

UNDER THE HOOD - MEETING THE DESIGN CHALLENGE OF THE FLUIDSCAN HANDHELD INFRARED OIL ANALYZER

Spectro Scientific



Synopsis

Direct imaging IR optics achieve the equivalent analytical capability as the FTIR spectrometer, and the unique chemometrics algorithms for accurate, repeatable and trendable TAN/TBN and water measurements. FluidScan delivers the power of a laboratory FTIR, Karl Fischer water titrator and a TAN/TBN titrator to reliability engineers who monitor the oil condition whenever and wherever they need it.

Introduction

Mid-Infrared (Mid-IR) spectroscopy is widely used for lubricant formulation and evaluation because of the detailed information on chemical composition provided by this technique. In recent years, it has been deployed as a condition monitoring tool in laboratories worldwide providing degradation information of in-service lubricants by measuring properties such as Oxidation, Nitration, Sulfation, Soot and Antiwear Additive depletion. It is widely accepted for this purpose with established ASTM standards (Table 1).

Figure 1 shows a typical infrared spectrum of an oil sample. The regions of the spectrum used to calculate typical oil condition parameters are highlighted to show how the IR spectrums are utilized for this purpose. Usually such spectrums are obtained in a lab with a Fourier Transform Infrared Spectrometer (FTIR), and the analysis is performed by a trained lab technician. Reliability professionals have not adopted FTIR spectrometers for use in the field due to the challenges of miniaturization, sample introduction and the need for direct, high-quality and actionable information without requiring the operator to be a trained oil analyst.

PROPERTY	ASTM METHOD	UNITS
Antiwear Additive	D7412	abs/0.1mm
Nitration	D7624	abs/cm
Soot	D7844	abs/cm
Sulfation	D7415	abs/0.1mm
Oxidation	D7414	abs/0.1mm

Table 1: Quantitative parameters extracted from oil Infrared spectra and the corresponding ASTM methods and units reported.

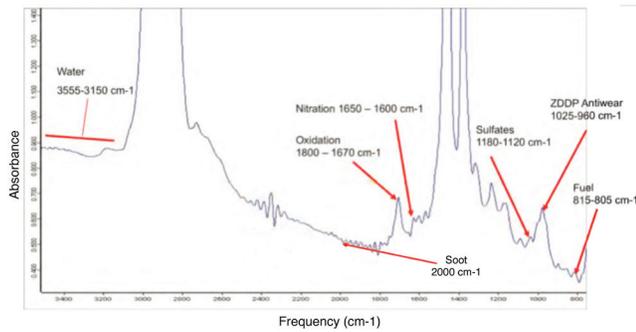


Figure 1: A typical infrared spectrum of in-service oil and parameters extracted from the spectrum. A laboratory FTIR spectrometer is a common tool to provide such information. A lab technician or data analyst then interprets the spectrum and provides quantitative information about the oil condition.

In response to the United States Department of Defense's need for a rugged field-based oil condition monitoring tool, Spectro Inc. developed FluidScan[®], a hand-held, infrared oil analyzer that helps confirm new oil is of the proper type and free of impurities and verifies that in-service oil is fit for use, by measuring the degradation of the oil chemistry, and contamination by other liquids such as water. It is an ideal solution for condition monitoring of in-service machinery oil in critical assets such as turbines, gearboxes and compressors and for the extension of oil change intervals for engines and back-up generators [1].

FluidScan is a revolutionary device that combines the power of a laboratory FTIR spectrometer, Karl Fischer Titrator and a TAN/TBN Titrator into a field-based, hand-held device, without sacrificing core analyses. Today FluidScan is widely accepted by the military and commercial service professionals as an ideal oil condition monitoring tool and is used to maintain critical assets around the world, including marine vessels, mining fleets and power generation equipment. The purpose of this article is to describe some of the original design considerations and how new technologies are used in FluidScan to meet the design criteria.

The design criteria

When the Spectro design team was given the task to design a hand-held infrared oil analyzer, a list of design criteria was set so the final device must have the following characteristics:

- Durability – eliminate moving parts for field use
- Size and weight – compact for hand-held usage, battery powered
- No solvent used in between tests to simplify operation in the field
- Direct and quantitative results are needed for users to make immediate decisions without the help of on-site oil experts. The list

includes typical oil degradation and contamination parameters such as oxidation, TAN, and water contamination for industrial oils, and oxidation, nitration, sulfation, antiwear additive depletion, TAN, water, glycol, soot, etc. for engine oils.

