

# Analysis of Synthetic Lubricants by Fourier Transform Infrared Spectroscopy

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## KEYWORDS

FT-IR/used lubricating oil, synthetic lubricants/mineral oil, fuel, glycol, ester, diester/PLUS/OMNIC Integra

## INTRODUCTION

Fourier transform infrared (FT-IR) technology is rapidly becoming a method of choice for used lubricating oil analysis. Historically, emphasis has been placed on the analysis of the more commonly used mineral oil based lubricants. However, the introduction of a wide variety of synthetic based lubricants has led to more demand for synthetic engine, gear box and hydraulic lubricant analysis as well. The components commonly determined in mineral oil lubricants, such as water, oxidation, fuel, glycol and antiwear, are also important for synthetic lubricants. Unfortunately, many synthetic lubricants are chemically very different from mineral oil lubricants; therefore, they cannot be analyzed with the same quantitative algorithms as are used for mineral oil lubricants.

There are several synthetic base oil types which represent different chemical structures including – polyalphaolefins (PAO), polyol esters (POE), polyalkylene glycols (PAG), and phosphate esters. These different chemical structures exhibit widely differing spectral changes as a result of the presence of oxidative breakdown products or contaminants. This application note discusses some of the issues related to the analysis of synthetic lubricants with particular focus on the determination of low levels of water.

In a typical analysis of used lubricants,<sup>1</sup> the new oil reference spectrum is collected and saved in a spectral database. When the used lubricant is analyzed, the new oil spectrum is subtracted from the used lubricant spectrum to obtain a difference spectrum. Figure 1 shows three spectra of a mineral oil based lubricant – the used oil, its new oil reference, and the subtraction result. The subtraction result or difference spectrum contains only information about what has chemically changed in the lubricant during its use. Note that the features in the difference spectrum are very small in comparison to the gross features of either the new or used

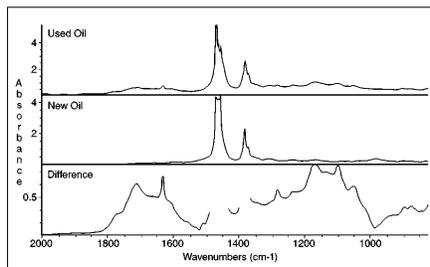


Figure 1

lubricant as indicated by the absorbance scale of the spectra.

Figure 2 is the same difference spectrum with annotation of the peaks typically used to calculate the main parameters of interest for used lubricant condition monitoring.<sup>2</sup> An alternate approach for this analysis is to obtain only the used lubricant spectrum, and relate changes in the spectrum to an information database of numbers for the unused lubricant to make decisions about its condition. Both techniques require knowledge of the spectral features of the lubricants being analyzed and work best for trending data over time. The later approach does not take into consideration, component to sample matrix interactions in the spectra.

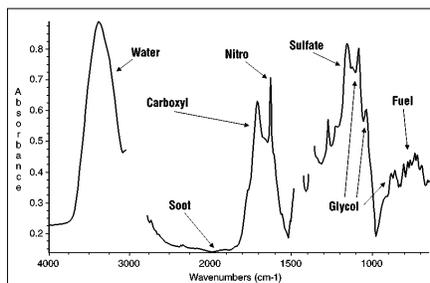


Figure 2

The demand for quantitative information for synthetic lubricants has been growing as the use of synthetic lubricants has been increasing. However, gathering this information is complex because synthetic lubricants come in very different chemical forms. In mineral based lubricants, there are variations in base stocks due to the differences in crude oil from which they are refined, but their chemical behavior is fairly consistent. With synthetic lubricants, the base stock is chemically very pure, but depending on which one is used and how the base stocks are blended, the spectral fingerprint and chemical behavior may vary widely. Some of the commonly used synthetic base oils include polyalphaolefins (PAO), diesters,

and polyol esters. The two former types are commonly found in non-aeronautical applications because of their lower cost, and they are often blended. The polyol esters, along with other ester types such as phosphates, are widely used in military and commercial aeronautic applications where their higher cost is justifiable due to their low flammability.

