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Use of FT-IR Spectrometry as a Replacement for Physical Property Testing of Railway Lubricants

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Abstract: The railway industry has long used physical property tests to determine the condition and suitability of lubricating oils for continued use in locomotive diesel engines and air compressors. This paper describes the adaptation and implementation of FT-IR spectral analysis as a means of determining lubricant physical and chemical parameters at Canadian National Rail (CNR). Specifically the paper reviews the application of traditional FT-IR measurements for fuel dilution, water contamination, insolubles loading, and oil oxidation, and describes the implementation of new measurement parameters for viscosity and total base number. A study of atomic emission and FT-IR data from over 8000 locomotive samples provides summary data on the reliability of the FT-IR for routine diesel engine oil analysis.

Key Words: Condition Monitoring, Oil Analysis, Railway, FT-IR, Infrared, Physical Property Test.

INTRODUCTION: The North American railway industry was one of the first to use oil property measurements to support engine oil condition monitoring. Routine property tests reveal the degree of contamination and degradation of the lubricant, and these data can be related to common failure mechanisms to determine the risk of damage and any required action. Canadian National Rail (CNR) operates a fleet of 1700+ locomotives. Oil analysis services are provided internally by

5 laboratories. The traditional tests used by CNR for diesel engine oil analysis were kinematic viscosity @ 100°C, total base number (TBN), percent pentane insolubles and percent water. In addition, atomic emission spectroscopy is performed to determine the level of wear metals and other data, such as coolant inhibitor contamination, dirt and silicas, etc.

In recent years, CNR has upgraded oil analysis technology in order to maintain high levels of data integrity, repeatability and reproducibility, and reduce costs. By mid 1993, CNR had state-of-the-art methods, data management and expert systems, and felt the next phase of improvement would be to find a replacement for the physical properties test methods. These methods were time consuming, potentially hazardous, subject to error, and required the operation of individual instruments for each parameter measured. While traditional property tests are available in automated forms, anticipated capital costs and labor savings did not justify renewal of these test methods. However, if a single instrument could be used to determine all property data, over \$700,000 per year would be saved at CNR in laboratory labor alone.

Recent published work [1,2,3,4,5] presented significantly improved FT-IR application software, and the new FT-IR systems showed promise as a single-instrument-replacement for the traditional oil condition tests. In addition to measuring oil contaminants, the new FT-IR system provided data about oil degradation (oxidation, sulfation, nitration, etc.).

CNR FT-IR DEVELOPMENT: Before considering FT-IR practical, the CNR Mechanical Department specified six parameters to be determined from each sample analysis. These are viscosity, percent fuel dilution, percent insolubles, percent water contamination, TBN, and oxidation level. Obtaining reliable FT-IR absorbance data for each parameter was only part of the task. CNR mechanical personnel were familiar with oil data in traditional units of measurement and wanted the absorbance data reported in the same units, and required the conversion of oil contaminant parameter data (fuel, water & insolubles) and the synthesis of viscosity and TBN from the FT-IR absorbance data. Moreover, a means to extract viscosity and TBN data was not commercially available and would require the development of suitable analysis and calibration methods. Oxidation was the only new parameter in the CNR program and is reported in integrated absorbance units.

All commercial FT-IR spectrometers offer a variety of infrared ranges, sensitivities, sample introduction methods and other features. After detailed review of the major FT-IR manufacturers instruments and capabilities, the Bio-Rad FTS-155 was selected in April 1994. Each instrument was equipped with a 100um flow transmission cell, an autosampler and a calibration matrix to convert absorbance data into the traditional units. To avoid the problems involved with spectral subtraction and the requirement for up-to-date reference oils, CNR chose a data trending methodology [1,2] where the area under the infrared curve for each oil parameter is measured and reported. The parameter trends are then calculated using prior measurements and engine usage data. Using this simple trending method, in conjunction with statistically based level and trend limits for each engine class, the need for operator interpretation of sample spectra was eliminated. In addition, the conversion of the spectra into properties data permitted interface of the FT-IR to the existing data management system without significant modification. This greatly reduced implementation costs.

