QUANTITATIVE FTIR CONDITION MONITORING - ANALYTICAL WAVE OF THE FUTURE?

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Introduction

The quality or status of a lubricant is directly related to the performance and reliability of machinery and the importance of condition monitoring so as to avoid excessive wear and downtime of equipment and critical components has been recognized (1). The chemical and physical parameters analyzed for are largely based on standardized analytical methods to provide an overall indication of the status of a lubricant. However, key ASTM chemical methods such as the determination of Total Acid Number (TAN), Total Base Number (TBN) and moisture (H_2O) are troublesome to carry out, being tedious, time consuming and trouble prone even in their automated forms. Today, there is more emphasis on structured condition monitoring to provide trending data so that one can take preventive action on the one hand, but not take unnecessary action on the other. This approach may extend drain intervals and reduce lubricant disposal and maintenance and failure costs. On the other hand, extensive testing is required and data management can become complex.

FTIR Spectroscopy

In this context, an instrument that has become increasingly prominent in lubricant analysis is the infrared spectrometer, specifically the Fourier transform infrared (FTIR) spectrometer. This analytical instrument effectively provides a spectral snapshot of the base oil and other constituents present. Its power is based on the fact that specific molecular functional groups absorb in unique regions of the mid-infrared spectrum, allowing identification of additives, contaminants and breakdown products. Although IR spectral information is meaningful to a spectroscopist, its meaning is not necessarily apparent to the non-expert. Even with this limitation, IR spectroscopy is still a very powerful tool, simply because it can provide substantial information about oil condition using a single instrument. Indications about the state of oxidation, nitration and sulfation and levels of soot, moisture, glycol and various additives, among others, is available. Extensive IR studies of lubricants and fuels have led to the establishment of standardized protocols to monitor selected condition parameters under the guise of the Joint Oil Analysis Program (JOAP). These protocols, and similar protocols under consideration by the ASTM, provide a comprehensive means of monitoring the condition of lubricants using a single analytical technique.

FTIR Limitations

Given the power of FTIR spectroscopy, one has to question why it is not used more, and more effectively. One of the key limitations in this regard is that the currently accepted methodology is *qualitative* rather than *quantitative.* At issue is the complexity and variability of formulated lubricants, making unambiguous quantitative IR data difficult to obtain. At present, FTIR spectroscopy is mostly used to track relative changes in an oil, the baseline being the fresh or new oil. By subtracting the spectrum of the fresh oil from its used or in-service oil counterpart, one can spectrally visualize what has changed at a molecular level, including moisture ingression, additive depletion, oxidation, soot buildup etc. Hence the JOAP protocols attempt to standardize the measurement of these changes in terms of absorbance or arbitrary units that can be correlated with machine faults, wear or failure. This type of spectral information can be rapidly collected on an ongoing basis and via trending can be associated with specific lubricant changes (e.g., oxidation, soot buildup). With the correct interpretation, lubricant replacement or additive replenishment can be made on the basis of oil condition monitoring rather than simply on the basis of time, thereby reducing oil consumption and machine wear caused by the use of oils which have exceeded their useful life. One of the main limitations of this approach is that the results may be completely off-track if the base oil formulation changes or the reservoir has been topped up with another oil formulation.

Why Quantitative FTIR?

In addition to providing a wealth of qualitative or semi-quantitative information, FTIR spectroscopy can potentially be employed in place of a variety of ASTM chemical methods. These ASTM analytical methods such as TAN, TBN and H2O are cumbersome and relatively inaccurate, but they provide values that are meaningful to the user. TAN is a measure of oxidative status, while TBN is a measure of reserve alkalinity, both measured as mg of KOH/g of oil, while water is reported in parts per million (ppm). The utility of FTIR analysis in the lubricant sector would be significantly enhanced by the capability to carry out quantitative measurements of this type, beyond its existing basic trending role. Hence *the best of both worlds lies in obtaining both trending and quantitative data using FTIR spectroscopy*, whereby one has both speed of analysis and more interpretable information.

