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Simple, in-use condition monitoring of lubricants using FT-IR

Sudhir Dahal, Liang Zhao, Gilbert Vial, and Andrew Fornadel, Shimadzu Scientific Instruments, Columbia, MD

1. Introduction

Engine lubricants play an important role in lubrication, cooling, cleaning, and rust prevention for vehicles, construction machinery, ships, airplanes, and other equipment with internal combustion or turbine engines. As the lubricant deteriorates through use, the lubrication performance will decline and the inside of the engine can wear, leading to a decrease in service life and potential engine malfunction. Lubricants deteriorate due to decomposition and chemical changes of oil components and additives caused by physical and thermal factors, as well as contamination by metal wear particles and incorporated fuel. Therefore, it is recommended to analyze the lubricant throughout its lifespan to assess its quality, utility, and remaining service life before an oil change is necessary. This is particularly important for heavy machinery that uses a large volume of specialized lubricants, which may be expensive.

These analyses can be accomplished with a number of instruments, but we will focus on the applications of FTIR for monitoring two major components of lubricant degradation: breakdown of the lubricants and their additives as well as incorporation of soot into the lubricant from combustion of fuels.

ASTM International specifies methods for evaluating the deterioration of lubricants through assessment of various parameters (Table 1). In this poster, we demonstrate the analysis and evaluation of lubricant deterioration, contamination, wear, and additives by an analysis method based on ASTM standards using a Fourier transform infrared spectrometer (FT-IR) and ASTM Method E2412.

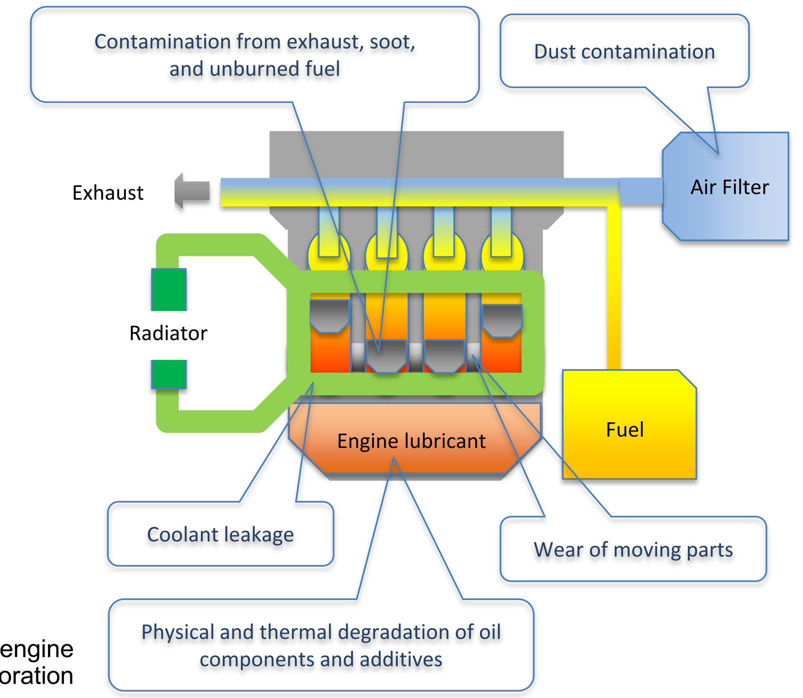

Figure 1: Typical causes of engine lubricant deterioration

Table 1: Examples of lubricant analysis items by FT-IR, GC, and ICP-AES

Condition Assessment		Instrument	Standard(s)
Deterioration	Oxidation	FT-IR	ASTM E2412
	Nitration		
	Sulfate by-products		
Contamination	Water	FT-IR	ASTM E2412
	Soot		
	Gasoline	GC	ASTM D3525 ASTM D7593
		FT-IR	ASTM E2412
	Diesel	GC	ASTM D3524 ASTM D7593
		FT-IR	ASTM E2412
	Coolant (B, Na, K)	ICP-AES	ASTM D5185
		FT-IR	ASTM E2412
	Antifreeze (Na)	ICP-AES	ASTM D5185
	Dust (Si)		
	Seal materials (Si)		
Wear	Metals (Al, Fe, Cu, Cr, Ni, Zn, etc.)	ICP-AES	ASTM D5185
Additives	Anti-oxidant (Zn, Cu, B)	ICP-AES	ASTM D4951
		FT-IR	ASTM E2412
	Anti-wear agents (B, Cu, K, S, Zn, etc.)	ICP-AES	ASTM D4951
		FT-IR	ASTM E2412
	Detergent inhibitors (Ba, Mg, Ca, etc.)	ICP-AES	ASTM D4951
	Corrosion inhibitors (Ba, Zn)		
	Anti-rusting agents (K, Ba)		
	Friction modifier additives (Mo)		

