

STLE 2007- Session: 3B - Condition Monitoring/Predictive Maintenance

FOURIER-TRANSFORM INFRARED (FTIR) SPECTROSCOPY – APPLYING THE
CORRECT METHOD FOR YOUR APPLICATION

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ABSTRACT

Lubricant condition and contamination testing by Fourier-transform infrared (FTIR) analysis has advanced considerably over the past two decades to include miniaturized infrared spectrometers for use as in-line sensors. However misconceptions and misapplications of the technology still prevail, even with the availability of the ASTM Practice E2412 which describes FTIR use for common in-service oils. What FTIR is capable of and how to choose the correct measurement parameters for your specific fluid application will be discussed.

INTRODUCTION

Lubricant condition and contamination testing by Fourier-transform infrared (FTIR) analysis has advanced considerably over the past two decades encompassing techniques for the measurement of the critical fluid failure modes as manifested in the different lubricant types e.g. crankcase oils, polyol ester oils, industrial ISO (turbine and hydraulic) oils. These techniques have even been incorporated into miniaturized infrared spectrometers for use as in-line sensors. Even with the advances and consensus as represented by ASTM Practice E2412 [1], misconceptions and misapplications of the technology still prevail. Comments such as the following are not uncommon.

- “Although FTIR can detect multiple parameters, detection limits are poor”.
- “FTIR does not detect water well – it needs to be verified by the crackle test”.
- “We only use our FTIR for soot analysis”.
- “Oxidation, nitration and sulfation parameters are not reliable”.

These comments imply misapplication or misuse of FTIR analysis and/or lack of information on measurement methods that have been developed by industry.

FUNDAMENTALS:

FTIR spectroscopy is an analytical measurement method to characterize and identify the structure of organic molecules. In oil analysis, we are analyzing in-service lubricants to detect the presence of any contaminants or by-products formed. The *lubricant*, the by-products and the contaminants, all absorb IR energy at specific and reproducible wavelengths. The key

word in this analysis process is “*lubricant*”. If the chemical structure of crankcase oils vary significantly from the chemical structure of gas turbine oils or industrial ISO oils, then it is not unreasonable to expect that the IR energy of the *lubricants* will be absorbed at different wavelengths. As well, different lubricant types can influence the response of some contaminants and by-products. An example is presented in the next paragraph. Work in the early and mid 1990’s by the US DOD [2, 3, 4] demonstrated that different wavelength regions of the infrared spectrum should be utilized depending on the type of lubricant. Figure 1 clearly shows the difference in the FTIR response to common lubricant types.

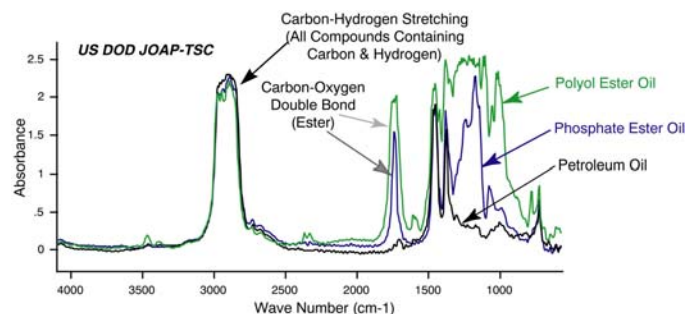


Figure 1: FTIR response to three common lubricant types

IMPACT OF LUBRICANT CHEMISTRY:

One of the more interesting findings of the DOD study was the difference in absorbance regions of water depending on the lubricant type. For example, 1000 PPM of water in a polyol ester (gas turbine) lubricant is found in a completely different region [3600 to 3700 cm⁻¹] than the traditional hydroxyl (O-H) stretching region [3250 to 3500 cm⁻¹] used for the measurement of water in a crankcase lubricant. The water contaminant behaves differently due to the difference in the *lubricant* chemistry. The crankcase oil is a long chain hydrocarbon that forms traditional hydrogen bonded hydroxyl bonds with water. The polyol ester lubricant is a hindered phenol and does not form these traditional bonds with water; instead water is observed as free hydroxyls and single bridge hydroxyls. Additives such as emulsifiers in some ISO fluids can also influence water behavior in a lubricant. The

significant differences in water behavior in the various lubricant types are the main reason why water measurement has been in dispute. This is a case where one size (measurement area) does not fit all. Each different lubricant type requires a unique measurement region for water. This has been verified by analysis of tens of thousands of in-service oil samples for the lubricant types discussed. [2, 3, 5, 6]

The issue with water measurement is also manifested in the measurement of other oil failure modes such as degradation. The FTIR regions of interest for breakdown / degradation by-products for petroleum and ester based lubricants are different. The ester peak (C=O) for polyol esters is observed in the same location [1800 to 1670 cm^{-1}] as oxidation by-product peaks for petroleum oils (see Figure 1). Thus reliable measurement requires specific regions for the respective lubricant type. These FTIR regions are associated with the functional groups of the oil, contamination or degradation by-products chemistry – and not with specific manufacturers' brands or viscosity grades.

Another confusion factor is the establishment of appropriate limits to define the point at which oil becomes unusable or unreliable, requiring maintenance action. Lubricant quantity (sump size) must be considered when determining FTIR limits, similar to the constraints on wear metal limits. The limits for a system that has 10 gallons of oil should not be the same as for a system with 100 gallons or more. Limits should be established by statistical analysis of sufficient samples covering normal through failure conditions.

INSTRUMENT FACTORS:

There are a number of instrument related factors that can affect the reliability of FTIR results and/or comparison between instruments / laboratories.

- Horizontal attenuated total reflectance (HATR) versus flow-through transmission cells – a 100 micron flow-through transmission cell is up to 20 times more sensitive than an HATR cell. [2]
- Spectral subtraction versus direct trending – spectral subtraction is very dependent on obtaining the correct reference fluid and has been found to generate “non-data”. [7] Spectral subtraction should only be used for new-oil analysis or for stoichiometric methods where the in-service fluid is also used as the reference. [8]
- Transmittance versus absorbance – Absorbance is linear in terms of the path length and concentration by the Beer-Lambert Law. This method also is the recommendation of ASTM Standard Practice E168-92. [9] Transmittance is not linear with concentration.
- Cell path length and composition – different cell path lengths or cell window composition can impact comparison between results.

- Apodization (data smoothing) techniques can also impact comparison between results.

CONCLUSIONS:

FTIR is capable of reliably measuring the level of water, soot, and fuel contaminants; the level of oxidation, nitration, sulfation by-products; and the relative amount of anti-wear and anti-oxidant additives. In the case of fuel measurements, the fuel level is dependent on the concentration of aromatic product in the fuel.

If the FTIR regions are selected correctly for the lubricant type, the measurements should be repeatable and reliable. ASTM E2412, Annex A1, clearly shows the FTIR regions of interest for common lubricant types. ASTM D2 committees are currently in the process of developing methods for crankcase oils based on ASTM E2412 where the instrument influences are removed to allow correlation of results between laboratories when different manufacturer instruments are used. FTIR can be a very powerful tool for detecting lubricant contamination and degradation by-products when used correctly for your specific application.

REFERENCES

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