FT-IR Analysis of Used Lubricating Oils – General Considerations

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Introduction

Infrared spectroscopy is a widely used technique for the analysis of lubricating oils. The Thermo Scientific Nicolet™ FT-IR spectrometer, coupled with OMNIC™ Integra™ software, provides modern laboratories with an intuitive package for routine infrared analysis of liquid samples. This application note details the application and the parameters used to derive the highest quality data.

Used Lubricant Analysis Using FT-IR

Infrared analysis of used lubricants provides useful molecular information about the changes in a lubricant and the mechanical compartment being lubricated. This makes the technique an effective trending and screening tool in modern maintenance programs. Information from infrared analysis can be used to complement data obtained by elemental analysis techniques, such as atomic emission or inductively coupled plasma (ICP) spectroscopy. In addition, it may reduce or replace the analysis requirements for certain traditional techniques that are tedious and time consuming. It must be stressed that infrared analysis is a trending and screening tool for multiple parameters of interest in lubricants and mechanical systems.

The parameters typically analyzed using FT-IR are listed in Table 1. This table presents the parameters of interest and information on obtaining and using them. The spectral plot in Figure 1 shows a used oil difference spectrum and labels the peaks of interest indicated in the table.

Parameter of Interest	Spectral Location (approx. cm^{-1})	Type of Measurement	Traditional Measurement
Soot	2000	Trending carbon load (diesel engines)	Total insolubles, Thermogravimetric analysis
Oxidation (carbon)	1700	Trending oil degradation	Total base number, Total acid number, Viscosity*
Nitration	1630	Trending oil degradation (engines only)	Total base number, Total acid number, Viscosity*
Sulfation	1150	Trending oil degradation (engines only)	Total base number, Total acid number, Viscosity*
Water	3400	Contaminant screening	Crackle test, Karl Fischer
Diesel fuel	800	Contaminant screening	Flash point, Viscosity, Gas chromatography
Gasoline	750	Contaminant screening	Flash point, Viscosity, Gas chromatography
Antifreeze (glycol)	880	Contaminant screening	Colorimetric assay, Gas chromatography
Antiwear additive	960	Additive depletion	Elemental zinc

Table 1

* This analysis relates to viscosity, but is not a replacement for this measurement.
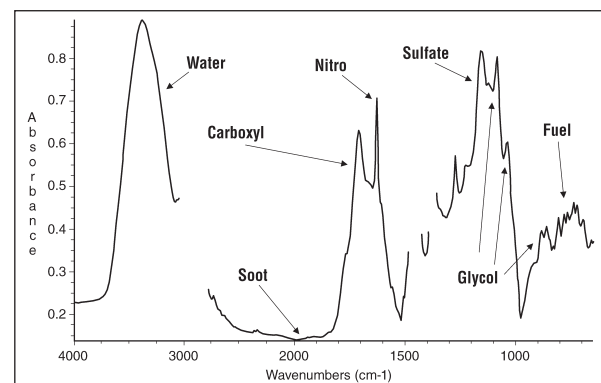

Figure 1: Used oil difference spectrum

Analysis Considerations

As a trending and screening tool, FT-IR analysis of used lubricants has limitations and must be applied with appropriate measures to assure proper generation and interpretation of data. First and foremost, numeric results from all of the parameters being determined (with the exception of soot), are affected by the molecular fingerprint of the base lubricant and additive package. That is to say, the additives and base oil have spectral features that interfere with the peaks that develop as the lubricant is contaminated or oxidized during use. The magnitude of the peaks that develop are typically smaller than, or of similar magnitude to, those found in the unused oil. This can be seen in Figure 2, which displays a plot of a new oil, the same oil used and the subtraction result (difference spectrum). The difference spectrum is shown with a much expanded y-scale.
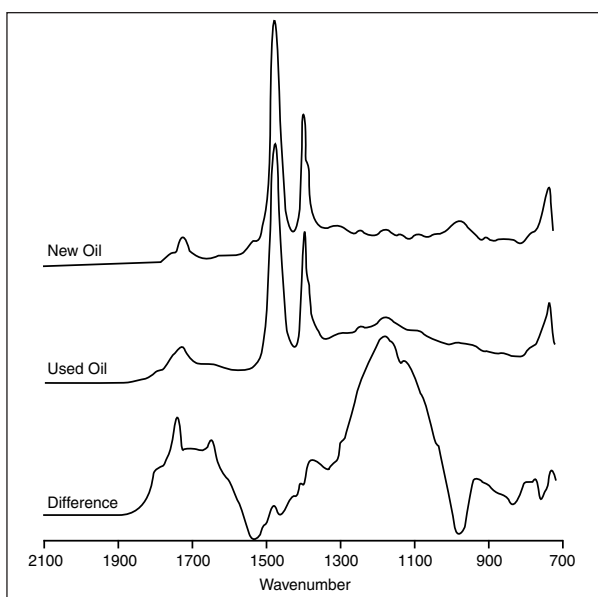