2. Molecular deterioration analysis

Infrared spectroscopy provides spectral data that reflect the molecular structure of a substance. By the analysis of lubricant by FT-IR, deterioration information due to compositional changes such as sulfation, nitration, and increase in carbonyl groups due to oxidation can be obtained. It also provides information about contamination by soot and other particulates as well as increases in hydroxyl groups due to moisture contamination. In addition, in the case of lubricants containing anti-oxidants or anti-wear components, it is possible to determine the degradation of additives due to the deterioration of the lubricants by assessing the spectral peak generated by those components. In this study, we evaluated lubricant deterioration using a compact and high-performance FT-IR and an easy-to-use liquid analysis cell.

IRSpirit FT-IR spectophotometer offers the highest S/N ratio in its class and high reliability using the technology inherited from the high-end model. The IR Pilot program simplifies routine analyses for all users. The combination of Pearl Liquid Analyzer and IRSpirit makes it possible to analyze lubricating oil with ease.

- Space-efficient with high expandability
- Easier to disassemble and clean than traditional liquid cells
- Accurate transmission path length

Figure 2: Combination of IRSpirit and Pearl Liquid Analyzer

2-1 Method

Used oil and new oil of Sample A and Sample B were analyzed by the combination system of IRSpirit and Pearl with 0.1 mm optical pathlength cell. Details of Sample A and Sample B are as follows.

Table 2: Sample Details

Sample A	Sample B
10W-60 gasoline engine lubricant Travel distance 3000 km Period of use: 3 months Used at high RPM range	0W-20 gasoline engine lubricant Travel distance 5000 km Period of use: 1 year Used at low RPM range

2-2 Results

As a result of FT-IR analysis, water contamination and deterioration due to oxidation and nitration were confirmed in Sample A. In Sample B, the amount of the anti-oxidant decreased, and no change in the spectrum indicating oxidation deterioration was observed. Presumably, oxidation of the oil was prevented by the anti-oxidant.

The analysis of lubricants by FT-IR does not require sample pretreatment, and the Pearl Liquid Analyzer makes it easy and quick to clean the cells for each analysis. In addition, data conforming to ASTM E2412 can be acquired with high reproducibility by the precisely maintained optical pathlength.

However, it is difficult to identify certain contaminants, such as fuel and coolant, at low concentrations because the FT-IR method is not as highly sensitive as other techniques. Various GC and ICP-AES methods are applicable to these detailed analyses.

