

White Paper

Using Infrared Spectroscopy for the Determination of TAN and TBN in Machinery Lubrication Oils

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Synopsis

Total Acid Number (TAN) and Total Base Number (TBN) values are commonly used to measure degradation of machine lubricants, in order to avoid machine wear, corrosion, varnish, clogged filters and other problems. Electrochemical titration has been the traditional method for measuring these values. However, this method is complex and costly, requiring relatively large amounts of sample, protective equipment, well-trained technicians, and disposal of hazardous reagents, among other difficulties.

This paper explores IR spectroscopy as an alternative method for measuring TAN and TBN values, using a 3-step process of library building, sample classification, and multivariate regression techniques. The authors present the principles of IR spectroscopy as it relates to TAN and TBN measurements, the advantages and disadvantages of the method, and specific examples of its application for various types of engines and lubricants.

Introduction

Why Measure TAN and TBN?

It is an unavoidable fact: Machine lubricants degrade over time. Thermal and mechanical stress, coupled with the inevitable contaminants, cause oil to reach a point where it can no longer perform its function as a lubricant. Degradation of a lubricant is primarily caused by the breakdown of chemical components in the oil which results in the formation of acidic by-products, formed by chemical reactions between the oil's base stock and additive components in an oxygen/nitrogen rich environment under extreme thermal stress. These acidic by-products lead to corrosion of oil wetted machine parts and the formation of varnish and sludge which can quickly clog oil filters.

It is therefore critical to monitor the level of acidity in the oil as it ages. The level of acidity is obtained by measuring either the acid in the oil (TAN) or the reserve alkalinity remaining from additives in the oil (TBN). Traditionally, TBN is used as an indication of alkaline reserve in diesel engines and TAN is measured directly in other applications like gears, hydraulics and turbines where acid formation is somewhat

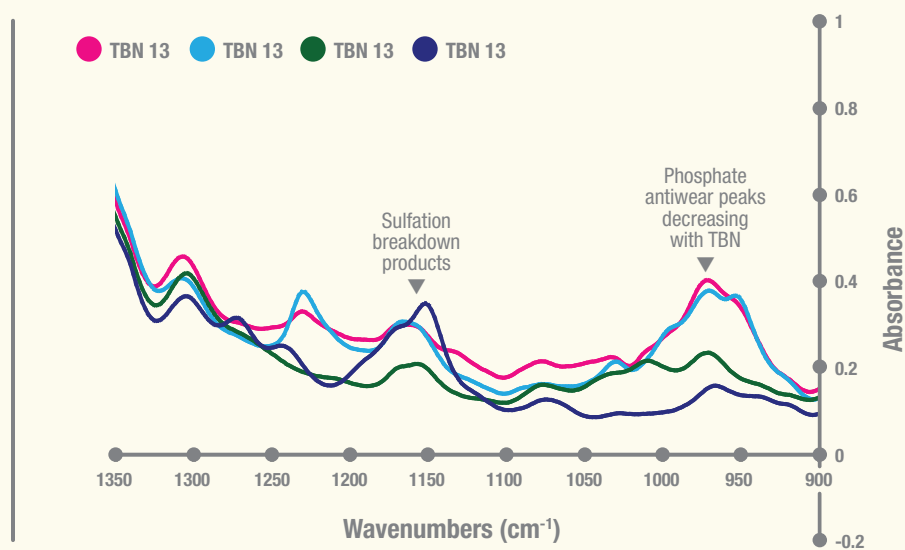
less aggressive the acid in the oil is measured directly. TAN and TBN are reported based on the amount of potassium hydroxide or equivalent needed to neutralize one gram of the sample (mgKOH/g).

Diesel engine applications are one of the most stressful on a lubricant, as the high temperatures and thermal stresses in the engine lead to the rapid formation of acidic by-products. Thus, oils used in diesel engines need to be equipped with a high reserve alkalinity additive package that consumes the acids created before they form sludge and varnish products and corrode machine components. This is why TBN is monitored in diesel engines.

