

Quantitative Condition Monitoring of In-use Oils by FTIR Spectroscopy

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Quantitative FTIR Condition Monitoring

Fluid Life operates three laboratories, two in Canada (Edmonton, AB and Brantford ON) and one in Minneapolis MN and has provided lubricant analysis services and reliability solutions for asset intensive industries for over 30 years. In the field of commercial lubricant analysis and condition monitoring, FTIR spectroscopy is extensively used as an automated fingerprint-based survey technique; largely for screening and trending of qualitative changes in lubricant quality parameters such as moisture, glycol, soot, oxidation, antioxidants and wear additives. It is an automated means of screening a large number of oil samples, in part to determine if additional quantitative confirmatory analyses are required, typically ASTM AN or BN FTIR-based BN determinations (1). However, after extensive development and testing of this approach, it was concluded that chemometric PLS-based direct FTIR BN determinations were inadequate in terms of accuracy and reproducibility and incapable of dealing with the variability in, and the variety of mineral oils we processed. As a consequence, Fluid Life investigated a more rigorous approach developed by Thermal-Lube in conjunction with McGill University (2). Their turnkey FTIR COAT (Continuous Oil Analysis and Treatment) system is based on the use of stoichiometric reactions similar to those used by the ASTM titrimetric methods.



Figure 1. COAT system used for the FTIR determination of ASTM-identical AN and BN results for in-use mineral oils.

The COAT system (Figure 1) is designed to deliver ASTM-identical results as separate methods, for either AN or BN at rates of up-to 100 samples/h. The evolution of this methodology has been extensively documented in the scientific literature (3) but its efficacy in a commercial setting has never been assessed or reported on. After substantive discussions with Thermal-Lube, Fluid Life determined that the COAT system and its methodology merited serious consideration and evaluation to determine whether quantitative FTIR analysis could be implemented and work in a commercial setting. Today, Fluid Life has four COAT systems in operation and has recently published a comprehensive assessment of the systems' operational performance in the Journal of Laboratory Automation (4). This article provides a synopsis of that assessment and summarizes the principles and performance of the methodology and those interested in more detail are referred to the original JALA article.

The Basic Concepts

The principle behind FTIR_{AN/BN} analysis is essentially identical to the corresponding ASTM titrimetric methods; the use of stoichiometric acid-base reactions, but using infrared-active organic acids and bases so that the products can be measured spectrally rather than titrimetrically (2). In the FTIR methods, the acid or base is delivered in a solvent which acts both as a reaction medium and a diluent thus substantially lowering the viscosity of the sample. As a result the sample is readily pumped from an autosampler vial (~20 ml) into a ~200 µm KCl infrared cell using a micro-pump rather than the peristaltic or syringe pump usually required to handle viscous, neat oils (5). A primary calibration is developed by gravimetric addition of a pure acid (e.g., oleic acid) or base (e.g., 1-methyl imidazole) to additive-free mineral oil which is reacted with the solvated infrared active base or acid. The appropriate spectral changes induced are then measured to develop a calibration curve. One practical impediment to using weaker acids and bases is that their "titer" (mg KOH/g oil) will be less than that obtained using the ASTM methods (6). This used to be an issue as it required one to change one's analytical frame of reference in terms of the AN or BN value used to condemn an oil, however, this problem has been resolved through the use of a unique mixed-mode chemometric calibration that ensures FTIR results are expressed in the identical terms as the corresponding ASTM reference procedure.

Calibration Basics

Mixed-mode calibrations are devised through a combination of "ideal" and "real" oils, the latter selected to be representative of the type of in-service oils routinely analyzed. Chemically pure standards (ideal primary standards) are gravimetrically prepared in mineral oil and used to calibrate and validate the expected FTIR stoichiometric response in terms of mg KOH/g oil. Such ideal standards do not contain soot, oxidative products, glycol, water, various residual additives and/or their byproducts which may be present in "real" in-service oils. The presence of such constituents can perturb the stoichiometrically-induced changes in the infrared signals of interest, affecting the predictions obtained and need to be accounted for. This is achieved through the use of chemometrics (7), specifically Partial Least Squares (PLS), which relates the spectral changes in the sample spectra to the corresponding ASTM AN- or BN-derived values

obtained from the "real" calibration standards. Because the final calibration devised is directly related to data obtained from samples analyzed by ASTM procedures, the results are expressed in ASTM terms, avoiding the issue of the weaker infrared-active acids or bases producing lower "titer" values. By combining both ideal and real calibration standards, PLS is able to differentiate between spectral responses directly related to the ASTM reference method results and spectral changes that do not correlate. It is important to note that this chemometric approach is quite different from that advocated for the PLS-based FTIR direct BN method (1). The direct BN method is not anchored by well-defined stoichiometric reactions as the FTIR_{AN/BN} methods are and relies solely on poorly defined spectral correlations which further deteriorate as the oil ages or is in extended service. Thus in the case of COAT FTIR_{AN/BN} methods, chemometrics is predominantly used to refine and account for any spectral variability or interferences inherent to "dirty" in-service lubricants and to ensure that the "titer" reflects that of the ASTM reference method used in its development. As a consequence, the COAT FTIR_{AN/BN} methods do not simply "estimate" AN or BN, but actually produce statistically equivalent ASTM results (4).