- Parameter sensitivity should be comparable to laboratory FTIR instruments
- Battery run time for at least one shift of continuous usage

It is worthwhile to note the difficulties in meeting all the design criteria. For example, a new sample introduction technique was developed to eliminate solvent usage in the field. In addition, much effort was put into balancing the requirement of size and weight, battery running time while ensuring the equivalency of analytical capability of the device to FTIR spectrometers for in-service oil analysis.

The final design

The final design of the FluidScan is illustrated in Figure 2. The centerpiece is a grating dispersive optical system [2], with a solid state wave guide to reduce the light leakage and improve signal-to-noise ratio. The optic operates in 2.6 μm to 14 μm wavelength range (corresponding to ~ 950 to 3850 cm^{-1} in frequency, which covers the portion of the IR spectra indicative of degradation, TAN/TBN and water and soot). There are two IR lamps in the system, one with a longpass wavelength filter and one with a shortpass wavelength filter coupled together with a beamsplitter. This design approach eliminates moving parts from the system with inherent durability and also eliminates any frequent recalibration needs for field use.

Sample introduction

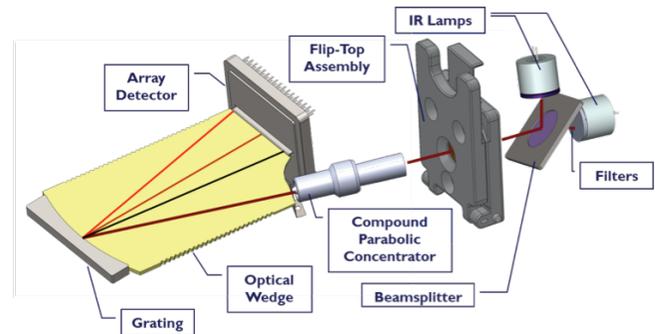


Figure 2: Schematic of FluidScan hardware, including IR source, flip-top cell, and grating optics. There are no moving parts in this design.

Simple and repeatable sample introduction is important for field-based oil analysis. A transmission cell is used and the amount of light absorbed vs. frequency passing through 100 μm of an oil sample is recorded. However, transmission cells are not suitable for field use as solvent is needed for cleaning after the sample is tested. To overcome this challenge, a new sample introduction technique was developed -- the flip-top cell. [3]. Shown in Figure 3, it looks like a clamshell that opens for sample introduction and cleaning and closes to form a 100 μm pathlength. The flip-top cell eliminates the need to use solvents for cleaning while maintaining same quality as a transmission cell used in laboratory environments.

In addition, both ZnSe windows of the flip-top cell are wedged so no parallel surfaces are in between the light transmission path (Figure 3). This eliminates any potential optical fringes making the signal much "cleaner" than traditional laboratory transmission cells. This is especially helpful for the measurement of water, with a result that detecting 100 ppm of water in oil is possible using infrared spectroscopy.

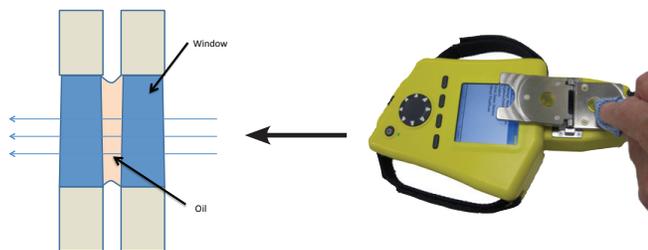


Figure 3: Flip-top cell (RHS) and schematic wedged window design (LHS).