In marine diesel applications the TBN is affected more by the type of fuel used rather than by oxidative by-products depleting the additive package. This is because the international marine shipping industry has far less strict sulfur requirements on the fuels they use, resulting in the lubricating oils requiring heavy additive

Figure 1:

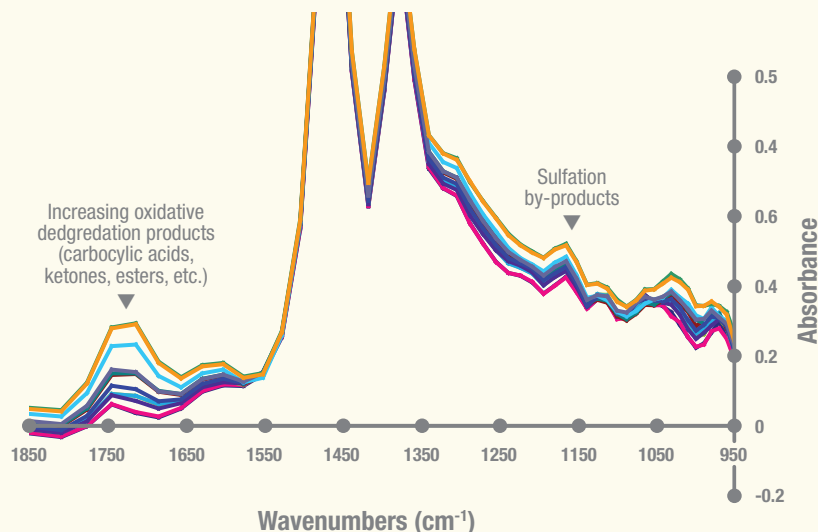
Spectra for oils with TBN values between 1-16 mgKOH/g, illustrating the complex behavior of the various additive and degradative infrared peaks, taken using a Spectro Q410 FTIR.



FluidScan Spectra of Gear Fluid with Increasing TAN

Figure 2:

Increase of TAN in a gear oil as reflected in the infrared spectrum of the fluid. This data is taken using a Spectro Q1000 FluidScan.



packages with a high starting TBN value. In some extreme cases, the heavy sulfur fuels require the starting TBN value to be as high as 70 mgKOH/g. The reaction between water and the high levels of sulfur in the fuel creates sulfuric acid which needs to be continually monitored by TBN in this application. It is common for marine diesel engines to be checked on a weekly basis for TBN and topped up with fresh makeup oil to keep the additive package level high.

The role of IR spectrum analysis

Both the basic additives in engine oils and the acid build up in other types of fluids can be seen as changes in the infrared spectrum of a sample. As seen in Figure 1, TBN changes are indicated in the IR spectra as decreases in absorbance peaks related to the basic additives that are present in the engine oils, as well as changes to standard degradation peaks. The additives most typically used are calcium or magnesium sulphonates, phenates and salicylates. All of these have peaks in the 1000 and 1900 cm⁻¹ region of the infrared spectrum.

The increase in TAN value for a lubricant is due to the build-up of organic acids, frequently carboxylic acids, created by the oxidative breakdown of the base oil. Oxidation products typically show absorbance peaks in the IR spectrum at 1600-1800 cm⁻¹. This can be seen in Figure 2 where the increasing peaks in the vicinity of 1600-1800 cm⁻¹ indicate increased oxidation, nitration, and acid oxidation products. While there is a complex mixture of acids generated, there is not a single absorption peak that correlates directly with TAN, but subtle changes across the spectrum can be detected and used to establish a correlation for TAN.

1. TAN and TBN by Infrared Spectroscopy

Infrared spectroscopy, both by directly probing the lubricant “as-is” [1,2] via relating the IR spectrum to a titrated TAN or TBN value using multivariate methods, and by measuring the lubricant’s response to a chemical reaction [3], has been used for some time to determine TAN or TBN of lubricant samples. The experimental setup involves measuring the absorbance of the lubricant through a 100 to 200-micron transmission cell using an empty cell background. The IR approach for measuring the TBN of reciprocating engine oils, due to their relatively uniform chemical composition, has been reported most commonly and is in use by some analysis laboratories as a TBN screening technique [4]. Still, questions on this subject continue to persist due to the lack of standard methods, as well as the overall chemical complexity of the lubricants themselves, which can make a “one size fits all” direct infrared method difficult. To date, only lubricant-specific calibrations for particular end-user applications are, in general, widely considered quantitative.