CNR Engine Oils: The engine oils used at CNR include multi-grade SAE 20W40 and single-grade SAE 40 blended with Chevron Oronite Division 2990 additive package at 17 TBN level. The oil is supplied by two different manufacturers and is produced by two different refining processes. The differences in the oils required the preparation of standards from both manufacturers to achieve good calibration reliability.

Calibration Standards: Calibration standards for each measured parameter were provided by the following organizations:

oxidation - Chevron Chemical Company, Oronite Additives Division,
10, 13, 27, 35, 64, 116 - ABS (integrated absorbance units)

viscosity - original oil manufacturers,
13.0 to 16.5 cSt @ 100°C in 0.5 cSt increments

TBN - original oil manufacturers,
1, 3, 5, 7, 10, 12, 15, 17, 20 total base numbers

%insolubles - CANAC International,
0.5% to 5.0% in 0.5% increments

%water - CANAC International, and;
0.05% to 0.5% in 0.05% increments

%fuel - CANAC International.
1.0% to 10.0% in 1.0% increments

The remainder of the paper will describe the extraction of oil condition parameters, the areas and baselines selected and the calibration methods used to convert the data into traditional reporting units.

Viscosity: At CNR, oil viscosity was measured by the ASTM D445 method, utilizing a calibrated glass capillary viscometer immersed in a heated bath at 100°C. Although multiple samples could be analyzed simultaneously, the method was labor intensive. In addition, experience has shown that the measurement is only reliable when the oil is relatively free of contamination such as free water. CNR required the FT-IR method to indicate viscosity changes due to fuel dilution and viscous shear. This was accomplished by analysis of changes in oil chemistry using PCR/PLS methods to integrate several measurements over the range 2500 to 650 cm⁻¹.

The viscosity calibration was established from prepared samples of 17 TBN 40 and 17 TBN 20W40 oils over the required viscosity ranges, with additional standards using both viscosity and fuel dilution prepared standards and 60-80 samples of used oil. The viscosity of the used samples was measured by the ASTM D445 method and the fuel concentration was calculated from the viscosity data. This calibration matrix provided the best correlation between FT-IR and ASTM D445 results.

Figure 1 shows the frequency distribution obtained from 4446 routine samples (one year of operation) from 175 EMD locomotive engines. Over 75% of the samples range from 14 to 15 cSt--the normal operating range of the engine oils used at CNR. Since the locomotive fleet ranges

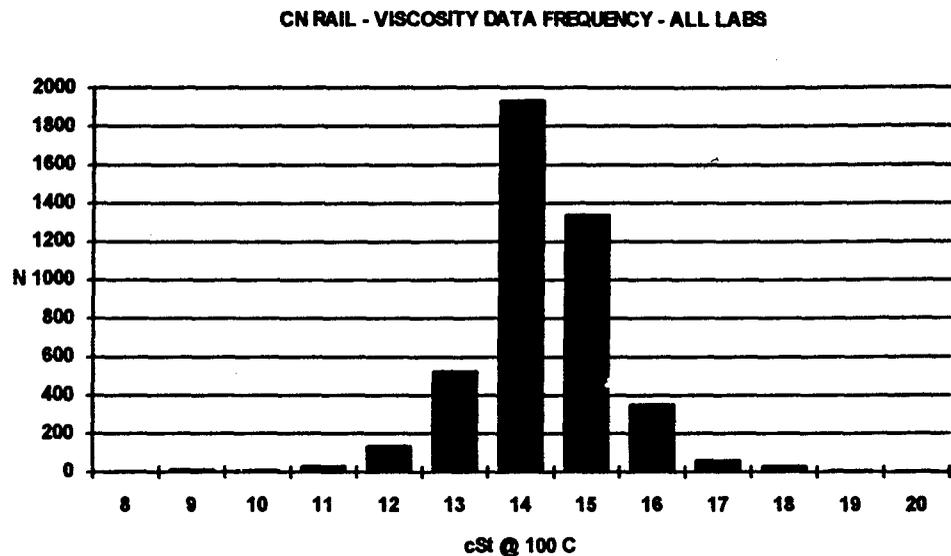


Figure 1. Frequency distribution for FT-IR predicted viscosity obtained 175 EMD engines.

