At elevated temperatures, oil exposed to oxygen from the air, will oxidise (chemically combine with oxygen) to form a variety of compounds. The majority of these are carbonyl containing compounds (C=0) such as Esters, Ketones and Carboxylic acids. Some of these compounds are dissolved by the oil, or remain suspended owing to 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. The increase in viscosity

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however, may be masked by other factors such as fuel dilution.

NITRATION - Nitration is another form of oxidation often termed nitro-oxidation. Nitration results from the reaction of oil components with nitrogen oxides (NO, NO_2 and N_2O_4) that are produced from the oxidation of atmospheric nitrogen during the combustion process. In addition to causing oil thickening, nitration products are the major cause of the build-up of varnish or lacquer.

SULPHATE FORMATION - The various oxides of sulphur and water, both of which are combustion by-products, react together to form sulphuric acid.

This acid is neutralised by the basic reserve in the additive package of the oil and normally results in the formation of metallic sulphates. An indication of the progress of neutralisation is obtained by monitoring the build-up of metallic sulphates in the oil.

Oil degradation by contamination

Detrimental contamination may occur from both external and internal sources.

INTERNAL CONTAMINATION - This mainly comprises soot and metallic particulates (wear metals). Both these contaminants occur on a continuous basis and will build up to undesirable levels at which time the lubricant should be discarded. The rate at which unacceptable levels of contaminant are reached will depend on the condition of the engine and its operating conditions.

EXTERNAL CONTAMINATION - The main contaminants in this category are unburnt fuel, coolant and dirt. These contaminants result from malfunctions and failures in the fuel, cooling and air intake systems respectively.

It is essential that these contaminants are detected early if catastrophic failures are to be avoided.

Infrared analysis of used oils

Infrared analysis on used engine oils can provide a great deal of information about what happens to an engine in service within a relatively short period of time. In a number of areas, infrared information is favoured over conventional oil analyses as it is regarded as having a greater diagnostic value. One should, however, exercise caution when interpreting data as engine design and operating conditions play an important part. A series of results from consecutive samples in which trends are evident has far greater diagnostic value than results from a lone sample. Important results that are available from infrared measurements and their interpretation are detailed below:

SOOT INDEX - The soot index is a measure of the level of partially burned fuel particles (soot) in the oil. The rate at which soot is deposited in the oil is dependent on engine design and operating conditions. An increase in the soot index will indicate poor combustion or an oil and filter change period that has been over-extended.

OXIDATION INDEX - The oxidation index measures the degree to which the oil has been oxidised and is a good indicator of oil degradation. A rapid increase in oxidation may indicate engine overheating or a depletion of the anti-oxidant additive in the oil due to an over extended oil drain period.

SULPHATE INDEX - The sulphate index measures the extent to which sulphur-based acids have entered the

Infrared radiation is part of the make-up of the electromagnetic spectrum.

oil. A rapid increase in the sulphate index could be due to depletion of oil additives, poor combustion or overcooling.

NITRATE INDEX - The nitrate index measures the build-up of nitrogen compounds in the oil. These compounds cause oil thickening and deposits that interfere with lubrication. Nitration is influenced by incorrect fuel/air ratios, improper spark timing, high loads, low operating temperatures and piston-ring blow-by.

WATER AND GLYCOL - Water and Glycol may be detected at relatively low levels by FTIR. The presence of glycol and water or glycol alone would indicate a coolant leak. Water alone does not necessarily indicate a coolant problem, as traces of water could result from condensation, if an oil sample has been taken from a cold engine.

Background to infrared analysis

The Electromagnetic Spectrum

Electromagnetic waves are waves that have both an electric and magnetic component. Well known examples of electromagnetic waves include X-rays, visible light, microwaves and even radio waves.

These waves all travel at the same velocity ("speed of light") but differ in the wavelength and frequency bands used to describe them. Figure 1 shows the whole range of electromagnetic waves arranged in order of increasing wavelength and depicts what is known as the electromagnetic spectrum.

