

Molecular Condition Monitoring in the Commercial World:
Objectives and Applications of FT-IR Analysis

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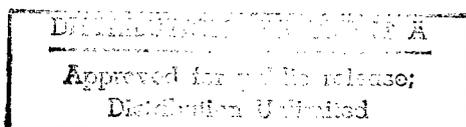
Abstract: Chemical and physical analysis of lubricants and hydraulic fluids is a common tool employed in equipment condition monitoring programs. Periodically checking these fluids for common contaminants and breakdown products allows a fast diagnosis of the general "health" of a machine or component, and thus permits maintenance activities effectively directed or deferred as necessary. A variety of different wet chemical and spectroscopic tests have been developed and applied to meet these needs. Condition monitoring of engine oils is perhaps the most common, with spectroscopic wear metal analysis complimented by molecular analysis by Fourier Transform Infrared (FT-IR). Much information has been presented in the past towards applying FT-IR analysis to engine lubricant condition monitoring. However, analysis of engine lubricants may only be a part of, or entirely unrelated to, other condition monitoring operations. Here, we will present additional information, examples, and statistical analysis of non-engine lubricants and machinery enrolled in commercial condition monitoring programs.

Key Words: Condition monitoring; Fourier transform infrared; contamination; degradation; lubricant properties; petroleum lubricants; synthetic lubricants.

Introduction: Condition monitoring of common lubricants is employed to diagnose the general "health" of a machine or component. Analyzing for common, known fault signatures, such as excessive wear metals, lubricant degradation, or lubricant contamination generates a fast and simple diagnosis of the condition of the lubricant, and thus the condition of the machine. This information allows timely and necessary maintenance to be either scheduled or deferred, as dictated by the machine condition. This approach, generally referred to as "condition based maintenance", is widely employed to maintain expensive mechanical systems while minimizing routine maintenance costs and oil consumption.

Condition monitoring has found the widest application in the protection of mobile equipment, most commonly diesel engines. Atomic spectroscopy was first applied in the analysis of wear metals in railway engines in the early 1940's. [1] Since that time, spectroscopic wear metal analysis of used diesel crankcase oils has become the most common instrumental technique employed in condition monitoring. Both original equipment manufacturers and larger customers today will specify allowable levels and

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trends of wear metals and elemental additives in the crankcase oils. These levels and trends will be determined by a combination of information and recommendations from the engine manufacturer, and can be modified by other factors such as age, usage patterns, and previous maintenance. Elemental analysis is often supplemented by a variety of other physical and spectroscopic measurements, such as FT-IR spectroscopy. Many manufacturers will specify allowable limits and trends in their engines based on infrared spectroscopy, and at least one company has developed and received a patent for a dedicated on-engine, infrared based oil condition sensor. [2]

While much work has been done on the application of FT-IR spectroscopy in engine condition monitoring, engines represent only a portion of the total range of machinery enrolled in commercial condition monitoring programs. Effectively applying FT-IR analysis to systems other than engines requires the same initial planning and data gathering steps as would be required in applying wear metal or other analysis tools. Three questions first need to be answered: 1) what are the characteristic faults or failures that can be detected? 2) What is the normal variance or distribution of these measurements? 3) Does the measurement have sufficient precision to indicate these failures? While past work on engine lubricants can be used as a starting point, straight application of infrared methods developed for crankcase lubricants will produce an ineffective evaluation. This may lead to the inaccurate conclusion that infrared spectroscopy is not beneficial for non-engine lubricant monitoring, when in fact, the crankcase oil analysis methodologies are not beneficial for gear boxes and hydraulic systems.

Besides routine condition monitoring of lubricants and fluids in-use, the commercial condition monitoring laboratories will work with machinery and lubricant manufacturers in evaluating formulation performance from real-world field data. While much work is applied before a formulation is released, it is most often supplemented from a wider range of equipment, conditions, and usage patterns than is possible in a laboratory test bed. In this area, routine FT-IR measurements are used in conjunction with other physical measurements on the performance of the lubricant in order to better understand which contaminants and breakdown products contribute most to the overall degradation of the lubricant characteristics.