We have approached this problem in three steps: First, we gathered hundreds of new and used lubricants of widely varying type and level of degradation into a sample library. We then recorded their infrared spectrum along with their TAN and/or TBN value using a standard ASTM titration technique (D4739 for TBN and D664 for TAN). Second, by using a standard multivariate classification technique called SIMCA (Soft Independent Method of Class Analogy),

we classified each oil type based on its infrared spectrum into distinct chemical “families”. Finally, we used either the Principle Component Regression (PCR) or Partial Least Squares (PLS) multivariate regression method to relate the known TAN or TBN to the infrared spectrum, each within a given chemical family. This results in a set of family-specific TAN- or TBN-to-IR calibration curves which show quantitative correlation across a broad range of lubricants, including gear, industrial, marine diesel, turbine, and reciprocating engine fluids.

The end-result is that by carefully classifying the chemical composition of the lubricant before it is processed for TAN or TBN, one can arrive at quantitative readings using infrared spectroscopy.

1a. Spectro Q410 FTIR and Q1000 Infrared Spectrometers

Obtaining TAN and TBN through infrared spectroscopy can be achieved, in principle, with a wide variety of approaches to obtaining the spectrum, from the now-prevalent FTIR method, to grating instruments, to emerging technologies such as tunable quantum cascade lasers. The only requirement is that quality spectra with sufficient resolution can be obtained between approximately 900-1900 cm^{-1} and 2500-4000 cm^{-1} , the areas over which the TBN and TAN calibrations can be obtained.

Property	Q410 FTIR	Q1000 FluidScan
Measurement Principle	FTIR	Grating
TBN calibration range (mgKOH/g)	0 to 50	0 to 60
Repeatability, TBN relative to D4739	better	better
Reproducibility, TBN relative to D4739	comparable	comparable
TAN calibration range (mgKOH/g)	0 to 20	0 to 20
Repeatability, TAN relative to D664	comparable	comparable
Reproducibility, TAN relative to D664	comparable	comparable
Standard Range (cm^{-1})	500 to 6000	900 to 4000
Resolution (cm^{-1} at 1000 cm^{-1})	2	20
Ambient Operating Temperature (Celsius)	18-35	0-50
Weight (Pounds)	15.5	3.5
Power (Watts)	50	1.5
Operating Software	PC-based	n-device

Table 1: Comparison of the Spectro Q410 FTIR and Q1000 FluidScan.

By carefully classifying the chemical composition of the lubricant before it is processed for TAN or TBN, one can arrive at quantitative readings using infrared spectroscopy.

Spectro has a complete product line including its Q410 FTIR spectrometer, a compact, benchtop instrument, and its Q1000 FluidScan, a handheld product targeted towards field applications. Both devices come with their own software packages which include TAN and TBN analysis. The software of both spectrometers and Q1000 hardware has been designed so that both provide quality TAN and TBN results. While the Q410 provides the power of the traditional FTIR for investigative oil analysis and automation for laboratory usage, the Q1000 is targeted towards end-users who need easy-to-use but accurate and reliable equipment on-site. A comparison of technical specifications for the two devices is shown in Table 1.

2. Advantages and Disadvantages of Using Infrared Relative to Existing Titration Methods for TAN and TBN

Monitoring the level of acidity in lubricants as they age has traditionally been done through electrochemical titration of a sample of the lubricant. These methods require relatively large volumes of sample (ranging from 0.1 to 20g), a well-trained technician, personal protective equipment and the use and disposal of flammable, corrosive, hazardous and toxic reagents (100 mL per sample, not including solvents required for washing and rinsing). These methods are time consuming: a TBN titration itself can take up to one hour. Time must also be budgeted for setup, sample preparation, function and quality checks on the instrumentation, in addition to clean-up and waste disposal.

