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Automated Acid and Base Number Determination of Mineral-Based Lubricants by Fourier Transform Infrared Spectroscopy: Commercial Laboratory Evaluation

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Abstract

The Fluid Life Corporation assessed and implemented Fourier transform infrared spectroscopy (FTIR)–based methods using American Society for Testing and Materials (ASTM)–like stoichiometric reactions for determination of acid and base number for in-service mineral-based oils. The basic protocols, quality control procedures, calibration, validation, and performance of these new quantitative methods are assessed. ASTM correspondence is attained using a mixed-mode calibration, using primary reference standards to anchor the calibration, supplemented by representative sample lubricants analyzed by ASTM procedures. A partial least squares calibration is devised by combining primary acid/base reference standards and representative samples, focusing on the main spectral stoichiometric response with chemometrics assisting in accounting for matrix variability. $\mathrm{FTIR}_{\mathrm{AN/BN}}$ methodology is precise, accurate, and free of most interference that affects ASTM D664 and D4739 results. Extensive side-by-side operational runs produced normally distributed differences with mean differences close to zero and standard deviations of 0.18 and 0.26 mg KOH/g, respectively. Statistically, the FTIR methods are a direct match to the ASTM methods, with superior performance in terms of analytical throughput, preparation time, and solvent use. $\mathrm{FTIR}_{\mathrm{AN/BN}}$ analysis is a viable, significant advance for in-service lubricant analysis, providing an economic means of trending samples instead of tedious and expensive conventional $\mathrm{ASTM}_{\mathrm{AN/BN}}$ procedures.

Keywords

condition monitoring, Fourier transform infrared spectroscopy, lubricant analysis, mineral oil analysis, ASTM, ISO, D664, D4739, D2896, lubricant quality, lubricant trending, equipment reliability, total acid number (TAN), total base number (TBN), $\mathrm{FTIR}_{\mathrm{AN}}$, $\mathrm{FTIR}_{\mathrm{BN}}$

Introduction

The Fluid Life Corporation (FLC) is a provider of oil analysis and reliability solutions for asset-intensive industries including mining, construction, transportation, industrial plants, and the oil and gas sector. For more than 30 y, FLC has provided quality analysis of in-service lubricants, coolants, and fuels and expert evaluation of test results, along with professional advice. It has a history of innovation, with patents pending as well as issued for the design of autoviscometers and viscometer tubes and was the first to market with fully computerized sample results and custom data-trending tools to identify equipment reliability trends and issues. FLC operates laboratories in Canada and the United States and has reliability consultants on site throughout North America. All three of its laboratories are highly automated and are accredited to International Standards Organization (ISO/IEC) 17025:2005 by the Canadian Association of Laboratory Accreditation (CALA) for tests on the laboratory scope of testing. In its ongoing drive for innovation and efficiency, FLC has invested substantial effort over the past 2 y to assess and develop the analytical potential of Fourier transform infrared spectroscopy (FTIR)–based technology as developed by the McGill IR Group and Thermal-Lube Inc. (Point Claire, QC, Canada) to measure acid number (AN) and base number (BN).

AN and BN are fundamental measures of oil condition, these being routinely used to monitor relative changes in acidity or reserve alkalinity, respectively, of new and in-service oils. The commonly used American Society for Testing and Materials (ASTM) titrimetric methods, D2896 and

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D4739 for BN and D664 for AN,[1–3] are problematic in terms of cost, maintenance, reproducibility, and reliability. Major disadvantages of these potentiometric titrations include the sluggish response of indicator electrodes to nonaqueous solvents, the fouling of electrodes, high maintenance, as well as high solvent consumption and disposal costs. Because the methods are rather cumbersome and relatively slow (approximately four to eight samples per hour), laboratories may choose to take shortcuts and decrease the analysis time by following modified versions of the ASTM methods. These shortcuts may include reducing sample mass, reducing solvent volume, decreasing the number of quality control (QC) standards, increasing the rate of titrant addition, and decreasing electrode rinse or soak time.

The McGill IR Group in collaboration with Thermal-Lube Ltd. have worked toward developing quantitative FTIR-based AN and BN ($FTIR_{AN/BN}$) methods by employing stoichiometric reactions similar to those used by the ASTM procedures but using weaker organic versions of the inorganic acids and bases normally used, so as to produce IR measurable changes proportional to the analyte concentration. Aside from eliminating the need for titration, the key to these methods is that sample dilution is part of the procedure, reducing sample viscosity and thus facilitating rapid IR cell loading from an autosampler as well as minimizing cell rinsing to eliminate carryover. Sample dilution in combination with spectral reconstitution was originally exploited to facilitate high-speed, automated, qualitative Joint Oil Analysis Program FTIR condition monitoring (CM) analysis[4,5] with dilution in combination with stoichiometric reactions used to develop quantitative $FTIR_{AN/BN}$ analyses.[6] Comprehensive reviews of the evolution of FTIR edible oil analysis[7] and CM methodology[8] provide a context for this article and describe the basic principles of automated FTIR analysis using the Thermal-Lube Continuous Oil Analysis and Treatment (COAT) Analyzer to facilitate CM, AN, BN, and H_2O analyses at rates of >100 samples/h. This article addresses the calibration, validation, and performance of the COAT FTIR system for quantitative AN and BN analysis in a commercial laboratory relative to the results obtained using the respective ASTM titrimetric methods.

$FTIR_{AN/BN}$ Methodology Overview

It is important to note that the partial least squares (PLS)–based chemometric approach[9] discussed herein is not to be confused with FTIR PLS-based direct BN method being used by some commercial laboratories to *estimate* the BN of neat oils.[10] Direct PLS-BN methodology relies solely on spectral changes and correlations in neat oils to develop a chemometric relationship between the FTIR spectral changes and ASTM BN results. In contrast, the $FTIR_{AN/BN}$ methodologies described in this article are defined and anchored by stoichiometric acid-base reactions using infrared-active reagents,[6–8] where PLS is used to account for spectral matrix, formulation, and contaminant effects and variability. The use of PLS in the $FTIR_{AN/BN}$ methods also ensures that the results are of the same magnitude as those of the ASTM reference methods, even though the acids and bases used in the $FTIR_{AN/BN}$ methods are weaker overall. Rather than *estimating* AN or BN, $FTIR_{AN/BN}$ methodology *predicts* $ASTM_{AN/BN}$ results.