Calibration Performance

Fluid Life invested significant effort in developing, assessing and validating its mixed-mode PLS calibrations and to validate their performance. As ASTM analyses are always ongoing, splitting samples and collecting the corresponding FTIR spectra and associated ASTM data was not that onerous a task or process, however, professional expertise was called upon for the chemometric calibration development. Prior to any calibration development, all sample handling, preparation and minimization of sample carryover required standardization, achieved largely through the assessment of calibration standards and analysis of standardized QC oils.

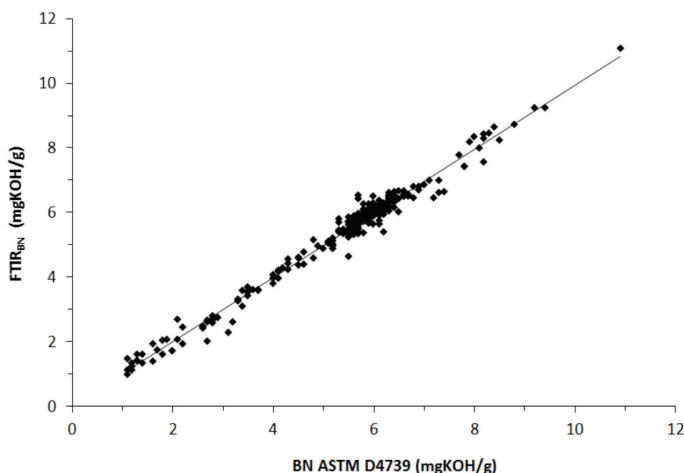


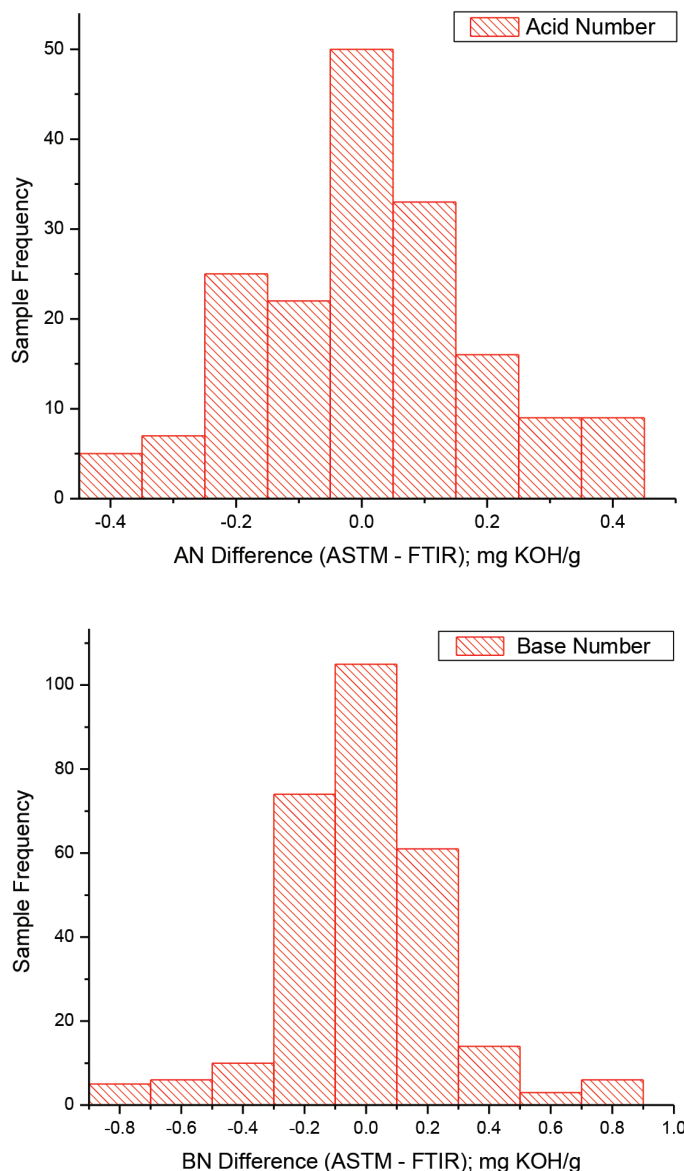
Figure 2. FTIR leave-one-out cross-validation calibration plot for BN derived using mixed-mode ASTM BN calibration.