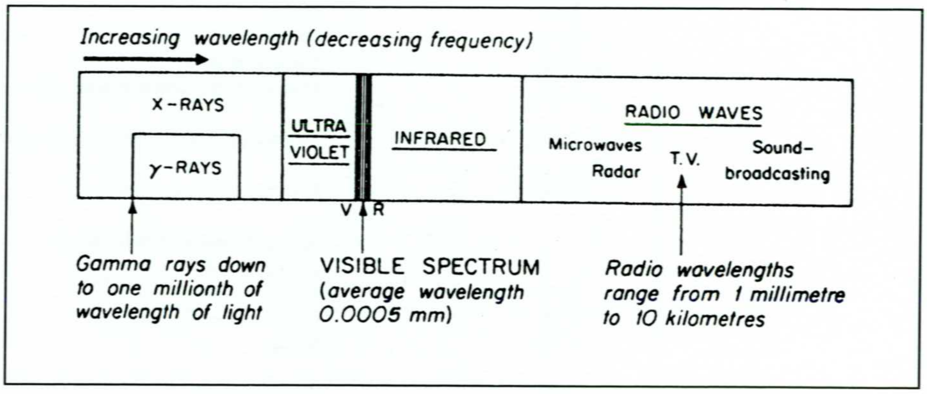
Infrared radiation

Infrared radiation is part of the make-up of the electromagnetic spectrum and covers electromagnetic waves with wavelengths between 0. 00008 cm and 0.04 cm. Chemists have adopted a more convenient method of describing infrared radiation in that it is described in terms of the number of waves that occur per centimetre. This number is called the WAVENUMBER and is actually a measure of wave frequency. Wavenumbers are calculated by dividing 1 by the wavelength expressed in centimetres.

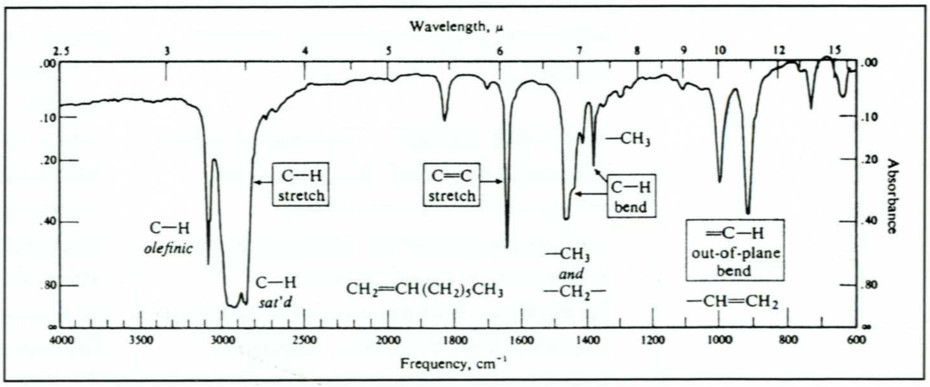
$$\text{WAVENUMBER (cm}^{-1}\text{)} = \frac{1}{\text{WAVELENGTH (cm)}}$$

Infrared analysis only uses a portion of the IR spectrum known as "Mid-range Infrared". It is defined as infrared waves having wavenumbers between 4000 and 400 cm^{-1}.

The Electromagnetic Spectrum. (Figure 1)



Spectrum of 1-Octene. (Figure 2)



Molecular vibrations and infrared absorption

The chemical bonds within organic molecules are in a state of continual vibration, with bonds stretching and contracting as well as bending relative to one another. When an infrared beam falls on a molecule, waves of specific frequencies (wavenumbers) are absorbed from the beam by the molecule, and result in changes to the molecular vibrations of the molecule. The actual frequencies of the waves absorbed depends on the types of bonds present in the molecule's structure. Different types of bonds within the same molecule would absorb different frequency bands while several identical bonds would all absorb the same frequency bands and give rise to stronger absorptions.

(Eg. A C=0 and a C-H bond in the same molecule would be expected to yield at least two different absorption bands while several C-H bonds in the same molecule would all contribute to at least a single relatively strong absorption band.) Chemical bonds within a molecule are therefore said to exhibit "characteristic infrared absorptions". Details of characteristic absorption for a number of common chemical bonds are given in Table 1. Some of these absorptions have been identified in the sample spectrum of a relatively simple organic compound, 1-Octene, in Figure 2.

Different types of bonds within the same molecule absorb different frequency bands.