In the past, in partnership with consultants, FLC did attempt to develop a reagent-less direct PLS-BN method for neat, undiluted oils but with very limited success.[11] A separate calibration was required for each customer, oil make, and grade, all of which increased costs and limited the application of the method. Confidence in the results decreased with the age of the oil, as interferences and contamination including soot, water, coolant, and dirt/dust increased. Wider development of the direct BN-PLS approach to determine BN on neat, undiluted oils was eventually abandoned because of overall poor performance and limited practical applications. Even so, the possibility of replacing cumbersome and slow titrimetric ASTM methods with an FTIR approach was clearly attractive. Based on the scientific literature regarding alternate stoichiometric $FTIR_{AN/BN}$ approaches, FLC decided to assess the only commercial system available that was designed for this methodology. Although the scientific basis for $FTIR_{AN/BN}$ analysis using ASTM-type stoichiometric reactions is persuasive, no commercial laboratory assessment of the performance of such an analytical system has been published to date. FLC currently has four operational Thermal-Lube COAT systems dedicated to carrying out automated high-throughput $FTIR_{AN/BN}$ analyses of new and used mineral oils and has determined that that these methods are accurate and commercially viable. The acceptance of $FTIR_{AN/BN}$ analysis in the analytical community is strongly dependent on its successful implementation within commercial laboratories as well as its integration into laboratory information management systems (LIMS).[12] FLC has chosen to share the basic concepts, benefits, and performance statistics with the lubricant analysis community at large via this publication. Although the details of the calibrations, methodology, and implementation are largely proprietary, the concepts and performance of the $FTIR_{AN/BN}$ methods as well as the substantive efficiency gains, significant reduction in one's environmental footprint, and lower analytical costs are all of general interest to the broader analytical community and are reported in this study.

Materials and Methods

Oil Samples

FLC routinely analyzes a wide range of new and in-service oils for AN and BN, these being representative of a wide range of suppliers, viscosities, formulations, and applications. For both AN and BN analyses, the oil samples were restricted to mineral-based oils, albeit other oils (e.g., ester) can also be analyzed using alternate calibrations and procedures.[13] In the case of BN analysis, the bulk of samples are in-use engine oils representing a wide range of equipment applications (mining, transport, generators, marine, etc.) using predominantly diesel (~70%) or natural gas (~30%) as fuels, with the majority being SAE grade 40 and 15W40 oils but extending to most other common grades with almost all major lubricant suppliers represented. In the case of AN, a mixture of new and in-service oils covering a wide range of suppliers and grades was included, including oil from engines, compressors, hydraulic systems, turbines, transmissions, and gear boxes.

Instrumentation

The instruments used were Thermal-Lube COAT systems, consisting of an ABB Bomem 3000 FTIR (Quebec, QC, Canada) integrated with a Gilson autosampler. The FTIR was equipped with a conventional 200 μm demountable CaF_2 cell coupled to a micro-pump, which aspirates the sample from the autosampler vials into the IR cell. The instrument was controlled by UMPIRE Pro (Universal Method Platform for Infrared Evaluation, Professional Edition), software proprietary to Thermal-Lube, which controls the autosampler, pump and spectrometer and carries out the spectral data processing to produce the final AN or BN values expressed as mg KOH/g. These data are passed to the LIMS system for final processing and report preparation. Each instrument is purged with dry air using a Balston Dryer to minimize water vapor variations in the spectra collected, with eight scans (~16 seconds) co-added to obtain a sample spectrum. The COAT system was modified to include a bulk solvent reservoir in conjunction with a computer-controlled solenoid valve to rinse both the lines and cells between samples.

Reference Methods and Quality Control

FLC's three laboratories are accredited by CALA to ISO/IEC 17025 for their scope of testing, and the company also participates in routine ASTM proficiency testing for ASTM D664 (AN) and ASTM D4739 and D2896 (BN), which were used as reference methods for this work. Slight modifications were made to the reference methods to accommodate the use of modern autotitrators. QC for these ASTM reference methods is strict because of the large number of potential interferences and included the analysis of solvent blanks, method blanks (base mineral oil), sample duplicates, and routine QC standards bracketing every batch of 10 to 15 samples. Routine, blind internal interlaboratory proficiency testing is performed monthly on samples and blanks between FLC laboratories. Certified reference material as per ISO Guide 34[14] is also analyzed routinely to ensure the methods meet all accuracy and precision requirements of the ASTM methods. In addition, the FLC LIMS ensures that samples are bracketed by a QC sample at both the start and end of each and every batch of samples. When a QC standard is outside its control limits, the LIMS system automatically documents the failure, rejects all sample data bracketed by that QC sample, and reschedules those samples for reanalysis. The LIMS system is also configured to automatically trend AN and BN QC data using control charts for blanks, QC standards, and sample duplicates for each instrument to provide real-time QC of these analytical operations.

$FTIR_{AN/BN}$ Sample Preparation

The original methodology as devised was predicated on the use of gravimetric sample preparation based on the assumption that volumetric preparation could limit accuracy because of sample viscosity variability. With rapid sample preparation being key to productivity, it was demonstrated that a volumetric syringe in conjunction with gravimetric calibration could dispense the required volume to within ±3% for a wide range of densities and viscosities, including ISO 680 gear oils. This constant volume syringe was used to dispense the correct sample volume into an autosampler vial after oil samples had been homogenized for 15 min on a platform shaker. For AN, the samples were first diluted 1:2.5 with mineral spirits (MS) using a repipette, and then a 1% sodium phenolate solution in 1-propanol (NaP/1-P) was added in a ratio of 2:1 to the diluted samples. This mixture was shaken and sonicated in a water bath maintained at 45 °C for 20 min and the vials loaded into the autosampler for analysis. For BN analysis, samples were diluted 4:1 with MS, and a 5% solution of aged trifluoroacetic acid (TFA) was added in a ratio of 2:1 to the MS-diluted samples. The samples were then shaken and loaded into the autosampler for analysis. Aging of the TFA solution for 48 h is required to ensure that the esterification of the propanol is complete to ensure stable spectra are obtained.[7]