In contrast, the direct infrared approach developed by Spectro requires no sample preparation, no reagents, and no solvents. Only 0.03 mL of lubricant is required to perform the analysis, and clean-up requires only a shop rag or towel. The measurement itself is completed in approximately 1 minute. Based on the fluid type, either TAN or TBN is reported in units of mgKOH/g. Clearly, this infrared approach offers the potential for substantial cost savings through reduced

labor, materials, and hazardous waste. At this point, the approach is predicated on having a fresh lubricant sample in order to classify its chemical family and thus provide quantitative TAN and TBN readings for the in-service or used lubricant. Once classified, however, samples of the new, in-service, or used lubricant may be analyzed continuously without the need to refer back to the new sample. Not all lubricants will be classified into a chemical family, as the library continues to be expanded. For these cases, established ASTM infrared methods must be used to assess oil degradation. However, at this point, >90% of the lubricants we encounter can be classified with the existing library. For an on-site operator, who knows and has their fresh lubricants of interest, the efficacy of the approach can quickly be confirmed by classifying their set of lubricants at the outset.

3. Performance of Infrared TAN/ TBN Approach Relative to Existing Titration Methods

There are several ASTM standard titration methods that detail measuring TAN and TBN for lubricants. ASTM D664 covers the potentiometric measurement of TAN for petroleum products, titrating with a solution of potassium hydroxide. TBN can be measured following either ASTM D4739 (using hydrochloric acid) or ASTM D2896 (perchloric acid method). The latter is used primarily for new oils and the former for tracking the decrease in TBN for in-service oils. The stronger solvent/titrant mix used in test method ASTM D 2896 will titrate weak bases and weakly basic degradation products in the sample that can have no protective value. It is for this reason that our infrared TBN values are correlated to ASTM D4739.

The repeatability and reproducibility of these standard methods for used oils are well-documented. Repeatability is the variability of measurements on the same sample by the same operator using the same measurement equipment. Reproducibility is the comparison of independent tests.

The direct infrared approach developed by Spectro requires no sample preparation, no reagents, or solvents.

For an in-service sample with a TAN of 2.0mgKOH/g, the comparison of independent tests (reproducibility) can yield results between 1.12 and 2.88mgKOH/g, with repeatability between 1.77 and 2.23 mgKOH/g.

ASTM D664 Reproducibility $R = 0.44 * x$
 ASTM D664 Repeatability $r = 0.117 * x$
 Where x is the average of two separate TAN readings

For comparison, the IR methods show typical TAN reproducibility relative to an ASTM titration measurement of 0.49 mgKOH/g at a 99% confidence interval in the normal operating range of TAN below 4 mgKOH/g. Thus for a nominal sample with 2 mgKOH/g, the results can be expected to range between 1.51 and 2.49 mgKOH/g, comparable to the ASTM method.

Repeatability is calculated at 6.8% RSD at the 99% confidence interval at the mid-range of the measurement window (0-10 mgKOH/g), which is similar to the ASTM method.

A typical calibration curve for turbine oils is shown in Figure 3. The figure depicts several different brands and states of lubricant breakdown.

For an in-service sample with a TBN of 10 mgKOH/g, titration results can range from 5.5 to 14.5mgKOH/g within the specification, with repeatability between 9.6 and 10.4 mgKOH/g.

ASTM D4739 Reproducibility $R = 1.54 * x^{0.47}$
 ASTM D4739 Repeatability $r = 0.22 * x^{0.47}$
 Where x is the average of two separate TAN readings

For TBN, both IR methods show typical reproducibility relative to an ASTM titration of 3 mgKOH/g at a 99% confidence interval over a range of 0-16 mgKOH/g. For a sample with a nominal TBN of 10 mgKOH/g this implies one would encounter a range of results between 7 to 13 mgKOH/g, again comparable to the ASTM method at this common level of TBN for new engine oils. Repeatability is 0.37% RSD at a 99% confidence interval, better than the ASTM D4739 method.