Petroleum EP Fluids: In plant machinery gear boxes, the most common faults which occur are contamination of the lubricant by water, and degradation of the lubricant by a combination of pressure and heat generated at the gear tooth contact points. There can be many other faults specific to the environment of the machinery that can be detected by FT-IR spectroscopy. Some of these can include dirt contamination in an ore processing line, or contamination from cutting fluids in an automated machining line. However, we will only consider the general contamination and degradation processes found in the majority of these systems.

As water is the most common compound found on the surface of the earth, it too is the most common contaminant in gear drives. Previous studies demonstrated that the infrared analysis methods developed for petroleum based crankcase oils were unsuitable for synthetic polyol ester turbine lubricants. [3] This is due to differences in the interactions

between the water and the detergent/dispersent package in crankcase lubricants, versus interactions between the water and the synthetic lubricant package in turbine lubricants. While petroleum based gear lubricants may be expected to respond in the same manner as the petroleum based crankcase lubricants, the extreme pressure (EP) additives in gear lubricants interact with contaminating water in yet another manner. Figure 1 shows this effect in an example of a petroleum based EP oil with water contamination. In these fluids, water contamination is detected by a constant offset in the baseline of the spectrum. The appearance of a distinctive OH stretch peak only becomes noticeable in extreme cases, as seen in Fig. 1. The infrared response for water contamination in a petroleum based EP hydraulic fluid is similar to that of the gear lubricants.

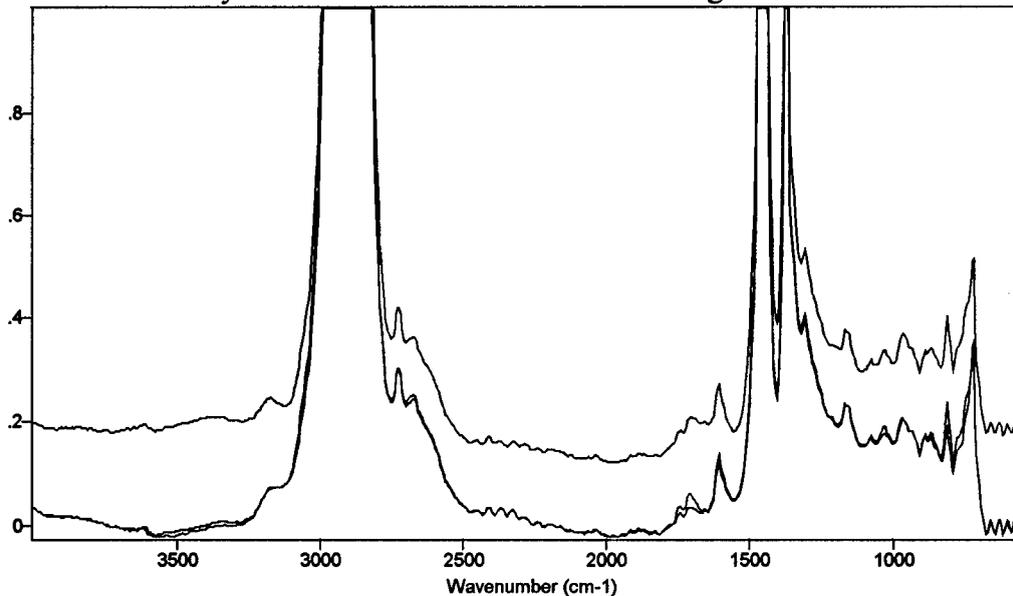


Figure 1. Water Contamination in EP Oil

In addition to water contamination, degradation of the oil due to the localized high pressures and temperatures generated will occur. Interaction with atmospheric oxygen and nitrogen under these conditions will produce oxidation and nitration in the oil. Figure 2 shows some examples of the buildup of oxidation products in some EP additive gear lubes. While those familiar with the infrared spectra of various synthetic lubricants may be tempted to identify the top two spectra as synthetics (based on the strong carbonyl band), these were originally EP petroleum lubricants like the lower spectra. In addition to the high infrared oxidation readings, oxidative degradation of the top lubricants was confirmed by high TAN (Total Acid Number) measurements.