Solving the signal-to-noise ratio challenge

In order to achieve equivalency to FTIR for in-service oil analysis, great effort had been put into improving the signal-to-noise ratio of the handheld device. It is noticed that the signal-to-noise ratio of a spectrometer is proportional to the power of the source as well as spectrum linewidth. In a system where the power of the source is limited, one can increase the spectrum linewidth (decrease spectral resolution) to increase signal-to-noise ratio. The analogy is to widen the aperture of a camera lens to increase the amount of light going into the detectors. The challenge here is to know how much spectral resolution can be reduced without affecting the quality of the

measurements. A typical FTIR spectrometer, such as Spectro Inc.'s Alpha Q410, has spectrum resolution of 4 cm^{-1} when configured for oil analysis. Such resolution is great for new oil analysis and fingerprint identification, but it is overkill for in-service oil analysis. The question is what resolution is needed for a device designed for in-service oil analysis. Parameters such as oxidation, sulfation, and soot are calculated from relatively wide absorption peaks (Figure 1). To determine the needed resolution, a comparison study was performed and shown in Figure 4, where multiple FTIR scans of the same oil sample at different spectral resolution are overlaid. Even at a resolution at 16 cm^{-1} , there is no significant distortion in the overall shape and heights of the peaks. A detector array was then carefully selected to balance the improvement of signal-to-noise ratio and decrease in spectral resolution to the determined level so that optimum device performance was achieved. Final hardware design accounted for trade offs between S/N ratio, resolution and speed of analysis to optimize the performance of the FluidScan.

To demonstrate the performance of the final device, Figure 5a and b shows comparison of oxidative by-product measurements on FluidScan and a laboratory FTIR. Even though the spectral resolution on FluidScan is not as good as the FTIR spectrometer, the signature of oxidative by-products are clearly identifiable on FluidScan and the changes of the features as oil degrades also correlates very well with those of FTIR. Figure 7 shows how the differential ICP results (large particles) for samples E and F compare to the XRF data for the same samples. Note that the XRF data is not shown in Table 1 above. The large particle portion correlates very well (within 3ppm) of the filtered XRF results (Figure 7).

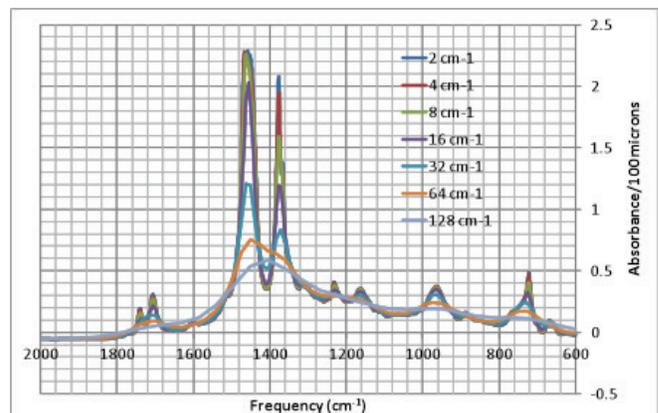
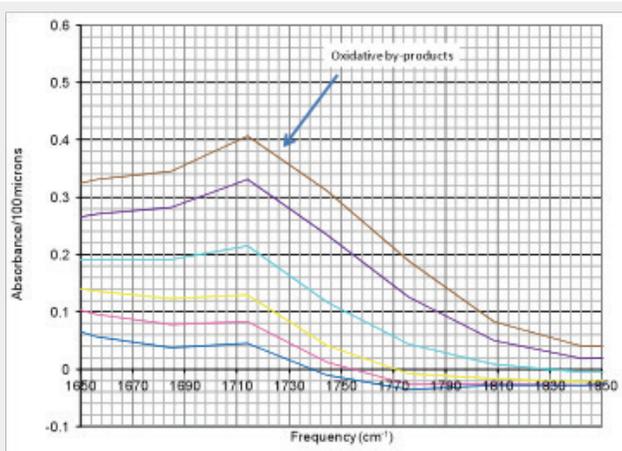
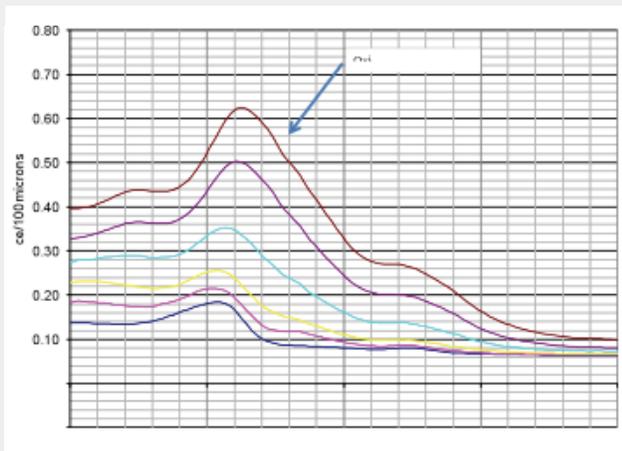