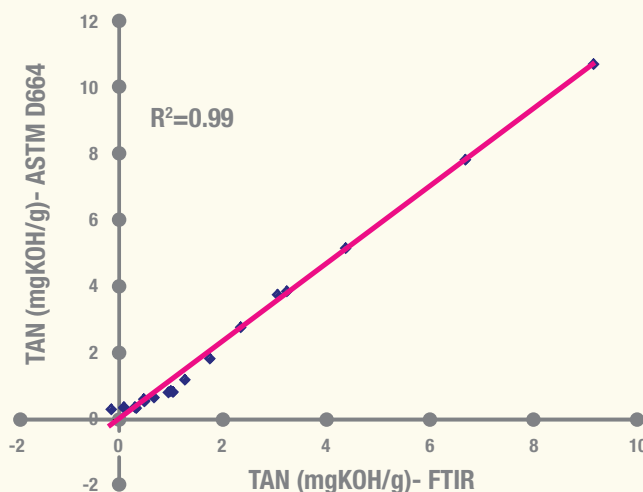
Figure 4 shows a calibration curve for reciprocating engine oils, based on a variety of different oil brands and states of degradation.

The usefulness of TAN and TBN measurements for monitoring oil degradation lies in consistent, frequent sampling and measurement. This practice produces many data points that show the trend in decrease in base reserve and increase in acidity over the lifetime of the oil. IR TAN and TBN measurements are quick and easy to perform and cost effective. Therefore, samples can be measured at short intervals and a close trend of the values can be followed effectively.

Titration vs. FTIR Acid Number Correlation

Figure 3:

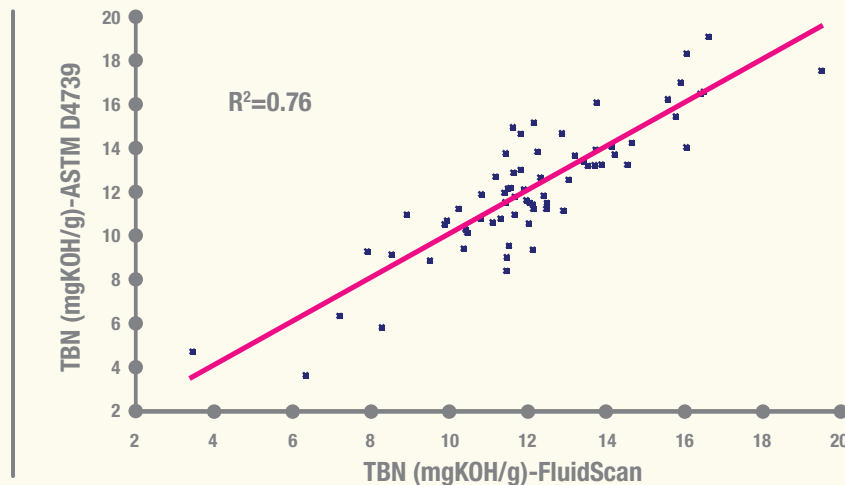
Relationship between ASTM D664 and infrared TAN values, acquired using the Q410 FTIR spectrometer.



ASTM D4739 vs. FluidScan

Figure 4:

Relationship between ASTM D4739 and infrared TBN values, acquired using the Q1000 FluidScan Spectrometer.



4. Example of TAN Correlation: Industrial Fluids

In order to illustrate the effectiveness of this direct infrared approach to providing TAN/TBN values, we investigate the case of the “Industrial” fluid family. The lubricants in this family are a collection of transmission and hydraulic fluids, and some gear oils. They all have base oils and additives that yield fluids with high shear stability and especially good low temperature flow properties. Despite differences in base oil and additive composition, for the areas that show changes with increasing TAN, the IR spectra of these fluids are similar, consistent with the SIMCA classification of these fluids into one common family.

The acid build-up that raises the TAN shows up in the same fashion in these fluids. This allows a single calibration to be used to calculate a TAN value from the IR spectra of the sample. The

calibration is generated from one fluid and then verified against other fluids in the class and in-service samples when available.

The calibration approach starts by choosing the most “central” fluid in the SIMCA classification, i.e. a fluid that has a classification score in the middle relative to other members of the family. Once the fluid is chosen, a matrix of degraded samples is generated from that fluid. The sample matrix encompasses the range of expected TAN values, degradation and contamination that would be expected in a real world application of these types of fluids. For this type of fluid, a range of oxidative degradation is created and various amounts of water are homogenized into the samples. The TAN values for all of these samples are titrated following ASTM D664, and

infrared spectra of each sample are acquired. PLS or PCR methods are then employed to create the calibration between the IR spectra and the titrated values. The results are shown in Figure 5, which indicate that an excellent calibration curve relating the IR spectrum to TAN is generated.