$FTIR_{AN/BN}$ Analysis and Calibration

Whether AN or BN is to be analyzed, the MS-diluted reagent solution is preloaded into the first two slots of the autosampler to ensure that a good-quality reference spectrum is obtained. This spectrum is subtracted from all subsequent sample spectra to remove the bulk of the solvent spectral contribution to produce a sample differential spectrum. The spectral subtraction is automatically adjusted for any significant displacement caused by the sample by measuring the overtone band of the solvent. A 5-5 gap-segment derivative is taken of the differential spectrum to both accentuate the spectral changes induced by the stoichiometric reaction as well as minimize any spectral contributions from the oil. A primary calibration is prepared using gravimetrically added reference standards (oleic acid for AN and 1-methylimidazole for BN) to an additive-free base mineral oil, which is diluted with MS and then treated with the corresponding reagent solution (1% NaP/1-P or 5% TFA/1-P, respectively). The differential second derivative spectra obtained are evaluated for their corresponding spectral changes in the regions where the spectral response is expected based on the following reactions:

$$\text{For AN: R-COOH (oleic acid) + Aryl-}\\ \text{O}^{-}\text{Na}^{+} \rightarrow \text{R-COO}^{-} + \text{Aryl-OH.} \tag{1}$$

$$\text{For BN: R-NH (1-imidazole) + R-}\\ \text{COOH} \rightarrow \text{R-COO}^{-} + \text{R-NH2.} \tag{2}$$

By measuring the spectral changes incurred as a function of concentration, a primary Beer's law calibration can be devised.[6] To produce a calibration more representative of the samples expected to be encountered, the spectra of real samples treated with the AN or BN reagent are collected, and the changes in the primary spectral region are related to the corresponding ASTM AN or BN data for each sample using PLS to develop a more robust relationship.

Thus, the PLS calibration is anchored using the same spectral region used in developing the Beer's law calibration but is supplemented with additional spectral information that correlates and/or contributes to a reduction in the calibration cross-validation error. This requires a substantive set of preanalyzed samples representative of the population of sample types expected to be encountered and the iterative examination of the correlation spectra; these are evaluated so as to optimize the calibration by eliminating outliers and minimizing the overall cross-validation error. This mixed-mode calibration, combining ideal and real representative samples, has the benefit of having a defined stoichiometric spectral anchor, with the supplementary PLS spectral regions used to account for matrix (formulation, soot, etc.) variability not accounted for using a simple Beer's law calibration.

Sample Handling and Data Processing

A wide variety of variables are involved in optimizing sample handling in any automated system, which may affect the results, requiring careful study and optimization to eliminate or minimize their effects. Key variables include sample handling and preparation procedures, reagent preparation and stability, sample volume, pump time, carryover, cleanliness of the cell, and path length, among others. The majority of these variables are unique to a laboratory's analytical objectives in terms of accuracy and throughput, and the details of these are beyond the scope of this article. Suffice to say, these elements were carefully examined and optimized, predominantly from a reproducibility standpoint, and further monitored using high- and low-value AN or BN oils as well as reference calibration acids and bases. UMPIRE was used for spectral data collection and processing to produce the gap-segment second derivative spectra, which were then used to develop the PLS calibrations[13] using commercially available PLS software.[15] The calibrations developed were then incorporated into UMPIRE so that the spectra could be processed directly using the PLS matrix to produce AN and BN data directly. This output was exported directly to the FLC LIMS system, where it was integrated into the company reporting system for further processing. One additional element that was incorporated was to spectrally identify anomalous oils, particularly phosphate esters, which cannot be analyzed as their absorptions strongly interfere with the measure(s) of interest. Although such samples are normally not in the analytical stream, they sometimes are inadvertently loaded, with their presence causing two problems: (1) meaningless high values and (2) potential production of a very substantive carryover effect, significantly biasing the next sample. For these reasons, additional algorithms were developed to identify spectrally samples of phosphate esters and to reject the results using the LIMS system, and carryover of esters (if any) was eliminated using a solvent wash system.

Results

Primary Calibration

Based on optimized sample-handling procedures, **Figures 1 and 2** typify primary calibration plots obtained for AN and BN using the pure reference acid (oleic acid) and base (1-methylimidazole), respectively, covering an AN range of 0 to 5 mg KOH/g and a BN range of 0 to 15 BN mg KOH/g. The corresponding best-fit linear regression equations obtained for AN and BN were

$$\text{FTIR}_{\text{BN}} = -0.387 + 54.23 * \text{Abs}_{1653\ \text{cm}-1}\\ \text{SD} = 0.19\, R^2 = 0.998. \tag{3}$$

$$\text{FTIR}_{\text{AN}} = -0.014 + 7.64 * \text{Abs}_{1589\ \text{cm}-1}\\ \text{SD} = 0.08\, R^2 = 0.998. \tag{4}$$

These plots clearly illustrate the simple direct stoichiometric relationship between the concentration of added acid and base and the resulting IR spectral changes taking place in the differential spectra. Analysis of these standards by the corresponding ASTM methods yielded results that matched the gravimetrically determined AN and BN values expected for the pure compounds within experimental error of the ASTM methods.

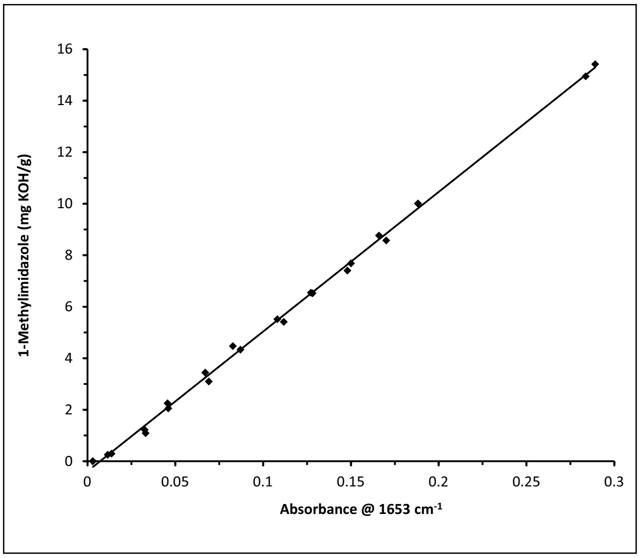

Figure 1. Primary $FTIR_{BN}$ calibration plot of duplicate 1-methylimidzaole calibration standards in mineral base oil versus absorbance at 1653 cm^{-1} obtained after its reaction with trifluoroacetic acid.