Figure 4: Overlay of oil FTIR spectra at different resolutions



5 (a) FluidScan spectrum



5 (b) FTIR spectrum

Figure 5: IR spectrum of degraded oil in the oxidation region. Even though the FluidScan spectrum lacks the fine details of an FTIR spectrum, it clearly shows the correlation of oil degradation to FTIR data. Furthermore, the calculated Oxidation parameter correlates well between the results from the two instruments

Correlation study of oil degradation measurement with FluidScan and laboratory FTIR instrument

Several inter-laboratory studies have been performed over the years to demonstrate the equivalency and correlation of FluidScan results to that of FTIR spectrometers. In one study, a random set of 37 in-service oil samples were chosen with various status and different characteristics to represent the real-world use case. Samples were vigorously shaken before testing. All tests were run by a single operator on a single instrument. The FTIR tests were carried out per the instructions of the individual ASTM test methods with

measurement units as listed in Table 1. Figure 6 a, b, c, d, e shows the correlation results between FluidScan and FTIR spectrometer for Oxidation, Nitration, Sulfation, Antiwear Additives, and Soot. Further rigorous statistical analysis according to ASTM D6708 “Standard Practice for Statistical Assessment and Improvement of Expected Agreement between Two Test Methods that Purport to Measure the Same Property of a Material” were performed on the results. The conclusion was that the FluidScan and FTIR measurements are equivalent. In addition, according to ASTM Interlaboratory Crosscheck Program round robins for inservice oils, variations observed from FTIR to FTIR are as large as or larger than variations observed on FluidScan to FTIR as reported in this study.

Chemometrics for TAN/TBN and water measurement in FluidScan

One major challenge in addition to the hardware design was to provide credible results on TAN or TBN measurements and water measurements, which is difficult using IR spectroscopy. One reason is that all oils are not created equal and if only one generic algorithm is applied to all oil, the results might be good for some oil but not for all others. If an oil-specific algorithm is developed, then it is a “mission impossible” to include all kinds of oils used around the world. To overcome the challenge, a classifier is introduced to classify oils into different families. Within a family, all oils share chemical similarities so one algorithm set can be applied. With this in place on FluidScan, users in the field can quickly match an unknown oil to a family and use a fine-tuned algorithm for parameter extraction.

Chemometrics are applied to FluidScan to yield information on TAN/TBN and water as those provided by laboratory titration methods. Chemometrics is the application of mathematical, statistical, graphical or symbolic methods to maximize the chemical information extracted from data. Chemometrics uses mathematical and statistical methods to improve understanding of chemical information, providing spectroscopists with efficient ways to solve the calibration problem for the of spectral data.

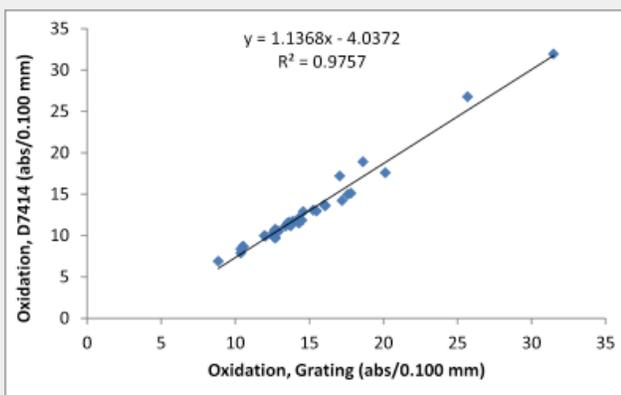
One example of chemometric calibrations for TAN of gas turbine oil is described here. As documented in ASTM E2412, infrared signatures relating to TAN in gas turbine oils have interferences from water contamination. To obtain quantitative readings with the FluidScan, a chemometric calibration using principal components regression (PCR) is used to automatically subtract the effects of the presence in water from the TAN area of the spectrum. This process involves the following steps:

1. Gather FluidScan spectra from a wide range of used samples.
2. Gather corresponding laboratory TAN and water readings.
3. Choose the spectral region of interest where the property has the highest correlation (eg. 3180 to 3750 cm^{-1} for TAN).
4. Perform principal components regression on the spectral region with the corresponding laboratory readings.
5. Assign the algorithm to a specific oil family so the same algorithm can be applied to oils with similar oils.
6. Oil specific offset and slope can be adjusted individually for each oil