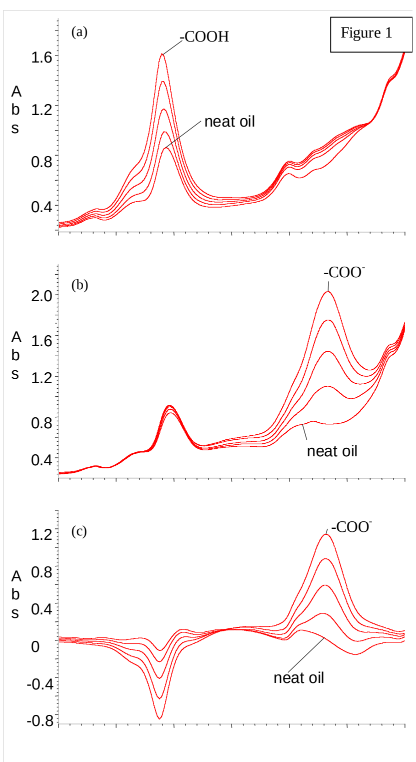
Quantitative IR spectroscopy has been undergoing extensive development for some time in the edible oils sector of the food industry (2), much of this work spearheaded by the McGill IR Group (3). Edible oils, like lubricants are formulated, change during storage and use, are modified during processing and undergo oxidation. The edible oil industry employs, tedious, chemical methods standardized by an official professional body, the AOCS (American Oil Chemists' Society), to evaluate the quality or condition of these oils also, much like the lubricant sector uses the standard ASTM methods. Similarly, the edible oil sector is in need of modern and more efficient methods of analysis for process and quality control functions that could be carried out on a single instrument. Mid-FTIR spectroscopy has been shown to deliver accurate results rapidly, improving substantially on the standard AOCS chemical methods. Thermal-Lube Inc., a specialty lubricant formulator, recognized that quantitative FTIR spectroscopy could provide similar benefits to the lubricant sector. Subsequently, a cooperative research program was instituted between McGill University and Thermal-Lube Inc, to develop a package of analytical methods for the lubricant sector.

Reference Oil Dilemma Solved

The research program focused on overcoming the main hurdle facing quantitative FTIR analysis of lubricants, *the need for a reference oil*. This stumbling block was overcome through the application of *differential spectroscopy in conjunction with the use of a specific stoichiometric reaction.* By recording the spectrum of the oil twice, once before and once after reagent addition and examining the differential spectrum obtained by subtracting one spectrum from the other, quantifiable information related to a particular constituent can be obtained. The FTIR TAN analysis is based on the conversion of the carboxylic acids formed as a result of oxidation to carboxylate salts using a strong base (4):

$$\text{R-COOH} \quad + \quad \text{KOH} \quad \rightarrow \quad \text{R-COO}^{-}\text{K}^{+} \quad + \quad H_2O$$

The oil is spectrally analyzed as is and after alcoholic KOH is added to it. Figure 1 illustrates what occurs spectrally. The series of bands in Figure 1a are indicative of a serial dilution of acid present (COOH) in an oil, while in Figure 1b the acid has been converted to its salt (COO^-). The difference spectrum in Figure 1c shows the overall loss of COOH (negative bands) and the formation of COO^-K^+ (positive bands). What is crucial about the differential spectrum is that because all the other constituents that may be present in the oil (additives, moisture, soot, etc.) are the same in both samples, their spectral contributions ratio out. The net spectral change observed is only what has changed as a result of the reaction. Unlike the ASTM TAN method, this FTIR method is specific for COOH as only this spectral change is measured. The amount of COOH can be quantitated in mg KOH/g oil, either by peak height or peak area measurements or by more sophisticated chemometric methods.



What is unique about the method is that it obviates the need for a reference oil, as the sample is its own reference by virtue of spectral subtraction. These concepts (but using different reagents) have also been used for the FTIR quantitation of TBN (5) and H_2O (6), to provide a means of obtaining meaningful, conventional quantitative data for these parameters (mg KOH/g and ppm, respectively).