Figures 3-5 are spectral plots of different lubricants that show the gross differences in their chemical structures. Figure 3 shows spectra for a PAO, a diester and a natural tallow oil. From this spectral data it is clear that the PAO is quite different from the tallow oil and diester in chemical structure. In fact, the diesters are much closer chemically to natural seed or animal oils, such as tallow oil, whereas the PAO lubricants are similar to mineral oils.

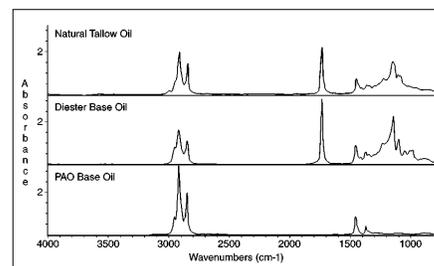


Figure 3

Figure 4 has three spectra showing an SAE 30W mineral-based engine oil and a SAE 10W-30 synthetic engine oil from Manufacturer A, and a 10W-30 synthetic engine oil from Manufacturer B. Note that the spectrum of the PAO base oil (Figure 3) is very similar to that of the mineral-based SAE 30W. The spectral differences between the synthetics and the mineral-based oils are apparent. Manufacturer B's synthetic appears to have a higher ester content as indicated by the relatively larger carbonyl peak at 1730 cm.<sup>1</sup>

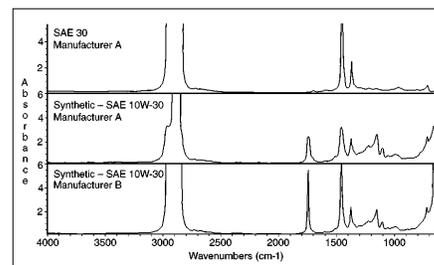


Figure 4

Figure 5 shows spectra of MIL-SPEC synthetic lubricants – L-23699 aeronautical

oil and H-83282 hydraulic oil. The L-23699 is a polyol ester based lubricant and is chemically similar to L-7808 and L-85734 aeronautical oils. The H-83282 appears to be a diester and would thus be closer in chemical form to the commercial synthetic engine oils shown in Figure 4.

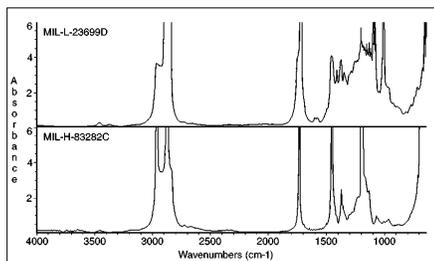


Figure 5

Due to their widely varying infrared spectra, synthetic lubricants present special problems for infrared analysis in used oil applications. First, the presence of oxygen in the molecular structure of ester-based lubricants causes spectral interferences that prevent the use of traditional quantitative algorithms. In addition, breakdown products from oxidative processes and interactions with other contaminants vary with different oil types. Only through controlled and consistent use of a given lubricant in either field tests or engine tests can an understanding of the lubricant breakdown products and the effects of external contaminants be established. However, it has been difficult to obtain study sets to build an understanding of the behavior of synthetic lubricants under conditions of use in the commercial non-aeronautical sector because the use of synthetics has not been consistent. The behavior of polyol ester based synthetic lubricants under breakdown and contamination conditions in military aeronautical applications has been described.<sup>3</sup> However, additional studies are needed for the characterization of the relationship of infrared spectral information to other contaminating materials under conditions of use. These studies are needed in order to accurately develop quantitative methods.

One key parameter of interest in lubricant condition monitoring is low level water contamination, since it affects the performance characteristics of all lubricants. Numerous FT-IR quantitative analysis methods have been described for various applications.<sup>4,5,6</sup> However, the purpose of this study was not to define a specific quantitative analysis algorithm for determining water in synthetic lubricants. Rather, it was to evaluate the parameters and scope of the problem

required to develop robust methods across a range of synthetic based lubricant products. Particular attention was paid to the interaction of a small set of synthetic lubricants with water, and the affect of these interactions on obtaining accurate quantitative results.