Ultimately, sample preparation itself simply consists of adding well-mixed oil to a vial using a calibrated syringe, dispensing the reagent by re-pipette, capping, vortexing, de-capping and loading the vials into the autosampler. COAT UMPIRE software controls the autosampler, pump and spectrometer, makes the spectral measurements, converts the spectral data to mg KOH/g oil which is transferred to the Laboratory Information and Management System (LIMS); typically at a rate of ~1 min/sample. A wide range of mineral oils were assessed with calibrations devised to determine if oil sub-classifications were required, e.g., based on oil type (i.e., hydraulic vs compressor) or fuel type (i.e., diesel vs natural gas). For BN, the bulk of the samples were in-service engine oils representing a wide range of equipment applications (mining, transport, generators, marine etc.) with ~70% using diesel fuel and the balance natural gas. The majority of these oils were SAE Grade 40 and 15W40 oils, but extended to most other common grades with almost all major lubricant suppliers represented. In the case of AN, a mix of new and in-service oils covering a wide range of suppliers and grades were considered, including oils from engines, compressors, hydraulic systems, turbines transmissions and gear boxes. From the calibration development studies, it was determined that one well devised general calibration was adequate for each of AN or BN for all mineral oils, regardless of their quality or soot levels. Figure 1 is illustrative of a typical leave-one-out cross-validation FTIR BN calibration obtained for ASTM D664 (HCl). Highly linear relationships were obtained for the FTIR_{AN/BN} cross-validation calibrations with SD's of 0.17 and 0.26 mg KOH/g for AN and BN, respectively, recognizing that the FTIR_{AN/BN} methods are limited by the reproducibility of the corresponding ASTM reference methods used as well as how rigorously they are executed.

Operational Performance

Prior to application of this new technology to customer samples, the FTIR_{AN/BN} methods were extensively validated. Precision, specificity, linearity/range and accuracy (with respect to the ASTM methods) were all determined. The method detection limit was calculated and QC limits established for all QC sample types (blanks, duplicates, high and low). After set-up and shake out runs to train operators and optimize sample handling and flow, the COAT® system was placed in the production mode and its performance assessed over a period of 6 months by randomly analyzing selected operational samples by both FTIR and ASTM methods. For AN, and BN, 177 and 284 new and used oil samples were analyzed, respectively, the former including oil from hydraulic systems, gear boxes, transmissions, engines, turbines and compressors while for the later diesel and natural gas-fueled samples predominated. Figures 2 and 3 are histograms of the differences between the individual ASTM and FTIR results for AN and BN.

What is noteworthy is that the analytical differences between the ASTM and FTIR methods are normally distributed in both cases, each having an overall mean difference close to zero with a variability reflecting that of the ASTM reference methods. These production sample results clearly indicate that the FTIR_{AN/BN} methods produce ASTM-identical results on average, reflecting the type of data one would normally obtain had one only used the ASTM procedure.



Figures 3 and 4. Comparative analytical test result distributions of differences between ASTM and FTIR results obtained for random operational samples for AN and BN, respectively.

Advantages and Benefits

Based on our comprehensive in-house assessment, the COAT system has proved itself of being able to produce ASTM-identical data. From an operational standpoint, one FTIR is roughly equivalent to ~9-10 titrators, assuming strict ASTM protocols are followed. Table 1 summarizes and compares the key operational variables of the two analytical methods, the advantage clearly being in favor of the FTIR system. As currently configured at Fluid Life, one analyst can analyze ~500 samples per 8 hour shift, a substantial throughput advantage.

Acid Number Variables	ASTM AN _{D664}	FTIR _{AN}
Sample Preparation Time ^a	120 sec/sample	60 sec/sample
Samples/hour	4-6/h	60 samples/h
Daily startup and preventative maintenance time ^b	Variable - up to 1h	< 5 minutes
Waste disposal volume	~130 ml	~25 ml
Base Number Variables	ASTM BN _{D4739}	FTIR _{BN}
Sample Preparation Time	120 Sec/sample	60 sec/sample
Samples/Hour	4-6/h	60 samples/h

Table 1. Comparison of sample preparation time, throughput, maintenance time and waste disposal volumes for the ASTM/AN/BN titrimetric methods vs. the FTIR/AN/BN procedures.

However, as FTIR_{AN/BN} methods are not sanctioned as official methods by any officiating body, ASTM or otherwise, these analyses are presented to clients as a cost effective, alternative means of obtaining quantitative ASTM-equivalent AN and BN data. Given the statistically proven equivalence of the FTIR_{AN/BN} results, clients can be provided with meaningful real-time AN and/or BN results at a reasonable cost. Quantitative real-time ASTM trending has generally been considered too expensive for routine monitoring applications, however, with efficient, lower cost FTIR analysis the door to AN and BN trending is now open. From our experience, it is clear that the COAT FTIR system has proven its efficacy and has provided Fluid Life with the ability to offer additional value-added quantitative condition monitoring information to its clientele which is effectively ASTM-identical. The utility and productivity of this new methodology is viewed as a significant advance in lubricant analysis technology and in our opinion could be of benefit to the oil condition monitoring sector as a whole.

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