across the country, the sample population includes measurements from all instruments. The low variability shown, thus indicates the high reproducibility in the FT-IR viscosity measurement.

Fuel Contamination: At CNR, fuel dilution was traditionally calculated from the ASTM D445 viscosity measurements and suffered from any problems inherent with that method. It was assumed that any decrease in viscosity was due to fuel contamination, although viscous shear and/or thermal cracking could result in the same symptoms.

CNR required the FT-IR to indicate the concentration of fuel contamination and report the data in percent. This was accomplished using PCR/PLS analysis over the range 850 to 760 cm^{-1} . The percent fuel calibration was established from prepared samples of used (uncontaminated) 17 TBN 40 and 17 TBN 20W40 oils spiked to cover the required range of fuel measurement. Figure 2 shows a classic example of a severe fuel dilution problem in engine CNR 5406. The viscosity and %fuel trends clearly show the sensitivity of the FT-IR measurements to the presence of fuel in the oil.

While the calibration model and frequency distribution data indicate a high correlation between viscosity generated and FT-IR generated fuel contamination data, in practice, the FT-IR failed to reliably indicate fuel contamination at laboratories located in Western Canada. The fuel measurement problem was found to be the result of a lower aromatic content in the fuels used in the Western Canada region. While the aromatic peak (810 cm^{-1}) of the fuel was measured accurately by the FT-IR, the level did not correlate with the actual fuel contamination as indicated by oil viscosity decrease. Since the current FT-IR method uses the 810 cm^{-1} peak for fuel quantification, the reliability problem was attributed to the variability in the aromatic content of the fuels used by CNR. As the spectra in Figure 7 shows, the 810 cm^{-1} peak of Western diesel fuel measures substantially lower than the peak from Eastern diesel fuel.

CN RAIL - UNIT 5406 - FUEL CONTAMINATION EXAMPLE

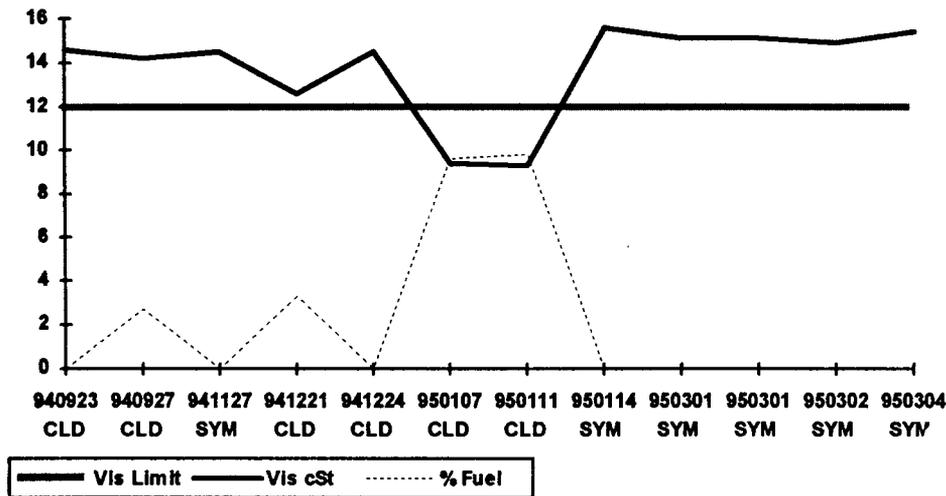


Figure 2. Unit 5606 fuel contamination. X axis in compressed date (yymmdd), with three character location code. Y axis in cSt @ 100C.