## EXPERIMENTAL

In an effort to assess the robustness of quantitative FT-IR calibrations for water determination in synthetic lubricants, standards were generated from a small set of unused synthetic lubricants. The synthetic lubricants used in this study included 10W-30, 5W-30, and 15W-50 from Manufacturer A, 10W-30 from Manufacturer B, MIL-L-23699D aeronautical lubricant and MIL-H-83282C hydraulic lubricant. The specific manufacturer of the MIL-SPEC lubricants was not known. These standards were analyzed via FT-IR and their spectra used to statistically evaluate various quantitative calibrations.

It must be pointed out that the analysis of water in lubricants has several important factors that make quantification difficult by optical techniques. Since water has low solubility in oil, standard preparation and analysis must be handled rigorously to obtain consistent results. Also the range of calibration must be kept small to obtain linear results. With these considerations in mind, all samples were prepared by weight using tap water and the lubricant of interest.

The range found to be best for maintaining linear calibration data was from around 0.025 to 0.5 wt. %. Each standard was sonicated for a minimum of 1 hour to homogenize the water with the oil at the various concentrations. Untreated clean oil for each oil type tested was analyzed along with the water spiked standards to be used as a reference oil in the cases where subtraction was done as part of the result calculation. The infrared absorbance spectra of each of the prepared standards and reference oils were collected on a Nicolet Impact<sup>®</sup> 400 FT-IR spectrometer at 4 cm<sup>-1</sup> resolution using 128 scans (about 2 minutes), Happ-Genzel apodization and no zero-filling. The flow-cell used was a BaF<sub>2</sub> transmission cell. A new instrument background was collected prior to every sample spectrum. Samples were pumped into the cell using the Spectra-Tech Programmable Liquid Uptake System (PLUS<sup>™</sup>). The cell was calibrated prior to use in these investigations and found to be 111 microns based on the fringe counting method for a clean, dry cell<sup>7</sup>

## RESULTS AND DISCUSSION

The sensitivity of mid-infrared measurements to the local chemical environment around particular bonds in a sample has led to its widespread use in research and development. However, when doing quantitative analysis on chemical systems the interactions of the chemical components within the sample matrix must be well characterized and modeled. Stated simply, the location and shape of peaks in the mid-infrared spectrum will shift based on a particular combination of chemicals in a sample that is analyzed.

Water is a chemical that is well known for its influence on and by other chemicals that it contacts through hydrogen bonding. This leads to variation in the spectral response to water in different chemical systems that would seem on the surface to be quite similar. Figures 6-8 are spectral plots that show the gross interactions with water exhibited by the synthetic lubricants used in this study. Each figure contains the spectra of the clean oil, the clean oil spiked with about 0.5 wt. % water and the spectral subtraction result.

Figure 9 compares the subtraction result spectra for each of the three previous water containing synthetic lubricants. Note that the behavior of the synthetic oils from Manufacturers A and B appear similar in the OH region (~3400 cm<sup>-1</sup>). The OH peak centered at about 3400 cm<sup>-1</sup> in these two lubricants is similar to that seen in mineral based lubricants (Figure 2). However, the MIL-L-23699 shows a very different interaction with water. This represents interactions with multiple forms of the OH functional group due to the presence of free OH groups within the molecular structure of the polyol ester base oil.

Calibrations were performed using the method described in the experimental section for each of the oil types. The region used for the calibration (3720 to 3117 cm<sup>-1</sup>) was based on that typically used for quantifying water in mineral oil lubricants. The goal of this exercise was to study how differing molecular interactions of the synthetic lubricants tested, affect the results of water quan-