TABLE 1: CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES [a]

BOND	*COMPOUND TYPE*	*FREQUENCY RANGE CM $^{-1}$*
C - H	Alkanes	2850 -2960 1350 -1470
C - H	Alkenes	3020-3080 (*m*) 675-1000
C - H	Aromatic Rings	3000-3100 (*m*) 675-870
C - H	Alkynes	3300
C = C	Alkenes	1640-1680 (*v*)
C ≡ C	Alkynes	2100-2260 (*v*)
C ⩦ C	Aromatic Rings	1500, 1600 (*v*)
C - O	Alcohols, ethers, carboxylic acids, esters	1080-1300
C = O	Aldehydes, ketones, carboxylic acids, esters	1690-1760
O - H	Monomeric alcohols, phenols	3610-3640 (*v*)
	Hydrogen-bonded alcohols, phenols	3200-3600 (*broad*)
	Carboxylic acids	2500-3000 (*broad*)
N - H	Amines	3300-3500 (*m*)
C - N	Amines	1180-1360
C ≡ N	Nitriles	2210-2260 (*v*)
-NO_2	Nitro compounds	1515-1560 1345-1385

[a] All bands strong unless marked: *m*, moderate; *w*, weak; *v*, variable.

Infrared spectra and spectrometers

A record of the frequencies at which infrared absorption takes place for an organic compound is a highly characteristic property of the compound and is called its INFRARED SPECTRUM.

An infrared spectrum of a compound will reveal information about molecular structure as the existence of specific groups of atoms may be confirmed from the presence of their characteristic absorptions. The instrument used to record infrared spectra is called an INFRARED SPECTROMETER. Modern FTIR spectrometers scan frequencies in an infrared beam and measure the radiant powers [P] of frequencies after the beam has passed through, and interacted with a sample in a sample cell. These values are compared against stored values of radiant powers [Po], obtained with an empty sample cell, and absorbance values calculated for output in an infrared spectrum. The output of spectra from a spectrometer is generally in the form of a plot of Absorbance vs Wavenumber, however most instruments will also output spectra in the form of Percent Transmittance vs Wavenumber. Absorbance is the preferred output for quantitative analysis as it is directly proportional to the concentration of the absorbing species.

For interest, the mathematical relationship between absorbance, transmittance and concentration are detailed in Figure 3.

Analysis of used oil spectra

Used oil samples are complex mixtures of a large number of different chemical compounds and include compounds derived from the original formulation of base oil and its additives, oil degradation products and oil contaminants.

As a result of this a used oil spectrum is complex and essentially the net sum of the spectra of all the individual compounds making up the sample.

In fact, because of this complexity, the spectrum of a used oil alone is of limited value, and it must be compared against the spectrum of the unused oil to be of significant analytical value.

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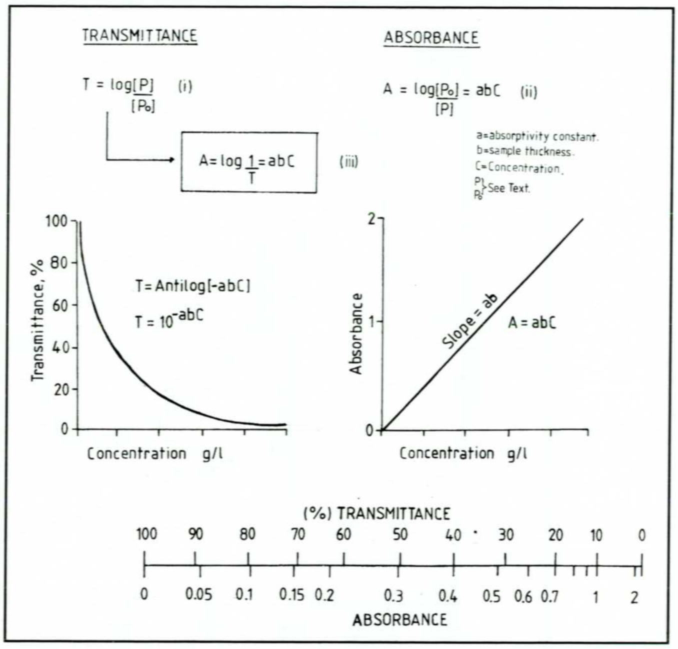
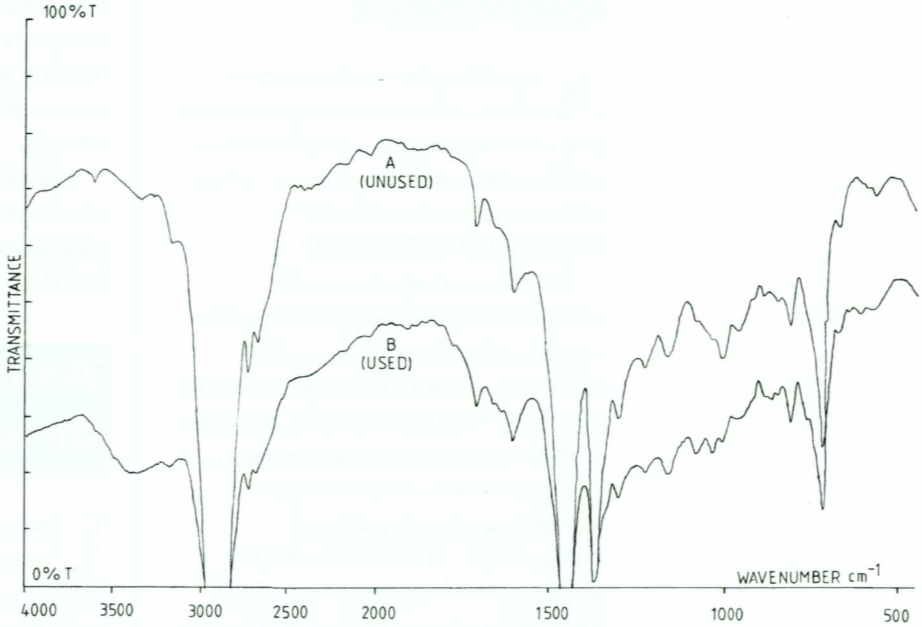
The relationship between absorbance, transmittance and concentration. (Figure 3)