Implementation

In order to make these measurements practical and useful for the general analytical situation, an FTIR analytical system was designed to carry out these analyses on a routine basis (7). This system consists of a rugged FTIR, computer and customized software as well as a sample handling accessory and reagent kits. As configured, the unit allows one to analyze for either TAN, TBN or H_20 in less than 5 min/sample (8). The precision of the analyses is ±0.10 mg KOH/g oil for TAN/TBN and ±40 ppm for H_20. These specifications are for a 200 μm pathlength cell, which can also be used for JOAP oil analysis protocols, extending the utility of the instrumentation. These methods are specifically for mineral base oils and are not suitable for synthetics, although specialized methods could be developed.

The Future: A Wave or a Whimper?

Quantitative analysis by IR spectroscopy has substantially advanced because of the inherent superiority of FTIR spectrometers over conventional grating spectrometers. More specifically, their very precise wavelength accuracy allows accurate quantitative data to be derived without the need for frequent recalibration. In addition, the combination of advanced chemometrics and spectral manipulation software has provided new analytical and discriminant abilities (9). These tools have made it possible to determine TAN, TBN and H_2O through the combined use of stoichiometric reactions and differential spectroscopy, to obtain meaningful, interpretable data. In the development of this FTIR methodology, TAN, TBN and H_2O were the more obvious and important candidates among many lubricant parameters a lubricant analyst might want to assess. There is certainly scope for other methods, including sulfation, glycol, fuel dilution and soot among others; however, extensive research and development will be needed for such methods to move into the quantitative realm. Experience should first be gained with the new methods developed to date, as it is only with their implementation that their benefits and limitations will become apparent. If these find acceptance and prove themselves, it will provide the impetus for other methods. The JOAP FTIR protocols have been around for some time but are still not as widely accepted or implemented as one might expect. Similarly, the concept of condition monitoring itself has been slow in coming of age. This conference with its condition monitoring theme is indicative of a growing recognition of new approaches to lubricant analysis. Only the future will tell if quantitative FTIR spectroscopy will become a part of the tribologists' standard analytical arsenal.

References

1. W. Robertson, ed., *Lubrication in Practice*, Macmillan Press Ltd., Houndmills, Basingstoke, U.K. 1984.
2. van de Voort, F.R., FTIR Spectroscopy in Edible Oil Analysis, *Inform* 5(9):1038-1042 1994.
3. van de Voort, F.R. and J. Sedman. FTIR Spectroscopy. The next generation of oil analysis methodologies? Inform 11 614-620, 2000.
4. Dong, J., F.R. van de Voort, A.A. Ismail, E. Akochi-Koblé, and D. Pinchuk. Rapid determination of the carboxylic acid contribution to total acid number of lubricants by Fourier transform infrared spectroscopy. Lubr. Eng. 6:12-20, 2000.
5. Dong, J., F.R. van de Voort, V. Yayalan, A. Ismail, D. Pinchuk and A. Taghizadeh. Determination of total base number (TBN) in lubricating oils by mid-FTIR spectroscopy. Lubr. Eng. (in press)
6. Dong, J., F.R. van de Voort, V. Yaylayan, and A.A. Ismail. A new approach to the determination of moisture in hydrocarbon lubricating oils by mid-FTIR spectroscopy. Lubr. Eng. (in press).
7. Dong, J., F. R. van de Voort, A. A. Ismail, and D. Pinchuk. A Continuous Oil Analysis and Treatment (COAT) System for the Monitoring of Oil Quality and Performance of Additives, Lubr. Eng. 53 (10), pp. 13-18 1997.
8. Dong, J., A.A. Ismail, F.R. van de Voort, D. Pinchuck. A novel method to determine TAN, TBN and moisture using FTIR spectroscopy. In JOAP International Conditioning Monitoring Conference. Mobile AL. 132-141, 2000.
9. McClure, G. L., ed., *Computerized Quantitative Infrared Analysis*, ASTM STP 934, American Society for Testing and Materials, Philadelphia, 1987.