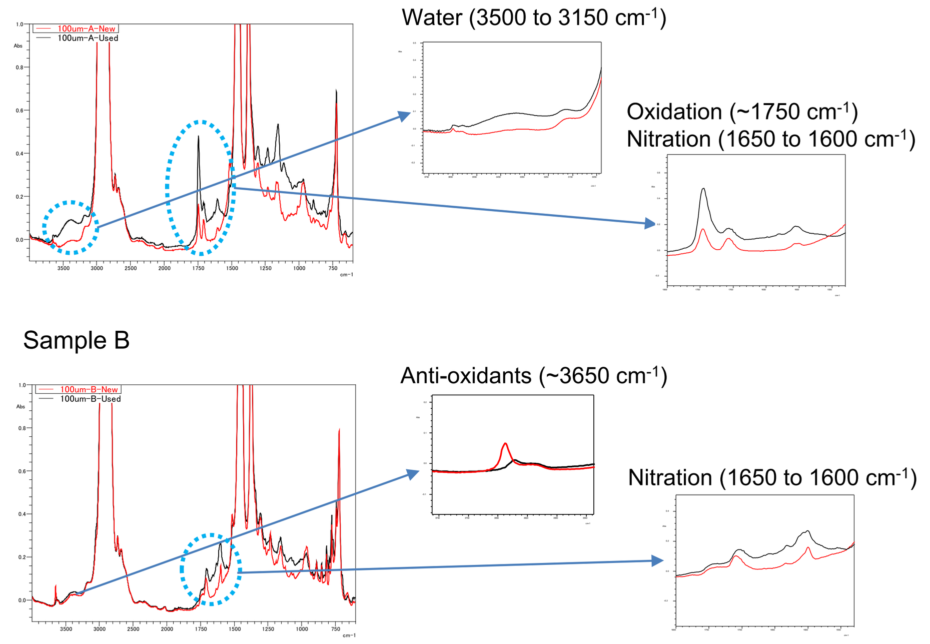

Figure 3: Spectra of Sample A and Sample B

3. Soot and particulate analysis

Soot and other residue may be incorporated into the lubricant as a result of incomplete combustion of fuel within the engine. Such a phenomenon is easily observed by the naked eye, comparing the honey-colored fresh lubricant with the dark brown to black color of used lubricants. In fact, lubricants and oil filters are intended, in part, to clean soot and particulates from the engine cylinders and remove them by filtration. Nonetheless, over time the lubricants and filters reach their capacity for removing soot and particulates. Excess particulate matter degrades the lubricant's performance.

Quantifying the soot or particulate content of a lubricant can also be performed by FTIR. Unlike quantification of molecular changes demonstrated in section 2, soot is largely composed of carbon and does not exhibit an absorption peak at a specific wavelength. Rather, the soot within a lubricant absorbs infrared radiation across the spectrum. As a result, the soot content can be inferred by a rise in baseline across the spectrum. For this study, we measured the baseline position at 1850 cm^{-1} as a proxy for soot content.

Figure 4: Combination of IRSpirit and QATR-S (left), drop of lubricant on stage of QATR-S (right)

3-1 Method

An IRSpirit with QATR-S attenuated total reflectance attachment was used to analyze a small amount of liquid sample placed on the QATR. Specific measurement conditions are provided in Table 3. Although ASTM E2412 specifies analysis for soot by absorbance at 2000 cm-1, we performed analysis at 1850 cm-1 to minimize interference with absorption by the diamond prism in the ATR. A calibration curve for soot was generated by analyzing 11 samples of known soot content (by mass %).

Table 3: Measurement conditions

Instruments	:	IRSpirit-T (KBr window plate) QATR-S (wide-band diamond disc)
Resolution	:	4 cm^{-1}
Accumulation	:	20 times
Apodization function	:	Sqr-Triangle
Detector	:	DLATGS

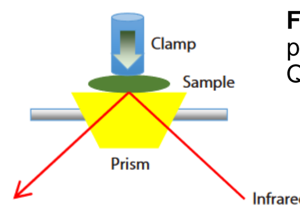

Figure 5: Diagram of light path through sample and QATR-S

3-2 Results

Eleven (11) samples of known soot content were analyzed to generate a calibration curve. The resulting spectra and curve are shown in Fig 6. The correlation coefficient of 0.998 indicate a strong linear relationship between soot content and absorbance at 1850 cm^{-1}.

Three (3) reference samples were analyzed against the calibration curve as "unknown" samples and the results are shown in Table 4. Samples 1 and 2, with higher soot contents, yielded results close to true values, whereas sample 3, with a low soot content of 0.02 mass %, reported quantified soot content higher than the true value. This is thought to be a product of baseline noise interfering with quantification.

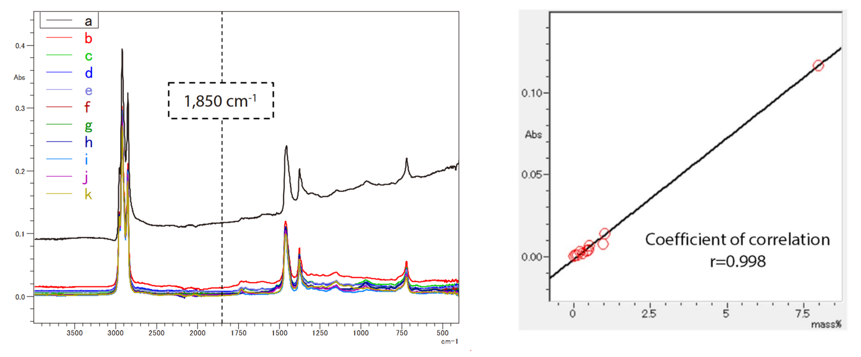

Figure 6: Calibration spectra (left) and calibration curve (right) for soot analysis

