

# Oil Condition Monitoring

## Using Spectrum OilExpress



### Introduction

The lubricant oil in a combustion engine operates in a very hostile environment, being dispersed over a large surface area where it is exposed to high temperatures and chemically reactive by-products of the combustion process. As a result, the oil must be monitored continuously to ensure an engine is operating with optimum efficiency.

The engine environment causes chemical degradation of the oil over a period of time. In addition, the oil is exposed to sources of internal and external contamination. Therefore, the measured parameters relate to both chemical degradation of the oil and to contamination, both of which can cause loss in

performance and failure of mechanical components.

Infrared (IR) analysis of used oils provides information on the state of the oil itself and the engine from which it comes. The analysis is performed by obtaining the spectrum of a used oil and comparing it with a spectrum of the same oil when it was new. Since the type of oil, engine design, and operating conditions have a significant effect on the infrared results, one should exercise caution when interpreting the results. The trend observed from a series of samples taken at regular time intervals from the same engine have a much higher diagnostic value than the results from a lone sample.

This application note describes how to monitor oil condition by IR analysis using the Spectrum™ OilExpress system.

### Indicators of Chemical Degradation

#### Degree of Oxidation

Oil exposed to oxygen at elevated temperature will oxidize to a variety of compounds, the majority of which are carbonyl compounds, including carboxylic acids. Carboxylic acids contribute to the acidity of the oil, depleting the basic additives present in the oil and contributing to corrosion. Oxidation can also increase the viscosity of the oil. The degree of oxidation is a good indicator of oil degradation. A rapid increase in oxidation may indicate an engine overheating or a depletion of the anti-oxidant

additive due to an over-extended oil change period.

### **High Nitration Value**

Nitrogen oxides produced from the oxidation of atmospheric nitrogen during the combustion process react with the oil. Nitration increases the viscosity of the oil and is the major cause of the build-up of varnish or lacquer.

A high nitration value, also known as NO<sub>x</sub> or nitro-oxidation, indicates incorrect fuel/air ratio, incorrect spark timing, excessive loads, low operating temperature or piston-ring blow-by.

### **Increasing Sulfate Value**

Sulfur oxides are produced by the combustion of sulfur compounds present in the fuel. These oxides react with water, also produced by the combustion process, to form sulfuric acid. This is neutralized by the oil's basic additives, forming inorganic sulfates.

A rapid increase in the sulfate value may indicate the use of a high sulfur content fuel, poor combustion, over-cooling or the rapid depletion of anti-wear additive.

### **Ester Breakdown**

Synthetic lubrication oils usually contain a high proportion of synthetic poly-ol esters. These esters are susceptible to breakdown in the presence of water and acids (hydrolysis). Ester breakdown contributes to the acidity of the oil and can result in the formation of crystals of the base poly-ol, leading to clogging of filters.

Ester breakdown may indicate the

presence of water from condensation caused by low operation temperatures or from a coolant leak.

### **Anti-Wear Additive Depletion**

Anti-wear additives most commonly used are zinc di-alkyl- or di-aryl dithiophosphates (ZDDP's). These additives are consumed during the normal life of the oil. Consumption of anti-wear additive is accelerated by the presence of water. A rapid loss of anti-wear additive may indicate excess loads or contamination by water from a coolant leak.

### **Types of Contamination**

#### **Soot**

Soot particles result from the incomplete combustion of fuel and since they are too small to be removed by the filter, remain suspended in the oil. Soot builds up continuously until it reaches an unacceptable level, that level depends on the type of engine and lubricant. Diesel oils tolerate higher soot levels than gasoline oils.

The rate of soot build up depends on engine design, type of fuel and operating conditions. A high soot value may indicate poor combustion due to incorrect fuel/air ratio, a clogged air filter or an over-extended oil change period.

#### **Water and Glycol**

The presence of water and glycol indicate a leak from the cooling system. It is essential to detect such a problem early to avoid a serious failure. The presence of

water alone does not necessarily indicate a coolant problem, but may be result from condensation due to a low operating temperature.

### **Unburnt Fuel**

Fuel measurement depends not only on the level of contamination, but also on the aromatic hydrocarbon content of the fuel. The amount of aromatic content in fuels vary in location and season, therefore a careful calibration is required for the fuel that is being used.

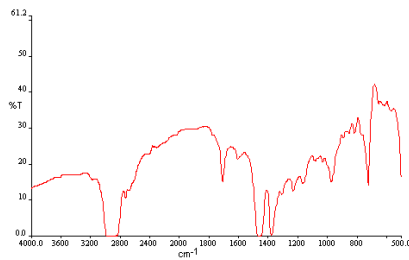
Fuel content may also be measured by flash-point determination. The flash-point method measures only the volatile components in the fuel. The IR method also measures the non-volatile components of the fuel which accumulate with time. The presence of fuel indicates poor combustion due to incorrect fuel/air ratio, clogged air filter or an ignition problem. It may also indicate an over-extended oil change period.