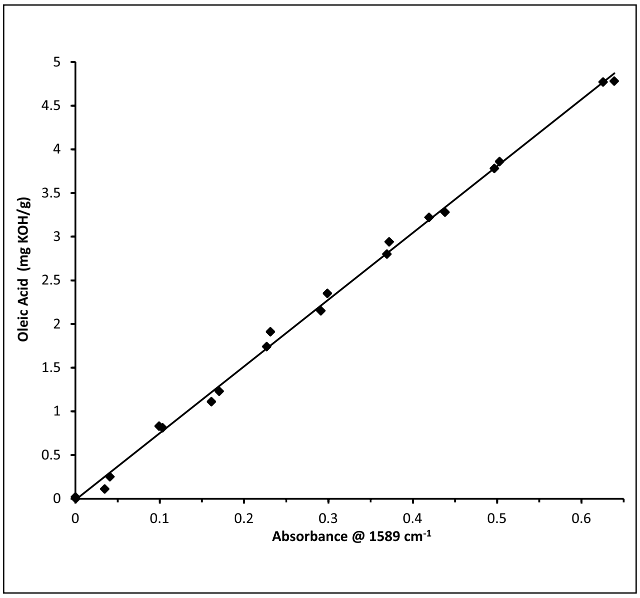

Figure 2. Primary $FTIR_{AN}$ calibration plot of duplicate oleic acid calibration standards in mineral base oil versus absorbance at 1589 cm^{-1} obtained after its reaction with sodium phenoxide.

PLS Calibrations

As noted earlier, PLS calibrations used in this methodology are developed to further generalize and account for the variability in real samples and to relate the spectral changes to the values obtained from the particular ASTM method used and implemented in the laboratory.

$FTIR_{AN}$ PLS Calibration. More than 200 oil samples for which ASTM D664 AN ($ASTM_{D664}$) data had been determined along with a duplicate series of oleic acid standards of known concentration were used to develop the AN PLS calibration. Correlation spectra of the pure standards, the ASTM samples, and the combinations thereof were compared and examined to determine whether other correlating regions could provide additional spectral information that could reduce the leave-one-out cross-validation error. Outliers were iteratively removed to obtain a smooth predicted residual error sum of squares plot while minimizing the number of factors used as well as the cross-validation error. By taking several independent routes and using a variety of sample subsets, their convergence to a similar calibration in terms of PLS factors and minimizing the leave-one-out cross-validation error provided a high degree of confidence that the calibrations obtained are workable and robust. As a final step, an independent validation set of representative samples was used to provide an estimate of the overall performance of the calibration in its ability to produce representative ASTM data. Unfortunately, a PLS calibration is a matrix and cannot readily be represented other than in performance terms by plotting the FTIR PLS predictions obtained versus the ASTM reference values. By definition, PLS-derived prediction plots will always have an average slope of ~1.0 and an intercept of ~0, the main arbiter being the standard deviation (SD) obtained between the IR predictions relative to the ASTM results, which in turn can be compared to the performance of the ideal sample, in this case, pure oleic acid. How far these SD values (ideal pure standards versus ASTM real samples) differ from each other is a measure of the total cumulative error from all sources and is based on the assumption that the $ASTM_{AN}$ method is "flawless." This is of course not the case, as the reproducibility of the $ASTM_{D664}$ procedure is ~±0.44***x** mg KOH/g for used oils.

Figure 3 presents a cross-validation plot of the FTIR PLS predictions versus ASTM AN, the best fit regression equation obtained being

$$\begin{aligned} \mathrm{FTIR}_{\mathrm{AN}} &= 0.018 + 1.002 * (\mathrm{ASTM}_{\mathrm{D664}}) \\ \mathrm{SD} &= 0.185\; R^2 = 0.960. \end{aligned} \tag{5}$$

The cross-validation SD for $FTIR_{AN}$ accuracy is ±0.185 mg KOH/g versus that of ±0.08 mg KOH/g for the oleic acid reference standards. The SD of the sample predictions relative to the ASTM data is in line with the reproducibility of the ASTM AN method, which is ultimately the limit of how accurate the predictive data can be, because the spectral information is referenced to those values. The reproducibility of the FTIR method for the standards is substantially better than that of the ASTM procedure. This is not surprising given that spectroscopic methods are generally known to be very reproducible. The argument has been made

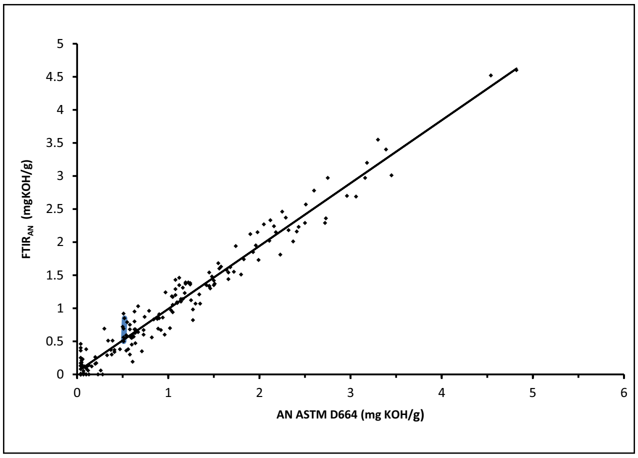

Figure 3. Cross-validation plot for the FTIR$_{AN}$ partial least squares calibration versus ASTM D664; oil types included natural gas engine, diesel engine, turbine, compressor, transmission, and hydraulic oils.

before[16] and is clearly proven here that FTIR$_{AN}$ analysis as structured for oleic acid serves as an accurate primary method. In terms of real samples, this is also true of the original split-sample (blank and reagent-treated sample) FTIR procedure originally developed,[6] in which matrix effects are ratioed out, but not for this single-sample method, in which matrix effects and solvent displacement can affect quantitation. Thus, for the single-sample approach, which is the case here, one has to rely on the ASTM reference method for quantitation and allow PLS to compensate for matrix effects and to include the solvent overtone band correction to correct for dilution/displacement effects.

FTIR$_{BN}$ PLS Calibrations. There are two ASTM methods commonly used to determine BN: ASTM D2896 using perchloric acid and ASTM D4739 using HCl. When a pure standard such as 1-methylimidazole is analyzed, the FTIR$_{BN}$ method and either of the two ASTM$_{BN}$ methods will produce the same result. However, for real oil samples, which may contain a variety of basic constituents having a range of pK$_b$, these will all react with the very strong perchloric acid but not necessarily with weaker HCl, thus resulting in differing BN values for the same sample[17] using the ASTM methods.