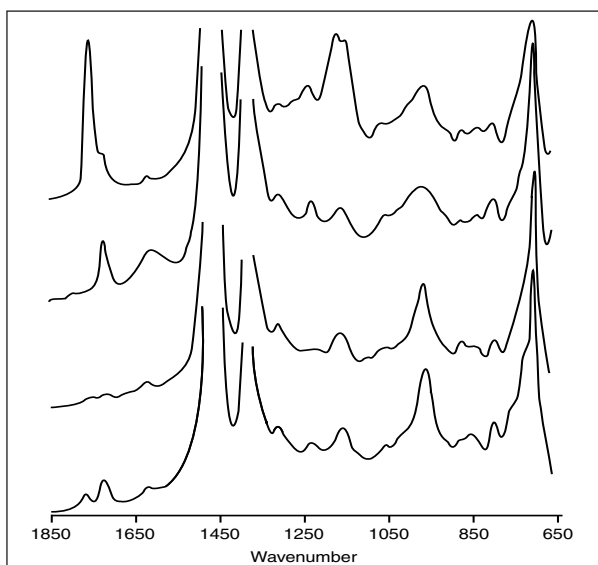Figure 2: New oil reference spectrum subtraction

Figure 3: Infrared spectra of four different new oils

Figure 3 shows four different new oils. The plot shows the differences in spectral features resulting from the variation in base oils and additives used to make the lubricants. These differences must be taken into account, or they will cause errors in the numeric values obtained from the analysis. Because of this, spectral subtraction of the proper new oil reference spectrum is applied to obtain correct used oil analysis results.

OMNIC Integra software provides advanced features for the creation and maintenance of custom, quantitative new oil reference libraries. In addition, when the new oil is not known, the autoreference feature is available to search a library for the best selection before reference subtraction. However, this option should not be used routinely since it may generate incorrect results, particularly for antifreeze, fuel and water, depending on the reference library contents. It should only be used if a reference spectrum is unobtainable.

Table 2 provides a relative sensitivity rating of the analysis components to the correct reference oil being used. Components with higher sensitivity will give a more significant error in the numeric values obtained when the incorrect reference is used. In the case of water, antifreeze, diesel fuel and gasoline, using the incorrect reference may produce false positive indications, or cause these components to not be detected. This is particularly true when autoreferencing is used because an unknown used oil with a contaminant is being searched against a clean oil library. The presence of the contaminant can make the spectrum of the unknown used oil appear more like another type of lubricant than the correct new oil reference.

Component	Relative Sensitivity
soot	insensitive
oxidation	fairly insensitive
nitration	fairly insensitive
sulfation	fairly insensitive
water	fairly sensitive
glycol	very sensitive
fuel	extremely sensitive
gasoline	extremely sensitive
ZDDP	extremely sensitive

Table 2

Considerations for Specific Analysis Parameters of Interest
Please refer to Figure 1 and Table 1 for this discussion.

Soot Particles

Suspended soot is the result of the incomplete combustion of fuel. This is usually only a consideration in diesel engines but could be indicative of carburetor or injector problems with other fuel systems. While it has no specific frequency of absorption in the infrared spectrum, soot causes a shift in the baseline of the spectrum due to absorption and scattering of light. Since there are no other spectral features in the region around 2000 cm^{-1}, this area is used to assess the level of soot in a sample. The baseline shift caused by soot is affected by the amount of soot present and the effective particle size. The effective particle size is a resultant of the nature of the combustion system and the dispersants in the oil. This makes it difficult to directly assess the quantity of soot, so factors that relate the amount of soot to the infrared value must be established with the engines and lubricants of interest.

Carbonyl Oxidation Products

The broad feature centered around 1730 cm^{-1} is due to the presence of carbonyl-containing degradation products of oil. These have been identified as lactones, esters, aldehydes, ketones, carboxylic acids and salts, as well as others. The broadness of the peak is because of the wide variety of materials present. The point of maximum intensity will vary as the oil and conditions of its use are changed. The increase in peak height that occurs as the number of hours the oil has been run in the engine increases has a greater significance in the measurement of degradation than total acid number (TAN) or viscosity.

Nitrogen Oxidation Products

The sharp feature at 1630 cm^{-1} is the result of nitrogen oxide fixation into the oil. The materials that create this feature are due mostly to nitrate esters. Nitrogen fixation products are most significant in gasoline and natural gas engines and some diesel systems that use exhaust gas recirculation.

Sulfur Oxidation Products

Another broad spectral feature, centered around 1150 cm^{-1}, is the result of sulfate compounds as well as overlap with oxidation products. Sulfate material is a result of the introduction of sulfur from fuels or from the oxidation of sulfur from the base oil and additives. This band is a fairly specific measure of over basing additive consumption and relates to total base number (TBN).