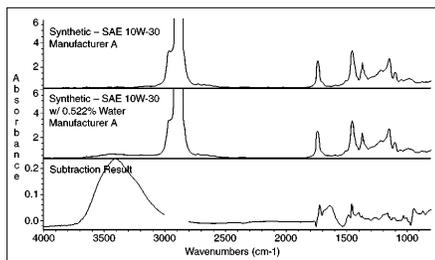


Figure 6

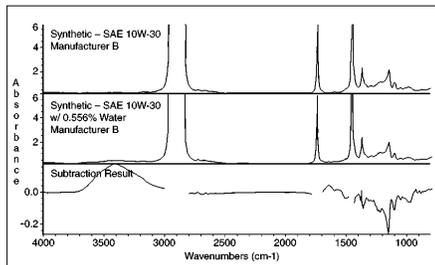


Figure 7

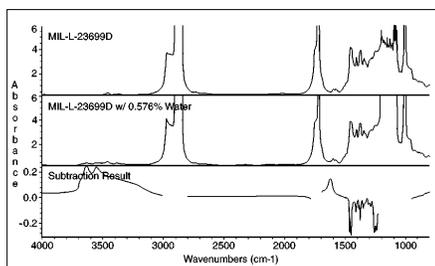


Figure 8

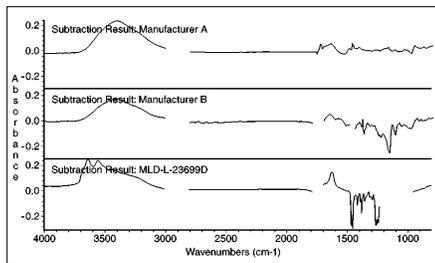


Figure 9

tification. Calculations were performed to generate predicted values for the standards calculated as unknowns for each data set. The average relative percent difference for a given set of results was used as a metric to indicate the total amount of deviation from the actual values used to calibrate for water in oil. This provides an indication of the amount of scatter found in the results. The average relative percent difference is the unsigned average relative percent difference between actual and predicted values and does not indicate any direction of bias.

Taking a simple case first, Table 1 shows cross-correlation data in which the unsubtracted spectra for Manufacturer A's 10W30 water standards were used to generate the calibration model. The actual versus predicted values were then calculated from the model for three lubricants from Manufacturer A and a 10W-30 from Manufacturer B. The

predictions for the 10W-30 from Manufacturer A were excellent, but predictions for the others were more widely scattered.

Sample No.	Mfr. A 10W-30		Mfr. A 5W-30		Mfr. A 15W-50		Mfr. B 10W-30	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	0.03	0.03	0.02	0.06	0.02	0.08	0.02	-0.03
2	0.09	0.08	0.08	0.09	0.08	0.11	0.09	0.01
3	0.17	0.17	0.13	0.15	0.12	0.15	0.13	0.05
4	0.13	0.13	0.17	0.19	0.16	0.19	0.18	0.08
5	0.25	0.24	0.25	0.26	0.25	0.28	0.31	0.17
6	0.37	0.39	0.38	0.39	0.37	0.36	0.41	0.26
7	0.52	0.51	0.55	0.57	0.54	0.53	0.56	0.31
Avg Rel % Diff:		5.27	26.71		49.16		79.24	
SD +/-:		4.98	50.04		87.90		66.64	

TABLE 1

By subtracting the new oil from the calibration, Table 2 shows analogous cross-correlation results in which data from the subtracted spectra for Manufacturer A's 10W-30 water standards were used to generate the calibration. The actual versus predicted values were then calculated for all water standards. This resulted in predictions for Manufacturer A's 10W-30 that were nearly the same as the unsubtracted spectra, as would be expected. However, the predictions for the others dramatically improved. It should be noted that the results of Manufacturer B's lubricant are worse than Manufacturer A's products, even for subtracted spectra.

Sample No.	Mfr. A 10W-30		Mfr. A 5W-30		Mfr. A 15W-50		Mfr. B 10W-30	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	0.03	0.03	0.02	0.03	0.02	0.03	0.02	0.02
2	0.09	0.08	0.08	0.07	0.08	0.06	0.09	0.06
3	0.17	0.17	0.13	0.13	0.12	0.10	0.13	0.10
4	0.13	0.13	0.17	0.17	0.16	0.14	0.18	0.13
5	0.25	0.24	0.25	0.24	0.25	0.23	0.31	0.22
6	0.37	0.39	0.38	0.37	0.37	0.32	0.41	0.30
7	0.52	0.51	0.55	0.54	0.54	0.48	0.56	0.36
Avg Rel % Diff:		5.24	10.43		16.11		27.01	
SD +/-:		4.69	15.25		9.32		6.64	

TABLE 2

The next experiment involved the results of a broader based calibration model that could potentially generate a more robust and universal calibration. Table 3 shows cross-correlation results in which data from the unsubtracted spectra for all water standards were pooled together and used to generate the calibration. The actual versus predicted values calculated for all water standards resulted in a model with a wide data spread. Using this approach would require one to accept fairly large variation in predictions.