Since the calibration must be robust across the range of samples, the calibration is tested against other fluids in the same family. A set of verification samples is generated similar to the calibration set described above. TAN values for these samples are obtained via ASTM D664 and

the newly-created infrared TAN calibration. As can be seen in the correlation data of Figure 6, the TAN of a transmission fluid can be predicted well using the calibration for the Industrial family.

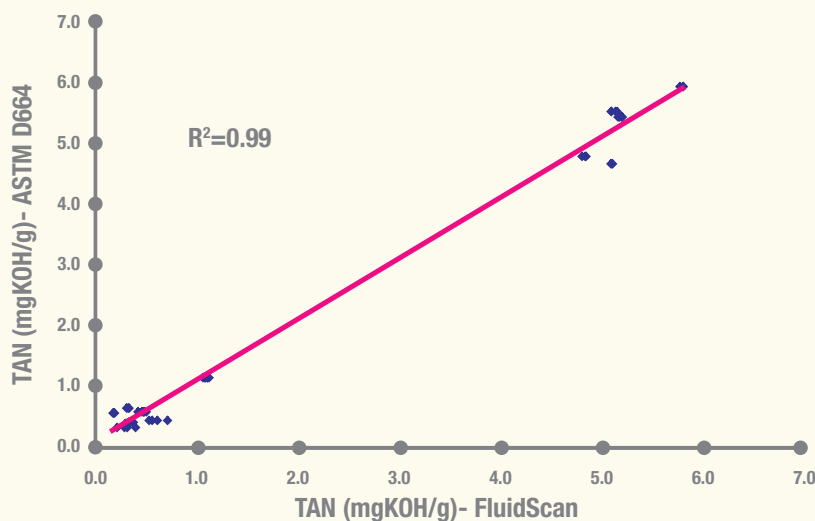
4a. Example of TAN Correlation: Heavy Gear Oils

An interesting calibration is that of a family of heavy gear oils which are particularly applicable for the Wind Turbine industry. These fluids have TAN values that initially decrease with service, as an acidic additive package is slowly depleted. Eventually, the buildup of acidic products outweighs the suppression of TAN due to the

Industrial Family TAN Calibration

Figure 5:

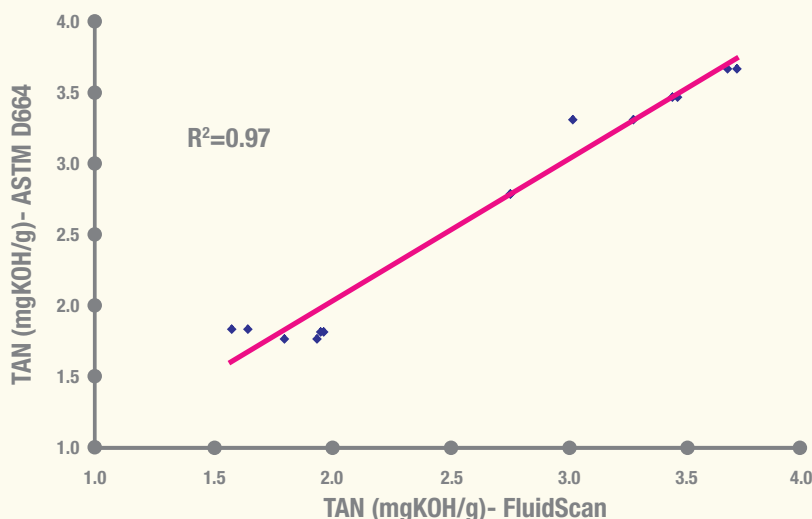
Industrial Family TAN Calibration using the Q1000 FluidScan.



Industrial Family TAN Verification

Figure 6:

Verification of Industrial Family TAN calibration by using another fluid in the family, using the Q1000 FluidScan.



additive package and the TAN begins to rise. For these fluids, the manufacturer specifies both a low and high TAN limit, consistent with how the TAN evolves in the oil.