Fuel Residue

The measurement of fuel residues or raw fuel is difficult by any method. The main difference between the fuel and base oil is in molecular weight or boiling range and the percentage of aromatic materials. Fuel has a lower boiling range and significantly higher percentage of aromatic material. Conventional methods make use of the lower boiling range, while the infrared approach examines the aromatic content to indicate if fuel is present. The spectral features around 800 cm^{-1} are used for this purpose.

The accuracy of measurement by any technique is strongly affected by the standard material used to calibrate the instrument and the level to which the fuel is evaporated within the engine crankcase. The infrared technique has the additional requirement of needing to match the new-oil reference properly, as discussed earlier. It is the change in base oil aromatic level that is the major factor leading to errors from reference mismatch. Gasoline contamination detection is less problematic than detection for diesel fuel because of the higher aromatic content of gasoline.

Even though calibrations are provided in the OMNIC Integra software, it is best if fuel is calibrated by the laboratory using the system. In any case, it is important to use at least one other independent test, such as viscosity, flash point, or gas chromatography to confirm an indication of fuel presence by FT-IR analysis.

Water and Glycol Contamination

These two contaminants have characteristic absorptions in the infrared that make their detection possible near the 0.1% level. While this is not as sensitive as some other techniques, it is at a level where problems from the presence of these contaminants in the crankcase could begin. Water is detected as a broad feature, centered around 3400 cm^{-1} that is caused by the hydroxyl (-OH) group. Glycol has a characteristic peak around 880 cm^{-1} as well as peaks at 1040, 1080, and 3400 cm^{-1}. The peak at 880 cm^{-1} is used to quantify because it is not subject to interferences to the same extent as the other bands. The other peaks in the spectrum related to glycol are used to confirm its presence.

Glycol will interfere with the quantification of the water level when present, but the converse is not true. Therefore, when glycol is present, water cannot be reliably quantified using FT-IR. This is not considered a problem because the presence of glycol has a greater significance to engine performance. As with fuel, it is extremely important to use at least one other test to confirm that water or glycol are present in a used-oil sample. Water can be confirmed by the crackle test or the Karl Fischer test. Glycol presence can be confirmed by a colorimetric test, and corroborated with elemental analysis results of sodium and boron.

Reporting of Data

The values determined from the infrared spectrum for the components discussed in the preceding section are reported in different ways because of the nature of the materials present. The following values are reported by OMNIC Integra software:

- Oxidation, nitration and sulfation components are not reported as concentration values, because there are many different chemical compounds formed that contribute to the measured absorption. Since no single product is formed, standard materials are not available to generate the calibration curves needed to relate absorbance to concentration. Absorbance values related to the thickness of sample exposed to light are reported. The units used for reporting are absorbance per 0.1 millimeter (ABS/0.1 mm), which relates directly to the peak intensities observed in the difference spectrum of a used oil. The information for these components is most useful in trend analysis.

- The carbon particles that form soot do not cause localized absorption. Instead, an offset of the spectral baseline due to light scattering and absorption is observed. The magnitude of this offset is determined by the particle size of the soot as well as its concentration. The particle size observed is affected by the engine type and lubricant. ABS/0.1 mm values related to the thickness of sample exposed to light are reported as well.

- Antiwear additive, typically various forms of zinc dithiodiphosphate, is reported in ABS/0.1 mm the same as the above oxidation components. However, the antiwear additive is reported as a negative value because in the used-oil difference spectrum the peak goes in the opposite direction of other peaks in the spectrum. This is due to the depletion of the additive compared to the original reference oil.

- Fuel, water, glycol, and gasoline are reported in percent values from calibrations with standards. The calibrations that are provided in the software for diesel fuel and gasoline may not accurately reflect the fuels in use in a particular region of the world. Because of this, these components should be calibrated with locally generated standards. In the case of water and glycol, these materials are typically very consistent. These components should not need to be routinely calibrated locally because of the difficulty of making and analyzing standards.

In practice, the approach taken to make use of the absorbance values for the uncalibrated components is to note their increase over time within an engine. From a plot or table of the change in absorbance with time, judgments about when to change the lubricant can be made. This is where experience with used lubricant analysis comes into play.

Table 3 provides an explanation of the units reported by the software with some typical and high results.

Component	Limit of Units	Typical Detection	Result	High Result
soot	ABS/0.1 mm	NA	0.22	0.70
oxidation	ABS/0.1 mm	0.02	0.1	1.0
nitration	ABS/0.1 mm	0.02	0.1	1.0
sulfation	ABS/0.1 mm	0.02	0.1	1.0
antiwear*	ABS/0.1 mm	-0.02	-0.05	-1.0
diesel fuel	weight %	2.0	NA	6.0
gasoline	weight %	1.0	NA	6.0
glycol	weight %	0.1	NA	0.3
water	weight %	0.1	NA	0.3

Table 3

* Antiwear is reported as a negative value since it represents the depletion of a material. "NA" means "not applicable"

Reference

Used Lubricating Oil Analysis manual, P/N 269-069403, Thermo Fisher Scientific, 2003.

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