Comparison of used and unused diesel lubricant. (Figure 4)

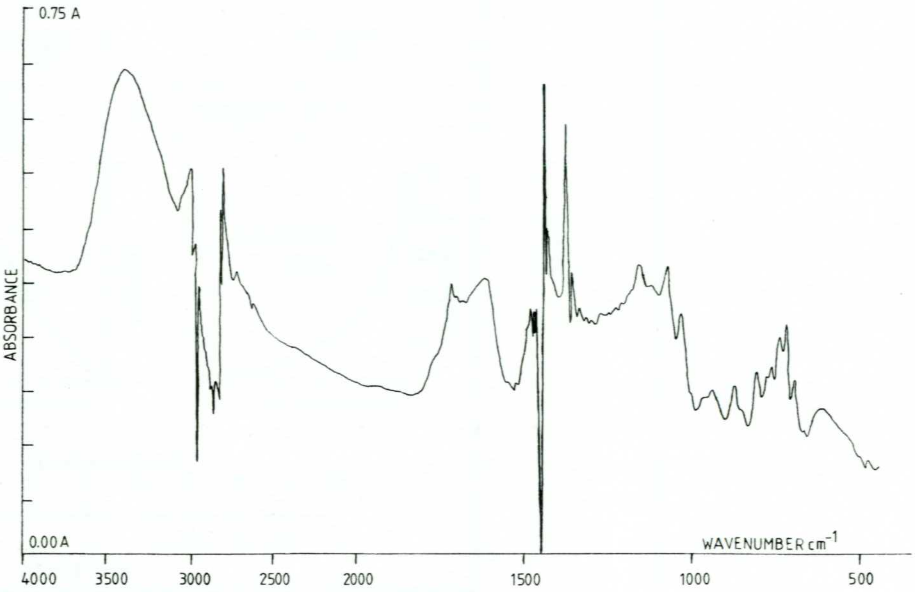


The difference spectrum may be regarded as a spectrum of degradation products.

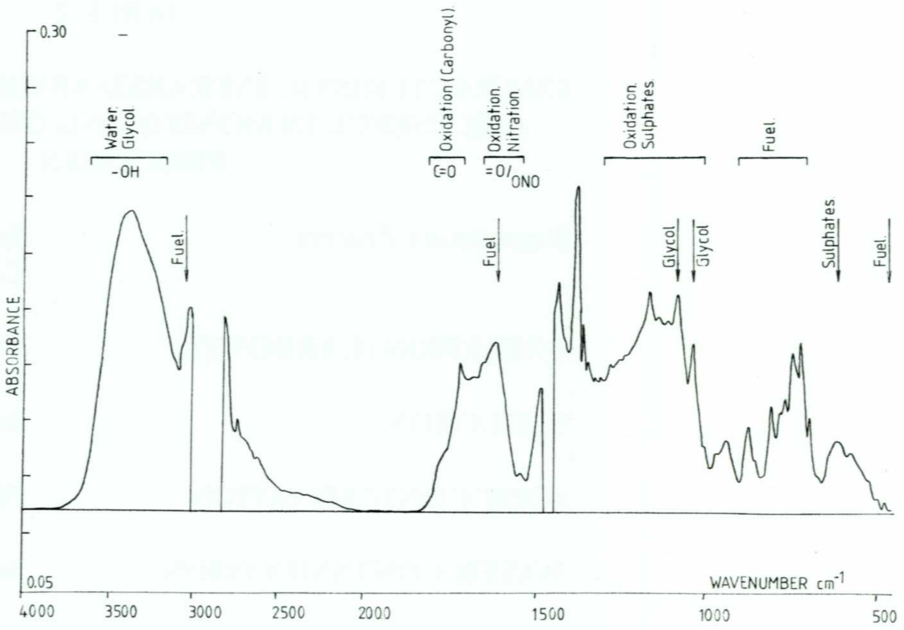
Figure 4. shows transmittance spectra from two oil samples that are superimposed on a common spectral grid. Spectrum A is that of a new oil (original fill) and Spectrum B is that of the same oil, degraded by a period of usage in a diesel engine. Apart from the displacement of transmittance values, caused by the presence of soot in sample B, there appears to be little difference between the two samples and it would be reasonable to expect the assumption that minimal degradation has occurred.