Table 4: Results of soot analysis of reference samples

Sample	Absorbance	Quantified Soot Content (mass %)	Actual Soot Content (mass %)
Sample 1	0.008	0.65	0.60
Sample 2	0.004	0.43	0.45
Sample 3	0.001	0.18	0.02

To ensure repeatable results from the FTIR, we performed 10 replicate analyses of 2 samples, with soot contents of 0.20 mass % and 3.93 mass %. The resulting spectra are shown in Figure 7. The coefficients of variation are 1.58% and 2.64% for 0.20 mass% and 3.93 mass %, respectively. The higher variability and drift in baseline of the sample with higher soot content is thought to be a result of suspended soot particles accumulating on the edges of the QATR-S stage. Nonetheless, repeatability was considered to be acceptable for the purposes of soot content quantification.

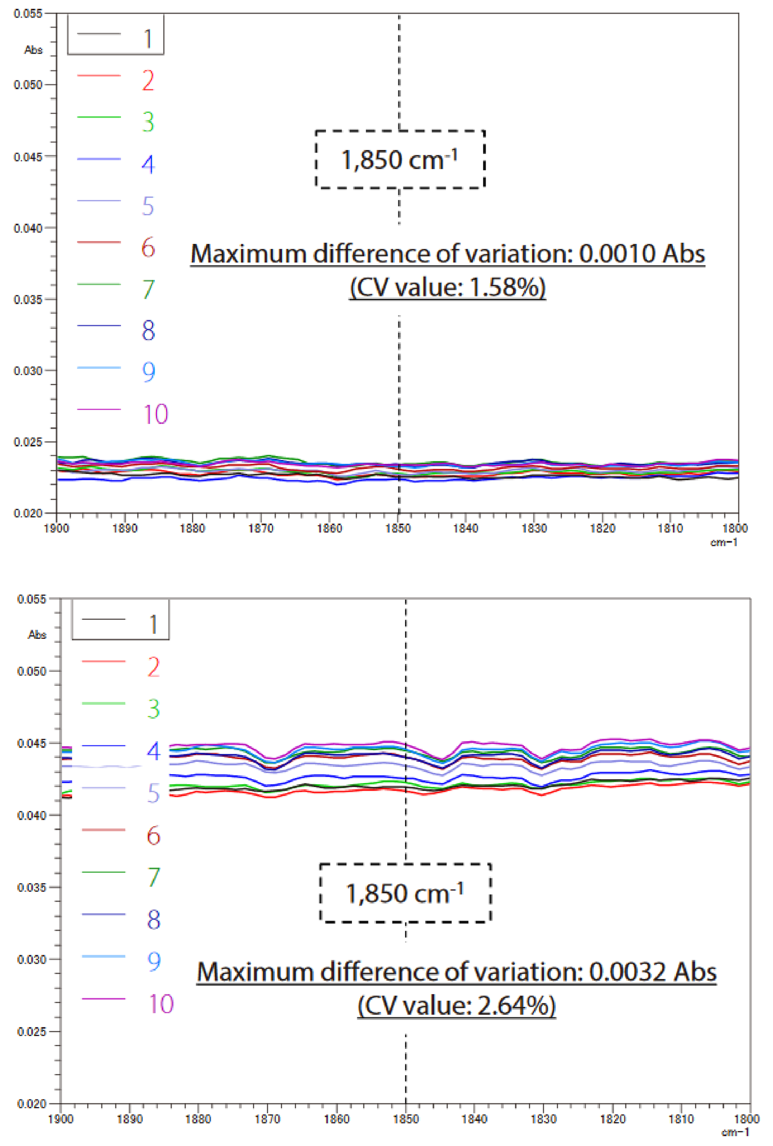

Figure 7: Spectra of 10 repeated analyses for samples with 0.20 mass % soot (top) and 3.93 mass % soot contents (bottom).

4. Conclusions

- The IRSpirit FT-IR with various accessories stage enable the simple, rapid analysis of lubricating oils to assess their quality, condition, and remaining life.
- With its small form factor, the IRSpirit can easily fit onto the benchtop, without major overhauls to laboratory infrastructure.
- Using the Pearl Liquid Analyzer, it is easy to assess molecular changes to lubricating oils, including oxidation, sulfonation, hydration, or degradation of additives designed to impede those processes.
- With the QATR-S, quick quantification of soot within the lubricant is enabled.
- The IRSpirit is compliant with industry standard test methods, such as ASTM E2412.