In the case of oxidation, nitration, and other degradation products, two different approaches can be taken towards determining normal and abnormal values. The first was hinted in the preceding paragraph: correlation of the infrared spectrum to a known physical measurement. While this has been demonstrated in the past, [4] generating and maintaining these correlation routines adds an additional burden to the condition monitoring operation. As will be demonstrated later, infrared spectroscopy is able to measure all the individual properties that determine the bulk physical nature of the oil. With this, then it only becomes necessary to determine the normal distribution of the

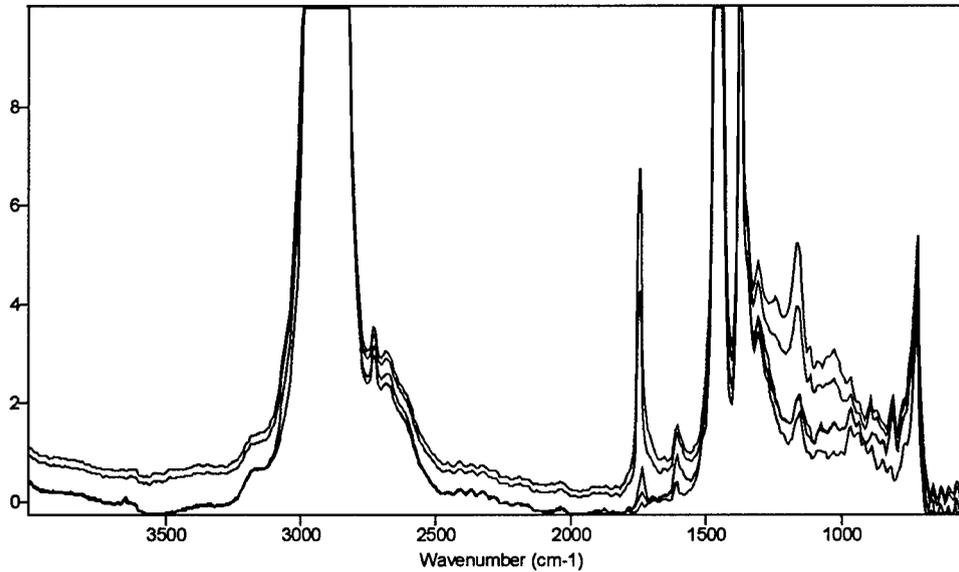


Figure 2 Oxidation Degradation of EP Oils

oxidation, nitration, and other degradation products that can be measured by FT-IR in these lubricants. Figure 3 shows the distribution profiles of the infrared measurements in a small population of EP gear oils. While not presented or proposed as strict limits in EP based gear box lubricants, the distribution profiles clearly show how normal (low to no degradation) and abnormal (excessive degradation) values can be discerned.

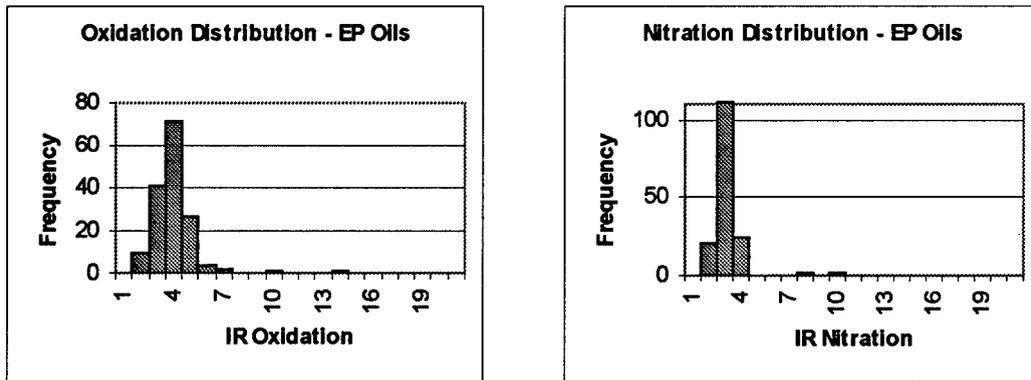


Figure 3. Oxidation and Nitration Distribution Profiles in EP Oils

Synthetic EP Fluids: Often, petroleum based lubricants and hydraulic fluids are unsuitable for some applications. In these, a higher degree of protection, wear resistance, inertness, or fire resistance is needed than can be obtained in a refined petroleum. Quite a large number of different formulations are available, ranging from simple synthetic hydrocarbons through very specialized chlorofluorocarbon ether lubricants. However, most of the synthetic lubricants are ester based compounds, and can be further divided into simple esters and phosphate based esters. [5] Starting with a synthetic based fluid, additional additives are blended to achieve the final degree of performance desired for a given application.