### **Using Infrared Analysis for Oil Condition Monitoring**

A used oil sample is a complex mixture of a large number of different compounds derived from the original base oil, its additives, oil degradation products and contaminants. The IR spectrum of a used oil sample is essentially the sum of the spectra of all of its components and consists of a large number of overlapping peaks that are very difficult to resolve (see Figure 1).

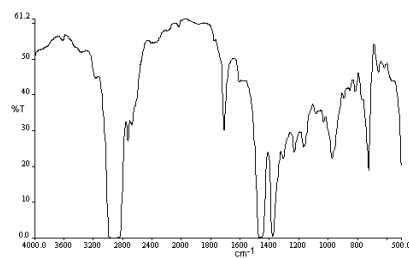
Used oil analysis is typically concerned with the changes that have occurred since the oil was changed. For that reason, a spectrum of the new (unused) oil is needed as shown in Figure 2.

The first step in the analysis is to convert the used oil sample and reference oil spectra to yield a *Figure 1 Spectrum of Used Oil*



*difference spectrum*, as shown in Figure 3. The difference spectrum represents the changes that have occurred in the oil since new and consists of spectra of chemical degradation products plus contaminants minus oil components that have been depleted or broken down.

*Figure 2 Spectrum of New Oil*



It is essential that the oil chosen as a reference is the same product as the used oil sample, otherwise

the difference spectrum will reflect differences between the formulations and give rise to spurious results.

The most significant observation of the difference spectrum is the slope, which is due to

*Figure 3 Difference Spectrum*



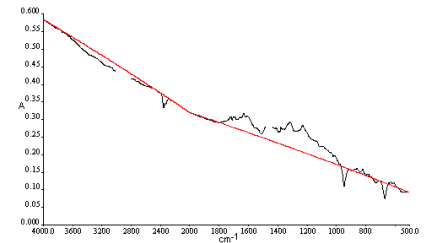
particulates, mainly soot, suspended in the oil. The soot values are found by measuring the absorbance at  $3800\text{ cm}^{-1}$  and  $1980\text{ cm}^{-1}$ . The  $3800\text{ cm}^{-1}$  measurement is sensitive to smaller particles than the  $3800\text{ cm}^{-1}$  measurement. The strong bands around  $3000\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$ , due to the base oil, have been removed from this figure for clarity.

The next step in the analysis is to remove the contribution from soot so that the positive and negative bands become visible. This is done by fitting a straight line (baseline) to the difference spectrum and then subtracting that straight line (see Figure 4).

The apparent kink in the baseline is due to a change in abscissa scale at  $2000\text{ cm}^{-1}$ .

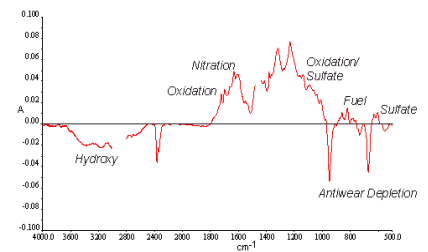
A baseline-corrected difference spectrum is then created to show the regions where some of the oil parameters were measured

*Figure 4 Baseline Fitting*



(Figure 5). The spectral regions and measurement units for the oil parameters are listed in Table 1.

*Figure 5 Oil Measurement Bands*



### Calculating and Reporting Oil Parameters

The Spectrum OilExpress system is controlled by the dedicated OilExpress software package. The software is delivered with three methods: one for mineral (petroleum-based) oils, one for synthetic (polyol ester-based) oils and one for the JOAP (Joint Oil Analysis Program).

Table 1 Summary of Oil Parameters

<u>Parameter</u>	<u>Spectral Regions</u>	<u>Measurement Units</u>
Soot:	3800 and 1980cm-1	Abs/cm
Hydroxy (Water and Glycol):	3650 - 3150cm-1	Abs/cm % Water
Glycol (Mineral oils):	1140 - 1000 cm-1	%
Oxidation (Mineral oils):	1720 cm-1	Abs/cm
NO <sub>x</sub> /Carboxylate (Mineral oils):	1650-1538 cm-1	Abs/cm
NO <sub>x</sub>	1630 cm-1	Abs/cm
Oxidation/Sulfate:	1150 cm-1	Abs/cm
Antiwear Loss (Mineral Oils):	700-640 cm-1	Negative Abs/cm
Antiwear Loss (Synthetic Oils):	1000-930 cm-1	Negative Abs/cm
Sulfate:	640-590 cm-1	Abs/cm
Fuel Contamination (Diesel):	820-800 cm-1	Abs/cm
Fuel Contamination (Gasoline):	780-760 cm-1	Abs/cm
Ester Breakdown (Synthetic Oils):	3720 - 3590 cm-1	Abs/cm

The latter was developed by the US military. The JOAP method will be discussed in detail in a separate application note.