Using the same pooled standard data approach but factoring out the new oil from the standard, Table 4 shows cross-correlation results in which data from the subtracted spectra for all water standards were used to generate the calibration model. The actual versus predicted values were calculated for all

Sample No.	Mfr. A 10W-30		Mfr. A 5W-30		Mfr. A 15W-50		Mfr. B 10W-30	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	0.03	0.05	0.02	0.08	0.02	0.10	0.02	0.00
2	0.09	0.10	0.08	0.11	0.08	0.13	0.09	0.03
3	0.17	0.19	0.13	0.17	0.12	0.17	0.13	0.07
4	0.13	0.15	0.17	0.21	0.16	0.21	0.18	0.10
5	0.25	0.26	0.25	0.28	0.25	0.30	0.31	0.19
6	0.37	0.40	0.38	0.41	0.37	0.38	0.41	0.28
7	0.52	0.53	0.55	0.58	0.54	0.54	0.56	0.33
Avg Rel % Diff:		25.00	51.34		73.34		51.36	
SD +/-:		37.47	83.87		123.81		24.54	

TABLE 3

Sample No.	Mfr. A 10W-30		Mfr. A 5W-30		Mfr. A 15W-50		Mfr. B 10W-30	
	Actual	Predicted	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	0.03	0.04	0.02	0.04	0.02	0.04	0.02	0.03
2	0.09	0.09	0.08	0.08	0.08	0.08	0.09	0.07
3	0.17	0.19	0.13	0.14	0.12	0.12	0.13	0.12
4	0.13	0.15	0.17	0.19	0.16	0.16	0.18	0.15
5	0.25	0.27	0.25	0.27	0.25	0.26	0.31	0.24
6	0.37	0.43	0.38	0.41	0.37	0.35	0.41	0.34
7	0.52	0.57	0.55	0.60	0.54	0.53	0.56	0.40
Avg Rel % Diff:		18.59	19.55		14.24		18.38	
SD +/-:		17.47	31.28		30.44		6.94	

TABLE 4

water standards, resulting in a model in which the average data scatter is improved greatly over the unsubtracted calibration model into a more acceptable range of variation.

Figure 10 is a graphical representation of the pooled data for unsubtracted spectra showing the relative scatter represented in Table 3. It is interesting to note the results of Manufacturer B's oil form a unique set of data points below the average line for all of the data.

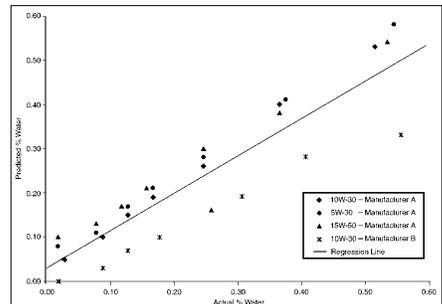


Figure 10

Figure 11 is a graphical representation of the pooled data for subtracted spectra showing relative scatter for all of the standards presented in Table 4. In this case, all results are tighter to the line except at the higher concentrations, where linearity begins to suffer owing to the difficulty in standards preparation at higher concentration levels.

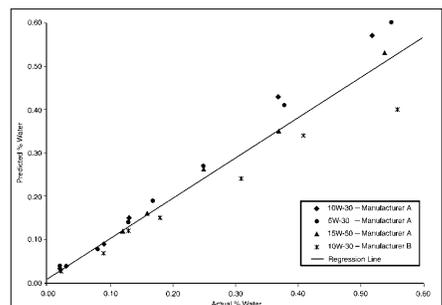


Figure 11

In order to relate the numerical and graphical data to the actual spectral data, Figure 12 shows a spectral overlay of Manufacturer B's oil clean and with increasing levels of water. This shows the spectral contributions due to the oil/water interactions in the water region of the spectrum. The level of this affect will vary in different lubricants. Note how the base oil spectrum also contains the broad peaks in the OH region. However, with the data shown for Manufacturers A and B's standards, it is still possible to generate a reasonable calibration curve to account for variation due to the interaction with water as long as proper reference information concerning the new oil is taken into account.