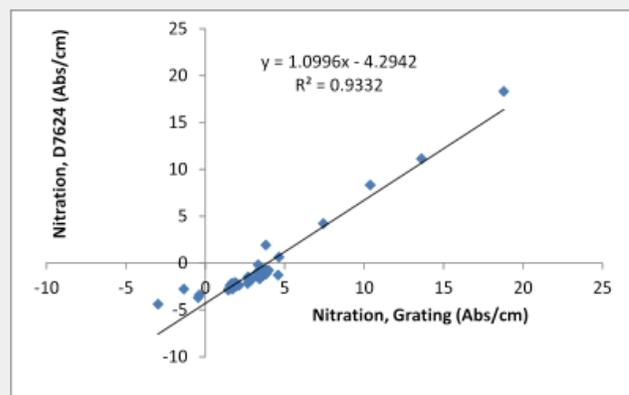
for allowing better correlation to laboratory titration methods.

This process produces a chemometric calibration which, when convoluted with an unknown spectra of turbine oil, yields the property of interest (e.g., TAN) in the units of interest (mgKOH/g). A similar process is used for water measurement to correlate to Karl Fischer Titration as well [3,4].

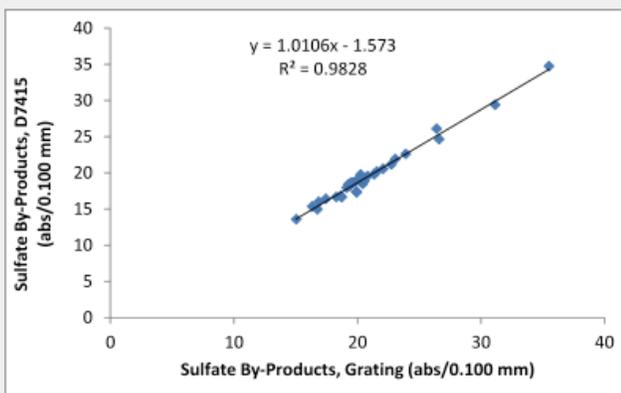
For more information on the use of FluidScan for water measurements and TAN/TBN measurements, please see the Spectro white papers "Measuring Water with FluidScan Fluid Condition Monitor" and "Using IR Spectroscopy for the Determination of TAN and TBN in Machinery Lubrication Oils".



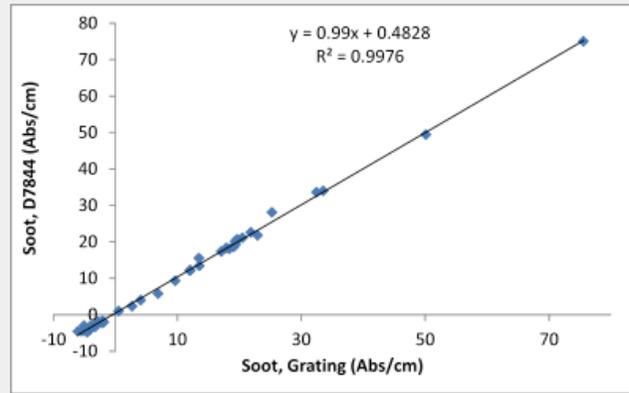
(6a): Correlation between FluidScan and ASTM D7414 for Oxidation.



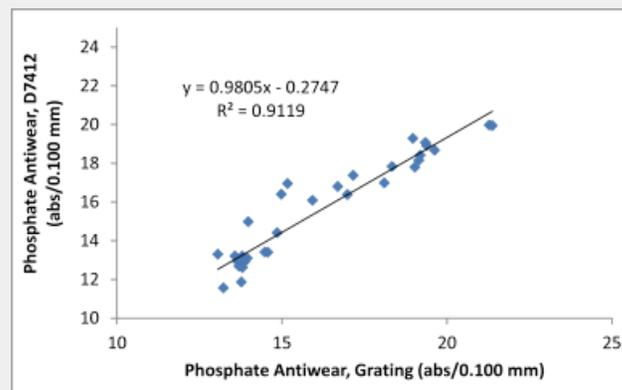
(6b): Correlation between FluidScan and ASTM D7624 for Nitration.