Generally, given the strength of perchloric acid, D2896 is considered to be more of a QC method used by oil manufacturers to monitor additives incorporated into lubricating oils, many of which are very weakly basic and otherwise difficult to measure. The determination of BN using HCl (D4739) is considered more practical and appropriate for used oil analysis and monitoring the metal carbonates incorporated into oils specifically to neutralize acid buildup due to oxidation and blow-by. FLC's experience with both methods has been that the ASTM perchloric method is more repeatable and reproducible than the HCl method, somewhat affecting the overall quality of calibration attainable. For the purposes of this article, only the results associated with the HCl method (ASTM$_{D4739}$), the dominant method used for in-service oil BN monitoring by the industry, are presented, albeit similar and somewhat better calibrations and results can also be obtained using ASTM$_{D2896}$.

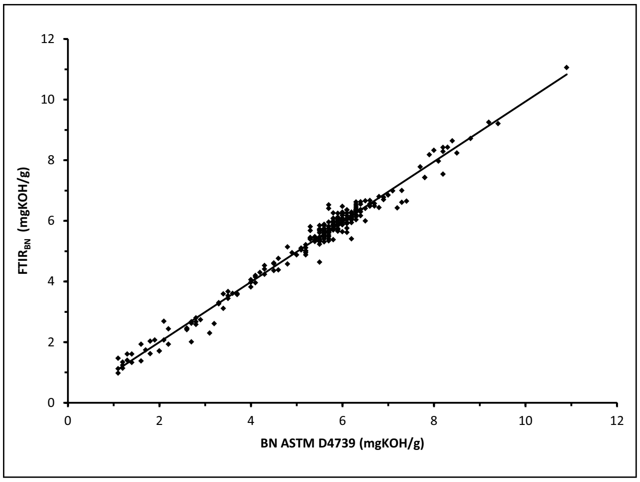

Figure 4. Cross-validation plot for the FTIR$_{BN}$ partial least squares calibration versus ASTM D4739; oil types included new and in-service natural gas (~30% of samples) and diesel engine–fueled oils.

FTIR$_{BN}$ PLS calibrations were derived for ASTM$_{D4739}$ (0.1N HCl) in a manner similar to that described earlier for AN. **Figure 4** illustrates the cross-validation plot obtained with the linear regression equation and accompanying statistics for the plot presented in eq 6.

$$\begin{aligned} \mathrm{FTIR}_{\mathrm{BN}} &= 0.099 + 0.978 * \left(\mathrm{ASTM}_{\mathrm{D4739\ BN}}\right) \\ \mathrm{SD} &= 0.258\, R^2 = 0.984. \end{aligned} \tag{6}$$

In the calibration development procedure, a number of subclasses of similar sample types were assessed with respect to quantitation, including, among others, high/low soot groupings, diesel-only versus natural gas–only engine oils, and whether separate calibrations would produce better results (lower cross-validation SDs). It was concluded that a single universal PLS calibration performed just as well as oil type–classified calibrations and that there was little to be gained by partitioning by sample type in terms of calibration development.

Operational Performance

Prior to application to customer samples, the FTIR$_{AN}$ and FTIR$_{BN}$ methods were extensively validated. Precision, specificity, linearity/range, and accuracy (with respect to the ASTM methods) were determined. The method detection limit was calculated and QC limits established for all QC sample types (blanks, duplicates, high and low). After setup and shake out runs to train operators and optimize