Extreme pressure additives are also commonly used in synthetic lubricants to improve performance under heavy loads. These blended synthetic fluids interact with water similar to the case of the EP additive petroleum oils. As seen in Fig. 4, varying degrees of water contamination is exhibited by a general baseline offset of the infrared spectrum of the sample. Here, the bottom traces represent oils with no water contamination, the middle set of traces represent water contamination in the 1000 to 2000 ppm range, and the top spectrum represents a sample that was found to have 9% (90,000 ppm) water. Note that this water contamination level is far in excess of saturation point of the oil, and the level was determined by the volume of water that settled out on standing. Thus, there is not a linear relationship in the infrared spectra between the lower levels of water contamination and this extreme case. However, if the objective is to "catch" water contamination in the 1000 ppm range, then establishing a perfect linear relationship for such an extreme condition becomes unimportant.

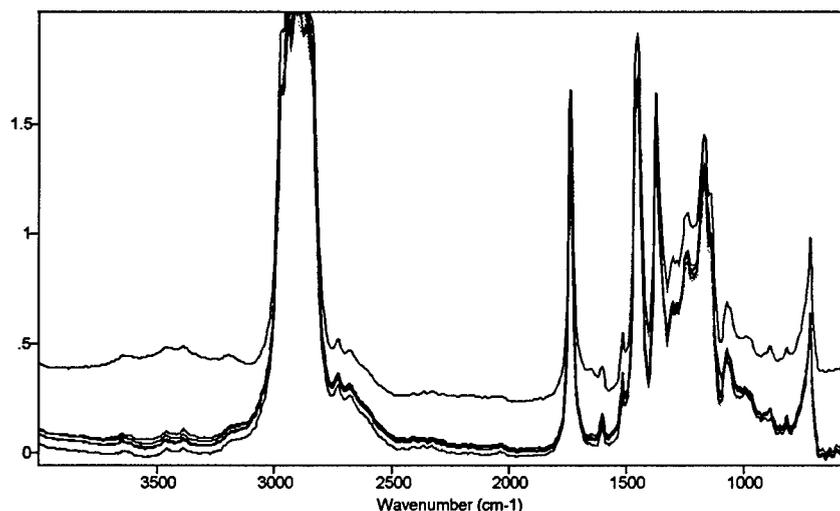


Figure 4. Synthetic EP Oils, Varying Water Contamination.

For the measurements of the chemical degradation of these synthetic fluids, such as from oxidative degradation due to heat, pressure, and oxygen, additional knowledge is needed. As different starting synthetic compounds will break down to form different products, then a simple, "one-size-fits-all" approach to measuring these degradation products will inevitably miss some cases of excessive breakdown while generating too many false alarms in other fluids. For example, simple and polyol esters will break down to form the starting organic acid and alcohol. Here, detecting this type of lubricant breakdown is performed by measuring the areas of the infrared spectrum where these functional groups appear. [3] Phosphate esters will break down to form organic acids, alcohols, simpler organophosphate compounds, and phosphate acids or salts. As the phosphate groups are generally strong infrared absorbers, a change in this area may be taken as a guide toward lubricant breakdown. Discussing all the different chemical breakdown infrared profiles for all the different classes of synthetic lubricants is beyond the range of topics that can be discussed in this limited paper. Work is progressing on further characterizing these fault signatures, and results will be presented later.