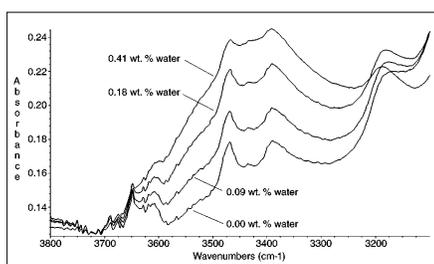


Figure 12

Another case investigated shows that this relationship can not be assumed to always hold true. Table 5 shows the data resulting from the original calibration when Manufacturer A's 10W-30 is compared to the MIL-L-23699 water standards. In this case, even with spectral subtraction, the data are farther from the calibration line than was

Sample No.	Mfr. A 10W-30		MIL-L-23699D	
	Actual	Predicted	Actual	Predicted
1	0.03	0.03	0.02	0.02
2	0.09	0.08	0.08	0.04
3	0.17	0.17	0.15	0.06
4	0.13	0.13	0.29	0.15
5	0.25	0.24	0.58	0.31
6	0.37	0.39	0.98	0.34
7	0.52	0.51	0.06	0.01
Avg Rel % Diff:		5.27	50.01	
SD +/-:		4.98	22.15	

TABLE 5

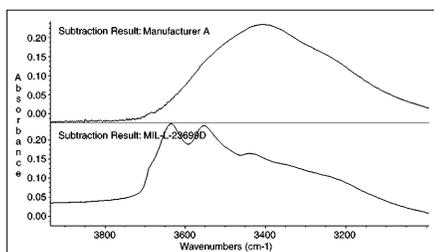


Figure 13

seen for the other synthetic lubricants studied. When one compares the spectral interaction of water with lubricants as shown in Figure 13, it is obvious that using standards prepared from Manufacturer A's 10W-30 to quantify water in MIL-L-23699 is not valid. The need to have a different software quantitation algorithm and separate calibration curve for this lubricant is obvious.

## CONCLUSIONS

Before presenting conclusions resulting from this study, it is important to point out some of the limitations of this work. First of all, a complete range of commercially available synthetic lubricants was not included. A representative set was chosen to address the issues of differences in the interaction with water. However this set would need to be expanded to characterize all synthetic lubricants on the market – not a practical consideration. In addition, reproducibility studies were not performed, and the data presented shows relative accuracy. Finally, the issue of interfering phenomena such as additive depletion, oxidation or the presence of other contaminants under conditions of real use was not addressed. These factors need to be addressed before a complete set of algorithms for quantitative analysis of synthetic lubricants can be properly developed.

There are important conclusions that can be made from this study. Primarily, that FT-IR provides a rapid and sensitive determination of water in synthetic lubricants. However, for this to be successfully implemented in a robust and accurate manner across a wide range of synthetic lubricant types, several important requirements must be met. First and foremost, a knowledge and understanding of the lubricant types and their interactions with water must exist and be built into the analysis and interpretation routines. Secondly, within the sample or data analysis protocol, referencing is required to obtain accurate data. The two types of referencing that can be applied are:

1. Spectral subtraction from a database of new lubricants' spectra as part of the analysis.
2. Having a knowledge base of spectral contributions by the new lubricants in the quantitative region or regions of interest.

It is obvious from the data presented that creating and maintaining separate calibration curves for each oil type (and new ones as they are developed) would be quantitatively ideal. However, this is an impractical consideration for the vast majority of used oil analysis laboratories since it is time consuming. This approach requires generating and maintaining individual calibration curves for each oil type, each consisting of 5 or more standard samples.

Reference subtraction only requires one clean oil reference spectrum stored in a spectral library. Based on the effort required to apply these two approaches and the quality of the quantitative information provided by each, spectral subtraction is the preferred technique.

With these considerations in mind and with careful implementation of quantitative algorithms for obtaining data from the FT-IR, the technique can become a vital part of an equipment maintenance management program. Since spectral subtraction more reliably accommodates water to oil interactions within a sample matrix, it is the preferred technique.

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