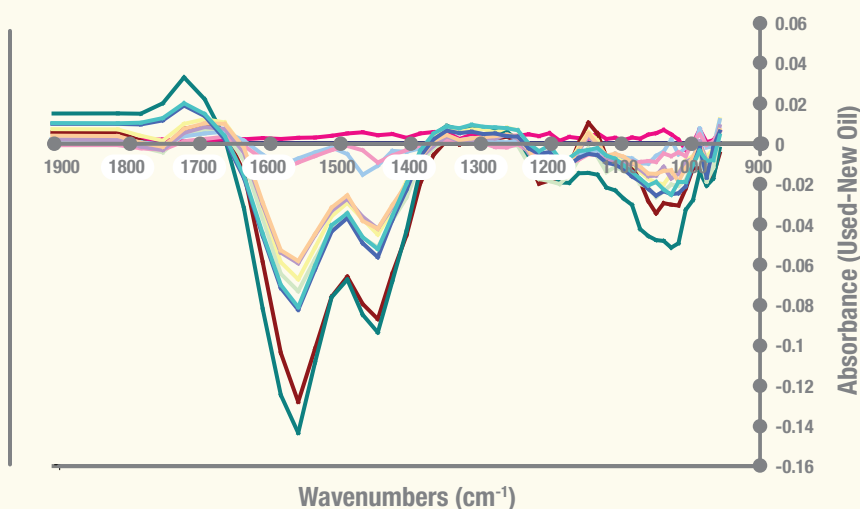
As can be seen in Figure 7 (plotted as a difference spectrum relative to the clean oil), the absorbance in the 1400-1600 cm^{-1} area decreases to a minimum level, consistent with the depletion of an additive package in the oil. The adjacent areas begin to show an increase in absorbance that grows stronger 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 8 shows that the infrared TAN has excellent correlation to the ASTM D664-determined TAN, indicating that the infrared multivariate analysis is able to account for and properly weight the various spectral effects observed.

Heavy Gear Oil - Spectral Differences Relative to New Oil

Figure 7:

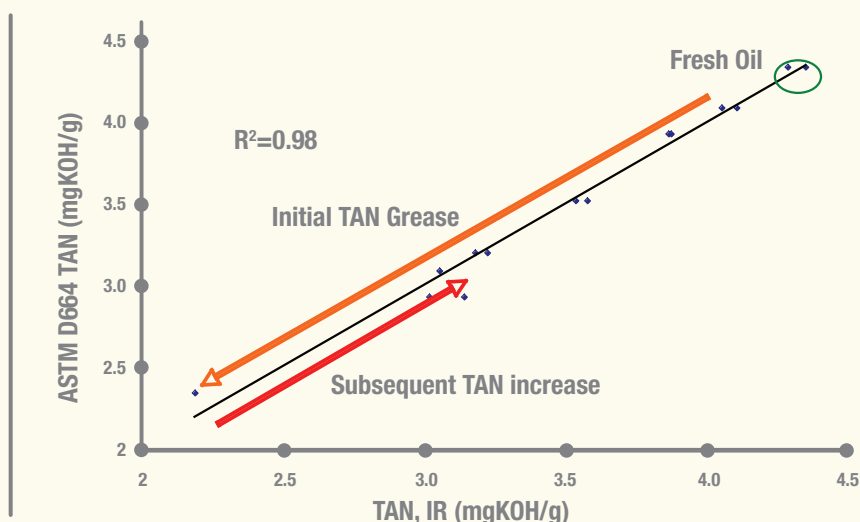
Spectral evolution of a heavy gear oil relative to the new fluid, which shows both increasing and decreasing absorbances at various frequencies as the oil becomes more degraded. Data obtained from the Q1000 FluidScan.



TAN of Heavy Gear Oil

Figure 8:

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. Data obtained using the Q1000 FluidScan.