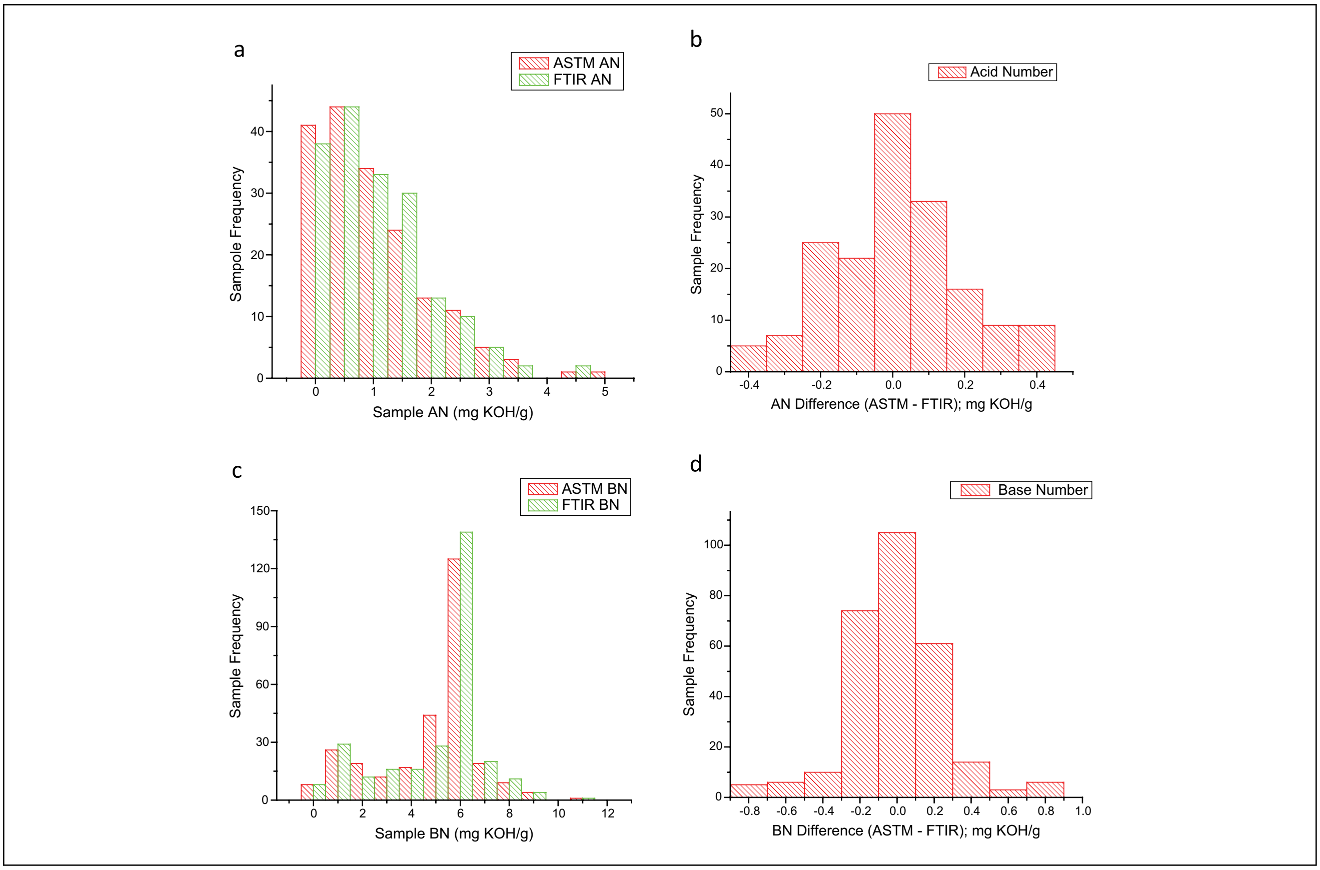

Figure 5. Operational AN (a) and BN (b) distributions for FTIR and ASTM production run analytical results and their respective difference distributions (c) and (d) obtained by subtracting the FTIR result obtained from that of the ASTM result.

sample handling and flow, the COAT system was placed in the production mode and its performance assessed relative to that of the ASTM methods in use by analyzing selected operational samples using both methods.

In-Service Oil Analysis: FTIR$_{AN/BN}$ versus ASTM$_{AN/BN}$ Methods. For AN, 177 used oil samples, including oil from hydraulic systems, gear boxes, transmissions, engines, turbines, and compressors, were analyzed using the FLC-devised quantitative FTIR$_{AN}$ method as well as by AN$_{D664}$. For BN, 284 samples of in-service engine oils (70% diesel and 30% natural gas) were analyzed following the FLC quantitative FTIR$_{BN}$ method as well as by ASTM$_{D4739}$. **Figure 5a and 5b** present comparative histograms of the FTIR and ASTM analytical result distributions for AN and BN operational samples, respectively, the range considered representative of the types of samples generally analyzed. AN samples have a more restricted range relative to BN samples, with most samples being at the lower end of the AN scale, dropping off exponentially as acidity develops in an oil over time and service. BN, being an additive, has a skewed distribution, starting off high and somewhat variably depending on the original amount of base added to the oil and is lost over time and service. **Figures 5c and 5d** are histograms of the differences in the analytical results obtained between the individual ASTM$_{AN/BN}$ and FTIR$_{AN/BN}$ methods. What is noteworthy is that the differences between the analytical results in both cases are effectively normally distributed; the statistics associated with these distributions are presented in **Table 1**. The latter indicates that the distribution sample means for AN and BN are obviously quite different and reflect the much lower values associated with AN analyses, which is an accumulation of an acidic reaction product, whereas BN reflects a basic additive loss. When one examines the difference in distributions resulting from subtracting the FTIR result from the corresponding ASTM result, the mean difference (MD) for both AN and BN methods are very close to zero, indicating that the methods are on average producing identical results. The standard deviation of the difference (SDD) is indicative of the variation of the differences around the MD, which is <0.2 mg KOH/g for AN and <0.3 mg KOH/g for BN. Converting the SDD data into a coefficient of variation (CV) relative to the mean of the sample value distributions, the CV for AN is ~18% versus ~5% for BN. Although the CV for AN appears significantly higher than that of BN, this is largely because the mean of the AN sample distribution is ~4.5 times lower than that of BN. If one normalizes the SDD of AN to a mean similar to that

Table 1. MD and SDD for $\mathrm{ASTM}_{\mathrm{AN/BN}}$ versus $\mathrm{FTIR}_{\mathrm{AN/BN}}$ Results Obtained for the Same Operational Samples Measured by Both ASTM and FTIR Methods.

Method	No. of Samples	Sample Means	MD	SDD	CV
AN	177	4.9062	0.0118	0.18453	17.55
BN	284	1.0532	–0.0061	0.26239	5.30

MD, mean difference; SDD, standard deviation of the difference; CV, coefficient of variation.

of BN, the AN method is in effect performing in a manner similar to, if not slightly better than, the BN from the standpoint of sensitivity. It is noteworthy to mention that these FTIR methods are primary methods in their own right and have substantially better precision than the ASTM titrimetric methods, which suffer from significant sources of interference and uncertainties but for historic reasons and convention have to be used as a basis for comparison.

Another means of comparing the relative performance of the methods is simply examining the best fit linear regression relationship between the FTIR and ASTM results. These relationships are presented in eqs 7 and 8.

$$\begin{aligned}\mathrm{FTIR}_{\mathrm{AN}} &= 0.039 + 0.9512 * \mathrm{ASTM}_{\mathrm{AN}} \\ \mathrm{SD} &= 0.17\, R^2 = 0.9609.\end{aligned} \tag{7}$$

$$\begin{aligned}\mathrm{FTIR}_{\mathrm{BN}} &= -0.024 + 1.0063 * \mathrm{ASTM}_{\mathrm{BN}} \\ \mathrm{SD} &= 0.26\, R^2 = 0.9844.\end{aligned} \tag{8}$$

These results clearly indicate that the operational data obtained for both methods are linearly related, with BN being almost ideal with a slope of 1.0 and AN within 5% of that value. Neither method has a significant intercept (bias), with the SD consistent with the difference distributions. Thus, statistically, the results obtained for representative commercial samples run in parallel by both the ASTM and FTIR methods are effectively identical and can be considered fully interchangeable.

Performance and Cost Benefits of FTIR

Modern autotitrators can analyze up to 50 samples/8 h shift/instrument versus 480 samples/8 h shift/instrument using the $\mathrm{FTIR}_{\mathrm{AN/BN}}$ methods, which is equivalent to 9 to 10 titrators. Thus, a significant reduction in capital and operating costs can be achieved using the FTIR approach simply by reducing the number of instruments required. This assessment is based on strictly following ASTM protocols. However, as noted, laboratories may choose to take shortcuts and decrease their analysis time using modified versions of the ASTM methods, but these tend to be at the expense of the accuracy that ASTM methods strive for. **Table 2** provides a general comparison of the relevant performance variables important to both the ASTM and FTIR methods from the perspective of a commercial laboratory. As is evident from the table, the FTIR methods have a significant advantage in every category, which ultimately ends up being reflected in a substantial lowering of the cost/sample analyzed, with these instruments being capable of analyzing ~500 samples per 8 h shift.