To compensate, the CNR FT-IR system at the Edmonton laboratory calculates the percent of fuel contamination from the FT-IR predicted viscosity data. The viscosity was not similarly affected by fuel aromatic concentration, and remained reliable. The FT-IR fuel contamination measurement is compared with the viscosity predicted fuel result and the larger value is reported. While lab-to-lab trending of fuel data was affected, it was determined that this was the best way to preserve engine components from fuel related damage modes.

Water Contamination: CNR laboratories traditionally used the crackle (hot plate) test and the presence of high levels of sodium and boron as the primary indicators of water in engine oils. Both methods suffer problems--the crackle test is non-quantifiable, insensitive and operator subjective, and any water ingress into the engine lubrication system may not be the result of a coolant leak, and thus, not show high sodium/boron levels.

As the most common contaminant found in diesel engine lubrication systems, water is also a very strong infrared absorber, and perhaps the easiest oil contaminant to detect. The hydrogen bonded O-H stretch vibrations (symmetric and asymmetric) of liquid water are found over the range of 3700 to 3100 cm^{-1} in petroleum based lubricants. [1] A general baseline over the range of 4000 to 2000 cm^{-1} will correct for the most common interferences, e.g. soot, insolubles, dirt loading, etc.

CNR required the FT-IR water measurement to indicate changes in concentration calibrated in percent. The calibration was accomplished using PCR/PLS analysis over the range 3700 to 3150 cm^{-1} . Prepared samples of 17 TBN 40 and 17 TBN 20W40 used (uncontaminated) oils were spiked with water to cover the required measurement ranges. Figure 3 shows the frequency distribution for the FT-IR percent water measurement for 175 engines over one year of operation.. As expected, most samples were free from serious water contamination. Figure 4

CN RAIL - WATER DATA FREQUENCY PLOT

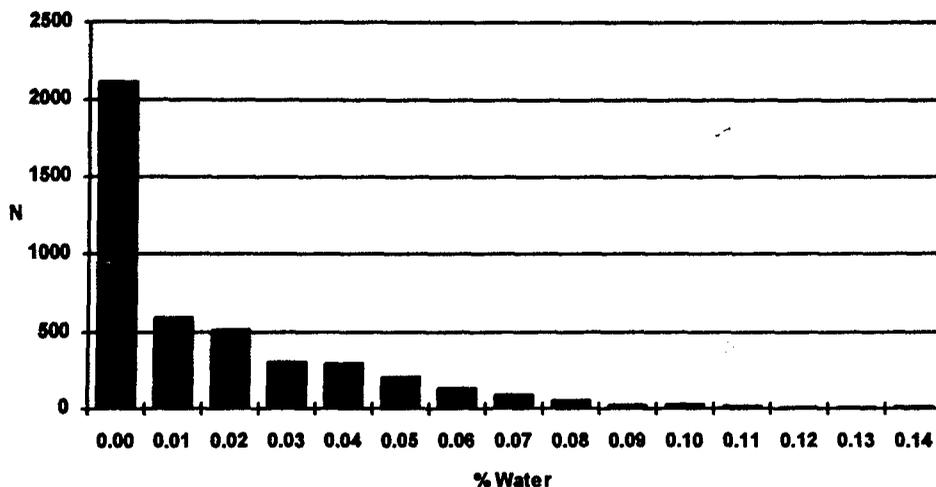


Figure 3. Frequency distribution of the FT-IR water measurement from 175 engines over one year of operation.

shows a classic example of two severe water leaks in engine CNR 5405. The percent water data is trended with the sodium and boron indicators of the coolant corrosion inhibitor. Notice the high correlation in the data trends.