(6c): Correlation between FluidScan and ASTM D7415 for Sulfation.



(6d): Correlation between FluidScan and ASTM D7844 for Soot.



(6e): Correlation between FluidScan and ASTM D7412 for antiwear additive.

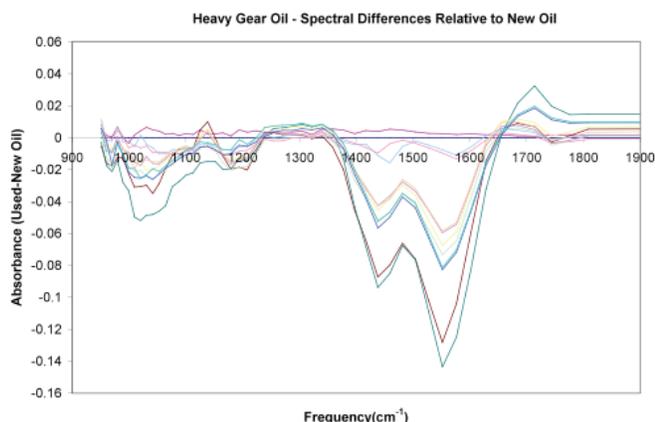


Figure 7a: Spectral evolution of a heavy gear oil relative to the new fluid, which shows both increasing and decreasing absorbances at various frequencies as the oil becomes more degraded.

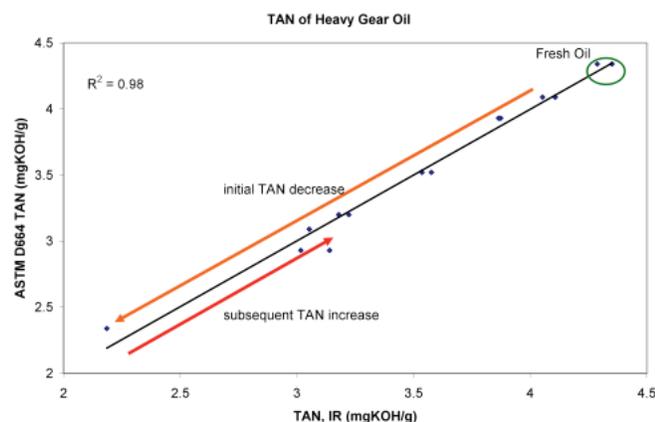


Figure 7b: Relationship between ASTM D664 and infrared TAN values for a heavy gear oil. This oil has a complicated evolution where the fresh oil's TAN initially decreases down to a minimum level, then begins to increase towards a maximum alarm value.

Examples of the power of such chemometrics are demonstrated in Figures 7a and 7b. As seen in above, (plotted as a difference spectrum relative to the clean oil), the absorbance in the 1400- 1600 cm^{-1} area decreases to a minimum level, consistent with the depletion of an additive package in the oil. The adjacent areas begin to show an increase in absorbance that grows stronger as the TAN starts to increase from its minimum value of approximately 2 mgKOH/g (from a clean oil value of 4 mgKOH/g), up to a value of 3 mgKOH/g in this dataset. The upper TAN limit is in the range of 5 mgKOH/g . Figure 7b shows that the infrared TAN has excellent correlation to the ASTM D664- determined TAN, indicating the infrared-based chemometric analysis is able to account for and properly weight the various spectral effects observed.

Summary

FluidScan, though small, is packed with innovations that deliver laboratory quality measurement to on-site oil analysis instruments. The patented flip-top cell provides easy-to-use, solvent-free sample introduction. Direct imaging IR optics achieve the equivalent analytical capability as the FTIR spectrometer, and the unique chemometrics algorithms for accurate, repeatable and trendable TAN/TBN and water measurements. FluidScan delivers the power of a laboratory FTIR, Karl Fischer water titrator and aTAN/TBN titrator to reliability engineers who monitor the oil condition whenever and wherever they need it.

References

- [1]: Spectro white paper: "Overview of FluidScan Handheld Oil Analyzer".
- [2]: US Patent, "Array detector coupled spectroanalytical system and graded blaze angle grating" US 7,495,761.
- [3]: US patent, "Spectrometer flip top sample head" US 8,384,895.
- [4]: Spectro white paper; "Using Infrared Spectroscopy for the Determination of TAN and TBN in Machinery Lubrication Oils".