Table 2. Comparison of Sample Preparation Time, Sample Throughput, Maintenance Time, and Waste Disposal Volumes for the $\mathrm{ASTM}_{\mathrm{AN/BN}}$ Titrimetric Methods versus the $\mathrm{FTIR}_{\mathrm{AN/BN}}$ Procedures.

Acid Number Variable	ASTM $\mathrm{AN}_{\mathrm{D664}}$	$\mathrm{FTIR}_{\mathrm{AN}}$
Sample preparation time[a]	120 s/sample	60 s/sample
Samples/h	4–6/h	60 samples/h
Daily startup and preventative maintenance time[b]	Variable, up to 1 h	<5 min
Waste disposal volume	~130 mL	~25 mL
Base Number Variable	**ASTM $\mathrm{BN}_{\mathrm{D4739}}$**	**$\mathrm{FTIR}_{\mathrm{BN}}$**
Sample preparation time	120 s/sample	60 s/sample
Samples/h	4–6/h	60 samples/h
Daily startup and preventative maintenance time	Variable, up to 1 h	<5 min
Waste disposal volume	~90 mL	~25 mL

[a] Sample preparation time includes vial labeling, dispensing sample, dispensing reagents, and mixing time and does not include reaction time.
[b] Cleaning titrator components (electrodes, stirrer, dispensing tip, autosampler) and verifying performance (buffers, titrant standardization, quality control samples).

$\mathrm{FTIR}_{\mathrm{AN/BN}}$ QC Performance and Procedures. QC samples including high and low reference standards, method blanks (base mineral oil), and duplicates are routinely analyzed at the start and end of each batch of FTIR sample batches to ensure the quality of results. AN and BN calibration standards are reanalyzed at fixed intervals to confirm linearity, and QC data are trended and analyzed to monitor ongoing analytical performance. **Table 3** summarizes the performance data of the high QC samples over a 2-mo period, during which both $\mathrm{FTIR}_{\mathrm{AN}}$ and $\mathrm{FTIR}_{\mathrm{BN}}$ had a mean recovery of close to 100% without any significant bias. These QC samples were analyzed during routine testing with minimal instrument maintenance aside from monthly cell cleaning and tubing replacement. The relative standard deviation (RSD) for both $\mathrm{FTIR}_{\mathrm{AN/BN}}$ QC results was <5% over a 2-mo period, indicating that the method is very robust, does not suffer from any significant interference, and is very precise. The percentage RSD for the QC samples analyzed using the corresponding ASTM methods over the same time period was 8.6% and 4.0% for $\mathrm{ASTM}_{\mathrm{D664}}$ and $\mathrm{ASTM}_{\mathrm{D4739}}$, respectively.

Table 3. Performance Data for Routine High QC Standards Analyzed over a 2-mo Period during the Normal Operation of the $FTIR_{AN/BN}$ Methods.[a]

QC Standard	No. of QC Standards	Standard Target (mg KOH/g)	Mean Recovery (%)	RSD (%)	ASTM Reproducibility Criteria (mg KOH/g)	Samples Exceeding ASTM Reproducibility
$FTIR_{AN}$ QC	96	2.0	102.5	4.390	±0.88	0
$FTIR_{BN}$ QC	139	7.7	100.6	3.599	±3.99	0

QC, quality control; RSD, relative standard deviation.

[a] All of the FTIR QC standards passed the ASTM criteria for reproducibility.

Uncertainty Assessment

Although ASTM does not generally require the calculation of an estimate of the uncertainty of a test result for standards, this is a requirement for ISO 17025.[18] Uncertainty provides a measure of the potential dispersion or variability associated with the result regardless of the method used to obtain the result.[19] The expanded uncertainty for both the $FTIR_{AN/BN}$ and $ASTM_{AN/BN}$ methods was calculated using concurrent experimental data including QC samples, reference materials, and sample duplicates, a summary of which is presented in **Table 4**. As can be seen, the $FTIR_{BN}$ method uncertainty is very similar to that of its ASTM counterpart, whereas in the case of $FTIR_{AN}$, it is significantly better, with the latter attributed to the higher precision of the FTIR method in dealing with samples with a much more limited range. Again, it is clear from these data that FTIR is performing as well or better than the ASTM procedures, and as such, the FTIR data can be used confidently for trend analysis.

Table 4. Comparison of Combined Expanded Uncertainty for Both the ASTM and FTIR Methods.[19]

Method	Combined Expanded Uncertainty (U)[a]
$FTIR_{BN}$	0.241
$ASTM_{D4739}$	0.237
$FTIR_{AN}$	0.152
$ASTM_{D664}$[b]	0.205

[a] Combined expanded uncertainty: $U = u_c{*}k$. See ref. 19.

[b] Buffered endpoint.

Discussion

ASTM D664 and D4739 are expensive to perform because the cost of reagents is high, the methods are time-consuming and prone to interferences, and the maintenance and sample preparation associated with the methods are time-consuming and costly. Because of the long analysis time associated with titrimetric procedures, a large number of instruments is required to test a relatively small number of samples (~1 instrument/40 samples/8 h shift), which leads to increased capital and operational costs. Computers and LIMS infrastructure as well as maintenance and repair costs also increase with the number of instruments. A significant amount of analyst time is required to set up and maintain the instruments, prepare reagents, weigh and load samples, and review the titration plots. Samples with contaminants or different additive chemistry may produce a poor titration graph (mV versus volume of titrant) and may need to be reanalyzed with a different sample mass. In addition, the titration methods use significant volumes of reagents that pose chronic health and safety risks and for which disposal may be difficult or expensive. ASTM D664 and D4739 specify that 125 mL and 75 mL of solvent, respectively, be used versus the ~25 mL of solvent required for the $FTIR_{AN/BN}$ methods. The use of FTIR spectroscopy leads to less chemical waste, lower costs, and less handling and dispensing of chemicals. The potential for lower costs, faster analysis, minimal sample preparation, lower maintenance, and the ability to process large numbers of samples unattended make these FTIR methods attractive. Furthermore, samples can be prepared and the instrument loaded by an analyst with little training or technical education, which may further reduce costs. Currently, as configured, one analyst can measure AN or BN on nearly 480 samples in an 8 h shift, and this capability has prompted FLC to operate a total of four COAT systems across its three laboratories.