CN RAIL - UNIT 5405 - WATER CONTAMINATION EXAMPLE

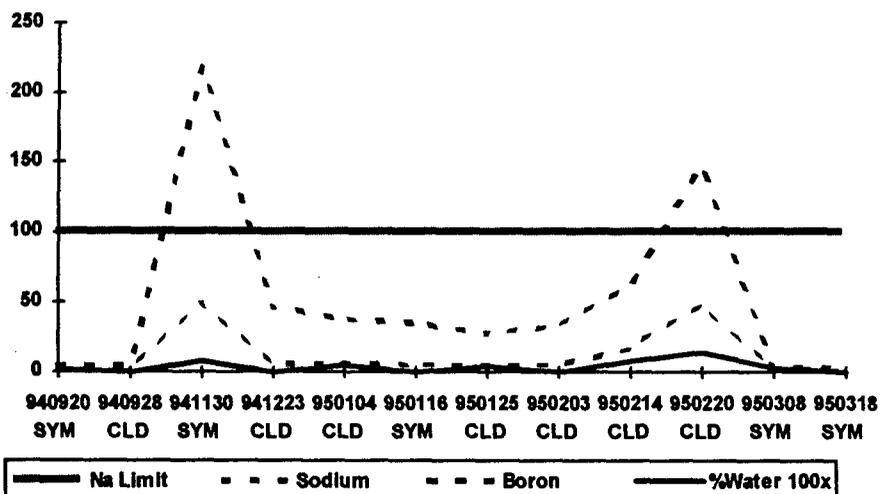


Figure 4. Unit 5405 water contamination. X axis in compressed date (yymmdd), with three character location code. Y axis in ppm for elements, % x 100 for water.

Overall, the FT-IR water measurements correlated well with other measurement methods such as emission spectroscopy (Na, B). In addition to coolant contamination, the FT-IR detected water which may result from other contamination sources. In these samples, the atomic emission data showed no change in Na or B levels. It is probable, these contamination occurrences were the result of condensation or fresh water ingress, and would have been missed prior to the implementation of FT-IR. While the Na and B trend data were routinely correlated to engine damage progress, the crackle test was only used as a go/no-go test. The FT-IR water contamination data can be trended over time and correlated to damage mode progress in a manner similar to the atomic emission data.

Insolubles: The FT-IR measurement of insolubles, such as soot, are not easily correlated to physical separation test methods, such as ASTM D-893 pentane and toluene insolubles [6]. The poor correlation is due to differences in particle size distribution, and differences in readings from the various ASTM methods, such as D-893, D-4055 and their many derivatives.

CN RAIL - INSOLUBLES DATA FREQUENCY PLOT

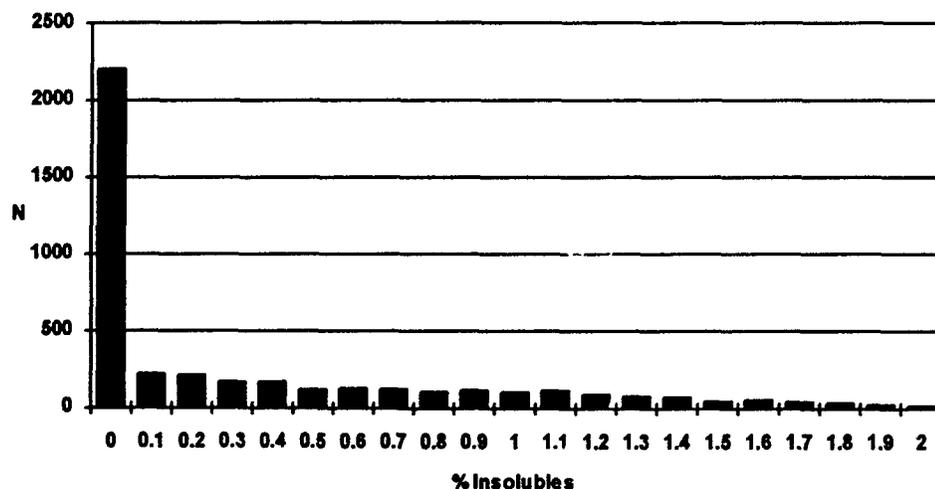


Figure 5. Frequency distribution of the FT-IR insolubles measurement from 175 engines over one year of operation.