This situation changes dramatically when a differential spectrum is viewed. Figure 5 shows the Difference Absorbance Spectrum of the same two samples in which very obvious differences are apparent. A DIFFERENTIAL or DIFFERENCE SPECTRUM is obtained by subtracting the absorbance spectrum of one sample from that of the other. This process is carried out by the spectrometer's internal microprocessor. Data for each sample is collected and converted into a numerical format which is

Difference spectrum including soot. (Figure 5)



Difference spectrum excluding soot showing important spectral regions. (Figure 6)



Oil analysis software calculates severity indices for various degradation processes.

subsequently subtracted to yield the difference data.

Difference data may be used for further calculations or be converted back to a graphical representation. Once in numerical form spectral data may be manipulated mathematically to yield vast amounts of information in a short time period.

Figure 6. shows the same difference spectrum that has been further enhanced by "soot correction". The soot loading is estimated from absorbance values determined at two specified wavenumbers and the values applied to a mathematical model. The mathematical model determines the shape of the "soot curve" to be subtracted.

The data in this corrected form now contains all the information about the "differences" that exist between the new and the used oil. and may be considered as being a spectrum of the degradation products that exist in the used oil. To convert this data into a meaningful form, the numerical data of the corrected difference spectrum is examined in various spectral regions by software routines that calculate numbers representative of the degree to which types of degradation and contamination has occurred.

Typical spectral regions of interest and the degradation processes they represent are detailed in table 2 and are represented graphically in Fig 6.

At Wearcheck, used engine oil samples are run on the Perkin Elmer FTIR and the resulting spectrum matched and compared to a new oil spectrum contained in a "new oil" library. The difference spectrum generated from this match is processed by the oil analysis software and "SEVERITY INDICES" are calculated for the various degradation processes. Severity indices are reported rather than concentrations owing to the complex and variable nature of the compounds that are being measured in each process. In the case of the simpler contaminants, such as Water and Glycol, concentration may be expressed directly. The software in use at Wearcheck calculates and reports indices for SOOT, OXIDATION, SULPHATES and NITRATES. Water and Glycol are also reported but are quantified where necessary by additional tests. Fuel dilution may also be measured but owing to the complexity of local supplies of fuel, the method is unreliable.

Where regular sampling is undertaken severity indices are particularly useful in monitoring

TABLE 2

CHARACTERISTIC INFRARED ABSORPTION BANDS THAT ARE USEFUL IN MONITORING OIL DEGRADATION PROCESSES

Degradation Process	*Spectral Region Centre (cm-1)*
OXIDATION (CARBONYL)	**1720**
NITRATION	**1630, 1553**
SOOT CONTAMINATION	**3800, 1980**
WATER CONTAMINATION	**3450, 1640, 770**
SULPHATE FORMATION	**1160, 606**
GLYCOL	**3370, 1087, 1043**
FUEL (AROMATIC)	**3052, 1605, 874, 811, 748.**

engine trends, determining oil change periods and determining the onset of potential problems. If oil is used over a prolonged period with minimal top-up, the severity indices would be expected to increase as concentrations of degradation products build up to unacceptable levels. The interpretation of these values however, requires considerable skill as numerous considerations such as engine type, engine conditions and operating environment must be taken into account.

The diagnostic department at Wearcheck has considerable experience in interpreting infrared results.

The diagnostic department at Wearcheck has considerable experience in interpreting infrared results and successfully identifying many potential problems in engines that would otherwise require extensive testing to detect.

At Wearcheck, Infrared analysis is a valued technique in used oil analysis.

References

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