As the $FTIR_{AN}$ and $FTIR_{BN}$ methods are not sanctioned official methods (ASTM or otherwise), these analyses are being marketed and presented to clients as a cost-effective, alternative means of obtaining quantitative AN and BN results. FLC presents the argument, borne out in the results presented in this article, that the $FTIR_{AN/BN}$ results effectively match those obtained by official ASTM procedures and can be used for CM and equipment reliability purposes with confidence. It is well understood that quantitative trend monitoring using AN or BN as determined by ASTM methods is a reliable means of monitoring oil deterioration; however, doing so has generally been too expensive for clients to make this a common practice. Using $FTIR_{AN/BN}$ analysis, clients can have rapid analytical turnaround as well as meaningful ongoing and timely trending information about lubricant degradation at a reasonable cost, which is a significant advance in terms of *quantitative* lubricant CM, and its impact could be far reaching for the industry if more widely accepted.

Although any new technology requires some degree of shakeout, the overall experience with the new $\text{FTIR}_{\text{AN/BN}}$ technology has been positive, having been shown to be rapid, robust, reliable, reproducible, and well suited to a high-volume commercial lubricant analysis laboratory. **FLC** concluded from its rigorous assessment of this technology and subsequent performance analysis to make a substantial investment in FTIR instrumentation. This is foreseen to bring significant benefits to FLC analytical operations, provide an expanded market for AN and BN trending, and provide clients with reliable information at a reasonable cost. Based on the information presented in this publication, it is the opinion of FLC that $\text{FTIR}_{\text{AN/BN}}$ merits serious consideration by officiating bodies, such as ASTM, for further interlaboratory assessment for its use as a potential alternative or adjunct to the standard titrimetric methods currently in use.

Abbreviations

AN: acid number
ASTM: American Society for Testing and Materials
BN: base number
CALA: Canadian Association of Laboratory Accreditation
CM: condition monitoring
COAT: Continuous Oil Analysis and Treatment
FLC: Fluid Life Corporation
FTIR: Fourier transform infrared spectroscopy
$\text{FTIR}_{\text{AN/BN}}$: AN or BN determined by FTIR
ISO: International Standards Organization
LIMS: laboratory information and management system
MD: mean difference
MS: mineral spirits
NaP/1-P: sodium phenolate in 1-propanol
PLS: partial least squares
SDD: standard deviation of the differences
TFA/1-P: trifluoroacetic acid in 1-propanol

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References

1. ASTM Standard D2896, 2011, Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration, ASTM international, West Conshohocken, PA, 2003, DOI: 10.1520/D2896-11.
2. ASTM Standard D4739, 2011, Standard Test Method for Base Number Determination by Potentiometric Hydrochloric Acid Titration, ASTM international, West Conshohocken, PA, 2003, DOI:10.1520/D4739-11.
3. ASTM Standard D664, 2011a, Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration, ASTM international, West Conshohocken, PA, 2003, DOI:10.1520/D0664-11A.
4. van de Voort, F. R.; Sedman, J.; Pinchuk, D. Improving JOAP FTIR Condition Monitoring Analytical Throughput By Sample Dilution. Joint Oil Analysis Program International Condition Monitoring Conference, *JOAP-TSC Technology Showcase and Conference Proceedings*; Pensacola, FL; April 18-22, 2004.
5. Garcia-Gonzalez, D. L.; Sedman, J.; van de Voort, F. R. Principles, Performance and Applications of Spectral Reconstitution (SR) in Quantitative Analysis of Oils by Fourier Transform Infrared Spectroscopy. *App. Spectrosc*. **2013**, *67*, 448–456.
6. van de Voort, F. R.; Sedman, J.; Yaylayan, V.; Saint-Laurent, C. The Determination of Acid and Base Number in Lubricants by FTIR Spectroscopy. *Appl. Spectrosc*. **2003**, *57*, 1425–1431.
7. van de Voort, F. R.; Ghetler, A.; Garcia-Gonazales, D. L.; et al. Perspectives on Quantitative Mid-FTIR Spectroscopy in Relation to Edible Oil and Lubricant Analysis: Evolution and Integration of Analytical Methodologies. *Food Anal. Methods* **2008**, *1*, 153–163.
8. van de Voort, F. R.; Sedman, J.; Pinchuk, D. An Overview of Progress and New Developments in FTIR Lubricant Condition Monitoring Methodology. *J. ASTM Int*. **2011**, *8*(5), 2–14.
9. Wold, S.; Sjostrom, M.; Eriksson, L. PLS-Regression: A Basic Tool of Chemometrics. *Chemometr. Intell. Lab. Sys*. **2001**, *58*, 109–130.
10. Wooton, D.; Thomas, D.; Barry, S. Using Infrared Spectroscopy in Used Engine Oils: Estimating Base Number. *Pract. Oil Anal*. **2005**, *11*. http://www.machinerylubrication.com/Magazine/Issue/Practicing%20Oil%20Analysis/11/2005.
11. Fluid Life Corporation. Base Number Directly by PLS [internal company document], 2011.
12. The Fluid Life Corporation, 1996, LabManager [computer software], Internal LIMS System, not available publicly at http://www.fluidlife.com/
13. van de Voort, F. R.; Sedman, J.; Cocciardi, R. A.; et al. FTIR Condition Monitoring of In-Service Lubricants: Ongoing Developments and Future Perspectives. *Tribol. Tans*. **2006**, *49*, 410–418.
14. ISO Guide 34:2009. General Requirements for the Competence of Reference Material Producers.
15. Serneels, S. Reliability of Multivariate Calibration. http://www.chemometry.com/Research/MVC.html.
16. Eshan, S.; Sedman, J.; van de Voort, F. R.; et al. Analysis of Base Content in In-Service Oils by Fourier Transform Infrared Spectroscopy. *J. Lab. Automat*. **2012**, *17*, 201.
17. Li, D.; Sedman, J.; Garcia-Gonzalez, D. L.; et al. Automated Acid Content Determination in Lubricants by FTIR Spectroscopy as an Alternative to Acid Number Determination. *J. ASTM Int*. **2009**, *6*, 1-2 JAI102110.
18. ISO/IEC 17025:2005. General Requirements for the Competence of Testing and Calibration Laboratories.
19. Eurachem /CITAC Guide CG 4. Quantifying Uncertainty in Analytical Measurement, 3rd ed., 2012