Lubricant Performance Research: Besides providing routine condition monitoring services, commercial laboratories are often tasked by lubricant manufacturers to provide field performance data on their (and their competitors) lubricants under real-world conditions. This research usually involves investigation of the performance of various blends and additive package levels, relating the field information to their own database of lubricant physical characteristics. One physical characteristic often used by lubricant manufacturers, blenders, suppliers, and purchasers, is the total base number (TBN) of a lubricant. This number is typically used to express the level or activity of the additive package, with higher numbers typically providing a greater degree of protection to the buildup of acidic breakdown products and contaminants. Previous work showed the power of FT-IR analysis, in combination with the mathematical analysis techniques of Principle Component Regression / Partial Least Squares, in accurately predicting the viscosity of railway lubricants based on the infrared absorbance spectrum. [4] While FT-IR spectroscopy is capable of measuring all the individual chemical compounds, and the interactions between the different chemical compounds, which determine the overall physical characteristic of a lubricant, these tools are often first needed to uncover the complex relationships between these compounds and complexes.

Based on this and other successful applications of FT-IR and PCR/PLS, one laboratory studied the factors by FT-IR spectroscopy that influence TBN in high-speed diesel crankcase lubricants. To verify that components measured in the infrared spectrum could be correlated to the physically measured TBN, a PCR/PLS "training set" of ~150 used crankcase lubricants from different equipment and applications was collected. This was then used to test the ability of FT-IR spectroscopy to measure all the important components in the oil, which affect the TBN. Figure 5 shows the correlation between the TBN as predicted from the FT-IR spectrum (y-axis) versus the physically measured TBN. While some scatter is seen across the range, the number of outliers was not judged significantly different from two independent physical TBN titrations.

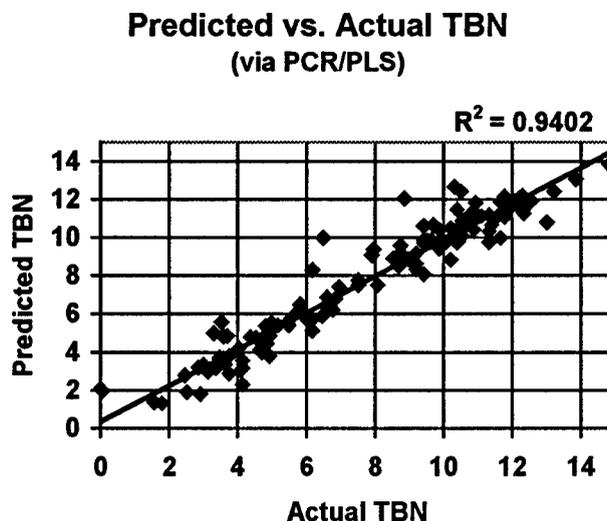


Figure 5. Predicted TBN by IR vs. Measured TBN

With this data demonstrating that FT-IR spectroscopy is recording all the various compounds and their interactions which affect TBN, further study was done to determine which chemical or functional groups contributed the most to the change in the TBN. These factors, presented in table 1, show that the additive package is very effective in interacting with, or neutralizing, oxidation and sulfation breakdown products formed in the oil. However, the surprise finding is that the nitration products contribute to the change in the TBN to a greater degree than the oxidation and sulfation products combined.

<u>Component</u>	<u>Relative Importance in TBN (Additive = 100%)</u>
Additive	100%
Nitration Products	73%
Oxidation Products	41%
Sulfation Products	9%
Oxidation / Additive Interactions	2%
Sulfation / Additive Interactions	0.5%
All Others	<1%

Table 1. Relative Contribution to TBN

This information can then be used to further investigate additive package performance, with the long-term goal of allowing “environmentally friendly” extended drain intervals without sacrificing engine protection. It should be pointed out however, that while FT-IR spectroscopy can successfully predict physical characteristics of a lubricant such as viscosity and TBN, research goals and routine condition monitoring goals often do not significantly overlap. As routine FT-IR analysis can measure all the individual components that affect the lubricant’s performance, it then only becomes necessary to measure these individual components, and relate them to a normal or allowed range. Developing, maintaining, and cross-checking calibration and correlation sets to predict physical properties will add a significant amount of work to a condition monitoring operation. However, it will not significantly improve the initial objective of a condition monitoring operation: judging the condition of a lubricant, and thus the machine, as an aid in maintenance planning.

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