CNR required the FT-IR analysis to correlate to the standard method developed by the Locomotive Maintenance Officers Association (LMOA). The LMOA method utilizes absorbance measurements from a UV-Vis-NIR spectrophotometer. The standard was established by a round robin analysis of sooted samples (0.2 to 6.0%) at a number of North American railway laboratories. Correlation of FT-IR generated percent insolubles with the LMOA standard was achieved by a PCR/PLS calibration over the range 3950 to 3700 cm^{-1} from prepared samples of 17 TBN 40 and 17 TBN 20W40 oils. In practice, the FT-IR analysis of used oil samples correlated very well to the LMOA method:

For values < 4%, Repeatability is 0.5% and Reproducibility is 1.3%
 For values > 4%, Repeatability is 0.75 % and Reproducibility is 2.0%

Figure 5 shows the frequency distribution for the FT-IR percent insolubles measurement. As expected, most samples were free from serious contamination

Oil Oxidation/TBN: In diesel engine lubrication systems, the oil is exposed to high temperatures and stresses in the presence of oxygen, resulting in the formation of partially oxidized compounds. Antioxidants are added to inhibit this process by serving as free radical scavengers. Oxidation by-products are generally acidic in nature and usually result in a depletion of the reserve alkalinity of the oil. The alkaline depletion has been traditionally monitored by measurement of the total base number (TBN). In keeping with past practice, CNR required both TBN and oxidation level be monitored.

Oxidation by-products in petroleum lubricants absorb infrared energy due to the C=O stretch from by-products such as ketones, esters, carboxylic acids, carbonates, aldehydes, anhydrides, and amides. A measurement region of 1760 to 1660 cm^{-1} was determined to be acceptable for the oils in use and a calibration curve was generated from prepared samples of 17 TBN 40 weight oil covering the range of 0 to 100+ integrated absorbance units. In practice the levels of oil oxidation remained low, due in part to the high oil consumption and frequent make-up oil, or periodic oil changes as are recommended by the individual engine manufacturers.

Obtaining reliable TBN data correlating to current standard methods was more difficult, in part due to the variability of results from current ASTM methods. The ASTM D4739 test was determined to be the most applicable for analysis of used railway engine oils. A TBN calibration method was accomplished by a matrix of 10 prepared samples. The analysis is performed over the range 1500 to 1420 cm^{-1} .