Figure 6 shows an example report generated by the Mineral Oil Procedure.

Spectrum OilExpress software also includes sophisticated tools for browsing through the entire results database (Figure 7) and also for carrying out trend analysis, in this example to track soot values for a particular engine (Figure 8).

### Automating Oil Condition Monitoring

The Molecular Spectroscopy Liquid Autosampler is an integral part of the Spectrum OilExpress, providing unattended operation and rapid sample throughput of up to 50 samples per hour. Designed to run samples with virtually no carryover (<0.1%), it handles a wide range of viscosities (4—2,000 centistokes, cSt).

The Autosampler uses a sealed transmission cell with zinc selenide (ZnSe) windows with a pathlength of 100 μm. The autosampler is fitted with syringe pumps, which provide much more

reproducible sampling and flushing than traditional peristaltic pumps. It offers a number of advantages over horizontal attenuated total reflectance (HATR), due to the limitations of the HATR technique.

### Advantages of the Transmission Cell over HATR

The cell pathlength of 100 μm is ideal for oil analysis. HATR has an effective pathlength of around 20 μm and a low light throughput, reducing sensitivity and increasing scanning time.

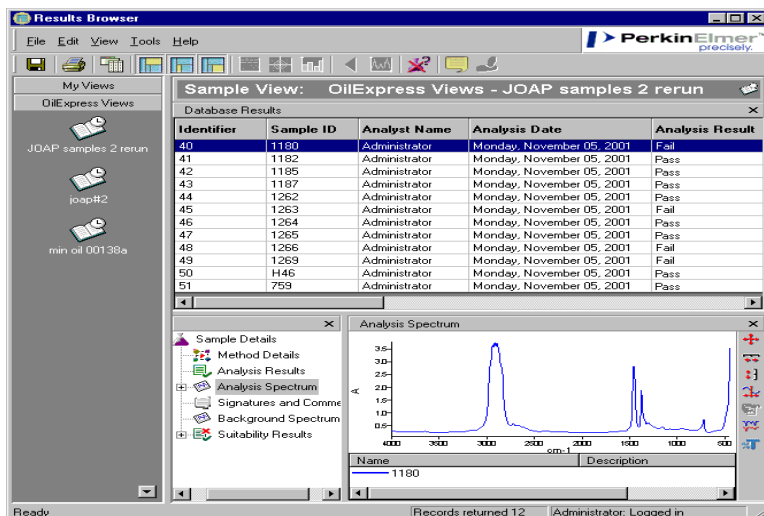
The syringe pumps allow rapid and thorough cleaning between samples and provide a very low sample carry-over of less than 0.1%. An HATR crystal requires time-consuming manual cleaning with flammable hydrocarbon solvent, exposing the operator to solvent vapors.

Used oils tend to be unpleasant to handle, they are irritating to the skin and often have a strong odor. The operator is not exposed to sample and solvent vapor during filling and cleaning of the transmission cell.

The infrared beam in the transmission cell passes through the bulk sample, easily detecting particulates like soot and suspended water and glycol. The HATR technique gives low values for soot because it ‘sees’ only a thin film of sample that is in contact with the crystal.

The transmission cell operates over a spectral range of 4000 to 500 cm<sup>-1</sup>. The HATR is limited to 650 cm<sup>-1</sup>.

Figure 7 Results Database Browser



### Conclusion

The use of IR for the analysis of used oils provides accurate information on the state of the oil itself and the engine from which it comes. Spectrum Express is a complete, easy-to-use system, optimized for this application, providing increased productivity and reduced running costs.

Figure 6

## PerkinElmer OilExpress Sample Report

### Sample Details

Sample ID	Mineral
Date/Time Analysed	Tuesday, July 17, 2001 19:09:47
Reference Spectrum	Ref Spectra Database/References/Diesel Engine Oil
Method	MineralOil
Analyst	Administrator
Batch Description	
Batch ID	
Cell Path Length	0.100893
Fuel Calibration	
Oil Type	Hydraulic
Oil Viscosity	
Position	1

### Analysis Results

Antiwear (A/cm)	0.00
Hydroxy (A/cm)	3.92
Nox (A/cm)	0.00
Nox vs Oxid (A/cm)	0.00
Oxidation (A/cm)	0.00
Soot 1980 (%T)	0.75
Soot 3800 (%T)	0.41
Sulf vs Oxd (A/cm)	0.00
Sulfate (A/cm)	0.00
Water (%)	0.12

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Figure 8 Trend Analysis