5. Example of TBN Correlation: Marine Diesel Engine Oil

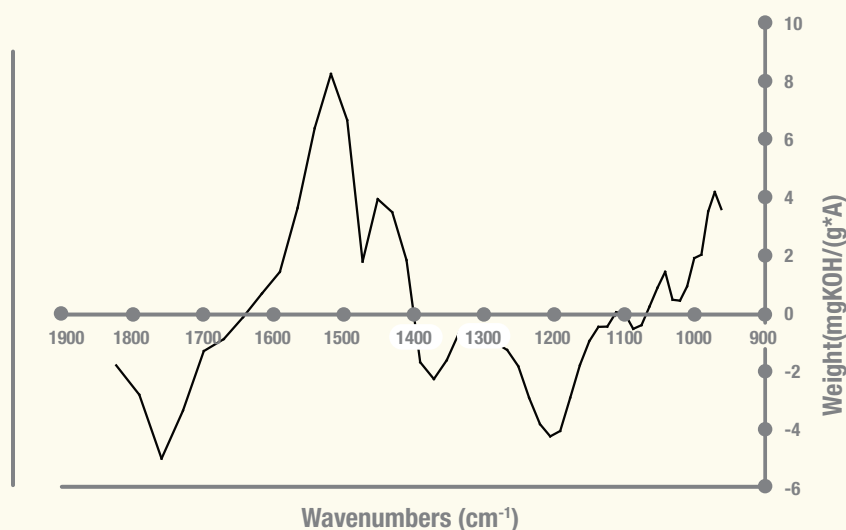
For the classification of marine diesel engine oils and reciprocating engine oil families, there is a strong overlap between the families for comparable TBN values. This is not surprising, as the main differentiator between the oils in both classes are the TBN-boosting additives such as detergents, soaps, and dispersants. The core calibration for the marine diesel engine oil family is obtained from an analysis of a variety of in-service and used diesel engine oil samples of commercial vehicles, including buses, trucks and small boats. This calibration accurately predicts TBN changes in the oil to levels exceeding 50 mgKOH/g all the way down to full degradation. Different from the TAN examples, we were able to obtain an excellent sample matrix from the in-service and used samples, without further treatment of the oil. This is always the preferred scenario, as these samples more fully represent the complex cycling that the oils undergo while in service, and thus are most likely to provide

accurate predictions, at least in principle. Figure 9 shows the TBN prediction vector for these marine diesel oils. The TBN value itself is obtained from a linear multiplication of this prediction vector with the actual infrared spectrum.

Finally, to illustrate the stability of the TBN measurement using the Q1000 FluidScan over a period of time, Table 2 shows the TBN of 5 different Marine Diesel Engines over a period from June 2010 to January 2011, as taken on-board by the Q1000 FluidScan handheld device. The TBN of the oil is checked monthly and fresh oil is added to the system to maintain a steady base reserve. The on-site capability of the FluidScan is well adapted for this type of application. These results show excellent accuracy relative to off-shore laboratory titration measurements over the entire period.

Figure 9:

Prediction vector for the
Q1000 FluidScan for
Marine Diesel Engine Oils



Date	Sampling Point/ Equipment	Product Type FluidScan	TBN mgKOH/g	TBN mgKOH/g Titration
June 2010	No. 5 Engine	Marine Diesel	14.7	15.3
July 2010	No. 5 Engine	Marine Diesel	14.6	14.2
November 2010	No. 5 Engine	Marine Diesel	14	13.9
January 2011	No. 5 Engine	Marine Diesel	13.9	13.6
September 2010	No. 4 Engine	Marine Diesel	14.5	15.6
January 2011	No. 4 Engine	Marine Diesel	13.6	13
June 2010	No. 3 Engine	Marine Diesel	14.4	14.5
October 2010	No. 3 Engine	Marine Diesel	14.3	14.3
September 2010	No. 2 Engine	Marine Diesel	14.5	15.8
December 2010	No. 2 Engine	Marine Diesel	13.4	12.8
September 2010	No. 1 Engine	Marine Diesel	13.7	14.9

Table 2: Correlation between on-site Q1000 FluidScan and off-shore laboratory titration methods over a period of time between June 2010 and January 2011, for five different shipboard engines.

6. Conclusions

The results presented in this paper show that it is possible, using the infrared spectrum of a lubricating fluid sample and software available on the Spectro Q410 FTIR and Q1000 FluidScan, to obtain reliable TAN or TBN readings for a wide range of lubricating fluids. This is achieved through a 3-step process of library building, sample classification, and multivariate regression techniques, all of which are built into the Spectro software. The expanding library and promising results relative to traditional titration methods indicate that this approach has wide applicability to both off-site laboratory and on-site oil analysis programs.

References

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