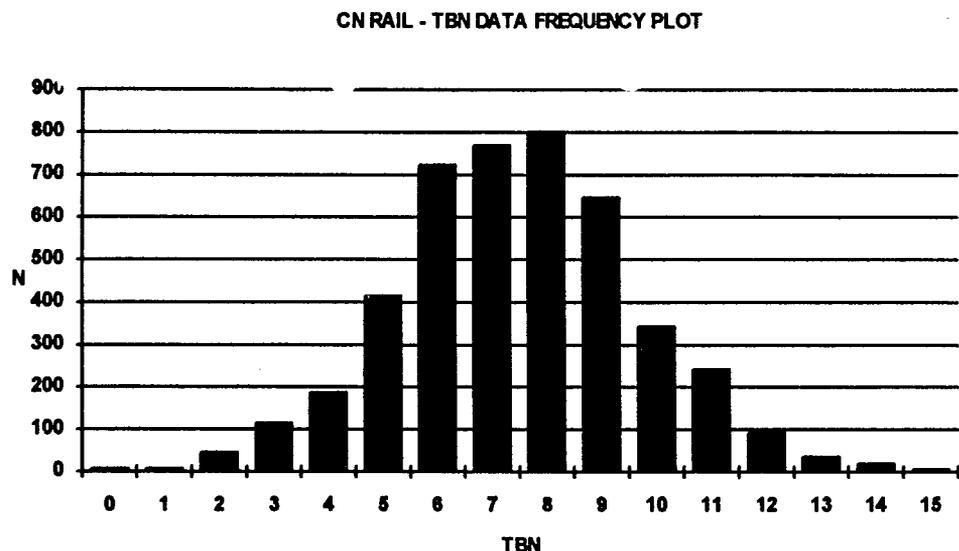


Figure 6. Frequency distribution of the FT-IR TBN measurement from 175 engines over one year of operation.

Figure 6 shows the TBN data frequency plot and indicates a relatively broad normal range spanning several base numbers. The FT-IR TBN area includes the CH₂ scissor band, a strong absorbance band, and its variability may be causing some of the variability observed. Overall, TBN showed a general correlation with oxidation data although high oxidation occurrences were not always followed by a reduction in TBN. Make-up oil additions are not reported and the effect of infusions of fresh oil could not be determined. In any case, variability in the TBN data did not impair the oil condition assessment reliability and further effort to improve the measurement was not pursued.

BENEFITS: During a 12 month period over which FT-IR analysis was used in conjunction with wear metal analysis, the CNR monitoring program detected 119 cases of fuel dilution and 325 cases of water contamination. This was based on routine sampling from 1600 locomotives sampled every 200 to 250 hours of operation, or about once every eight days. Analyzing 80,000 samples / year with a total program cost of \$1,200,000.00 translates to roughly \$15.00 / sample. Historical data from CNR indicates that a fuel contamination problem which is allowed to progress to failure will cost an average of \$17,000 to repair, and water contamination which is allowed to progress to failure will cost an average of \$30,000 to repair. Assuming that the fuel and water contamination problems were not caught prior to failure, the 444 problems detected above could of incurred in excess of \$11.7M in repair costs to CNR. Based on the laboratory operating costs and cost avoidance estimates, CNR is able to achieve roughly a 10:1 return on investment in their oil analysis condition monitoring program. An extended analysis of the financial costs and benefits in the CNR program has already been presented [7].

CONCLUSIONS: FT-IR analysis provides CNR with a fast, easy to operate method to determine engine oil properties data and is used to complement atomic (wear metal) analysis for a complete two-instrument oil condition monitoring program. The experience at CNR indicates the flexibility of FT-IR analysis software allows easy creation and implementation of new measurement parameters and was easy to interface to the existing computer infrastructure.

Viscosity measurement by FT-IR is practical. Although anyone attempting to duplicate this method should consider that, CNR maintains tight lubricant specifications and, while oils may be blended by different manufacturers, a single additive package is specified. TBN measurement by FT-IR also appears to be practical, although the above consideration also applies.

Contamination measurements met or exceeded the physical property tests replaced with the exception of fuel dilution measurements which appear to be dependent on the level of aromatics in the contaminating fuel. This problem was corrected by using the viscosity as an alternative fuel dilution indicator.

Calibration of the FT-IR to generate oil condition data in standard engineering units is practical, however, each instrument must be calibrated individually and may require re-calibration should significant maintenance alter an instrument's measurement profile. The major problem with using calibration matrices is the general lack of off-the-shelf standard fluids. Standards prepared by individual FT-IR users may lack global consistency and this can lead to poor correlation between

different users' instruments. Poor correlation among users will entrust the new FT-IR method to the old controversies surrounding the lack of correlation among the various physical tests which are variously in or out of vogue. However at CNR, the calibration matrices developed met all goals established for the program. In addition, other authors have presented an alternative to calibration [1,2,3]. This methodology suggests the development of new alarms and limits based on the FT-IR absorbance data rather than converting the absorbances to engineering units so the data can be used with existing alarms. The choice seems to lay with the user.

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