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Titrimetric-Equivalent Acid Number (AN) Determination of Lubricants by FTIR Spectroscopy

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Summary
This article previews a generic, manual quantitative Fourier-transform infrared spectroscopy (FTIR) method for determining Acid Number (AN) capable of delivering deterministic ASTM titrimetric-equivalent data for new and in-use lubricants. The method is universally applicable to any lubricant type, differentiates between weak and strong acids, does not involve the use of chemometrics and is capable of analysing ~20 samples/hour using any FTIR spectrometer equipped with a transmission flow cell or open architecture accessory. The generic nature of the AN method could provide a mechanism for standards bodies (ISO/ASTM) to consider it as well as similar approaches used to determine Base Number (BN) and moisture (H_2O) by FTIR spectroscopy.

Introduction
In 2015 LUBE Magazine reviewed a commercial automated FTIR system configured for lubricant condition monitoring (CM) analysis with additional capability to determine AN (or BN), both using pre-diluted samples to achieve higher analytical speeds (1). Recently, a generic, manual AN version has been developed, readily implemented on any standard FTIR without recourse to instrument-specific or proprietary software to obtain ASTM titrimetric equivalent results (2).

Almost every lubricant CM laboratory has either a dedicated autosampler – based or stand-alone FTIR to carry out lubricant CM screening by ASTM D7418, E2412 or its founding methodology, the Joint Oil Analysis Program (JOAP) protocol (3). These trending methods are relied on to screen lubricants to either accept their continued use or follow up with more determinative methods; typically, titrimetric AN (D664) or BN (D2896/D4739) analyses if an oil is deemed questionable. These methods are effectively opposite sides of the same analytical coin, with AN rising over time/use as acids are produced by heat, pressure and oxidation in non-combustion applications commonly used in turbines and compressors, while for combustion engine applications, the added base present expressed as BN, drops as it is consumed by both strong combustion byproduct acids and weaker acids produced by oxidation. Currently, proprietary neat-oil chemometric (4) and diluted-oil stoichiometric FTIR approaches/methods (5) exist to determine AN, however both are problematic in not having universal applicability to provide accurate and reliable deterministic results for any oil type. A generic FTIR-based method has recently been developed that overcomes these limitations; its principles, benefits, limitations and performance are compared here to methods currently in use.

Chemometric AN by FTIR – Neat Oils

Almost all current FTIR AN (and BN) methods are based on the direct analysis of neat-oils using chemometric, Partial Least Squares (PLS) based methods. These require calibrations being available or developed as software add-ons to laboratory CM systems (6) and stand-alone FTIR systems, but are most common for on-site FTIR (7), grating IR (8) and filter Infrared (IR) analysers (9). The latter have built in chemometric calibrations, targeting users with machinery infrastructure requiring local monitoring rather than sending samples to a commercial CM lab for analysis. Such instruments come with generalised Library chemometric calibrations developed by the instrument supplier relating AN/BN titrimetric data to correlating spectral features of in-use oils representative of a particular oil-type, class, or family (8). Many of these systems are cited or listed as following designated ASTM approved protocols (e.g., D7418, D7417, D7889) which provide a veneer of official approval. These protocols, however, relate specifically to operational qualitative attributes rather than quantitative capabilities (e.g., predicting AN or BN) often associated with ASTM approved procedures. As a result, users tend to place undue reliance on the predictive ability of such instrumentation assuming the outputs to be representative of ASTM titrimetric procedures.

Advanced chemometrics can only model so much on a correlation-only basis without having a substantive cause-and-effect spectral signal to work with, lacking in most circumstances aside from being restricted to the oils modeled in the calibration. The veracity of the predictions is heavily reliant on proper selection of the representative oil-type, additive package, and lubricant application to have a reasonable expectation of obtaining rough and ready estimates of AN or BN. Thus, anyone using direct PLS-only approaches and instrumentation must be quite cautious in reporting, relying, and acting on chemometric-based analytical results if they are to be used for critical determinative in-use lubricant assessments.

Stoichiometric AN by FTIR – Diluted Oils

The stoichiometric AN approach, which relies on dilution of a sample containing a basic reagent to react with acids in oils has been limited to specific automated CM systems. Here a spectrally active base in a carrier solvent is added to an oil to elicit a spectral response proportionate to the acidity present in an oil, mimicking ASTM D664. Designed for high throughputs labs, it is also oil-type restricted, involves a chemometric element (1) and is not suited for on-site analysis.

A new manual stoichiometric FTIR AN method has been developed to generically address on-site capabilities as well as overcome the universality limitations associated with oil-specific direct chemometric methods and their associated accuracy and validation issues (2). The manual stoichiometric AN method has some unique benefits, including being independent of oil-type as well as being capable of acid differentiation. It is limited to ~20 samples/h because it uses a split-paired *vs*. the single-sample approach of the automated version, with both relying on a base to react with acids much like ASTM D664, but determines the reaction "endpoint" spectroscopically.

Concept

In the AN stoichiometric methods, a primary calibration is devised by adding oleic acid to a neutral hydrocarbon matrix and treated with NaPhenolate delivered via a solvent carrier. In the new manual method, the oil sample is split into two equal portions, with a reagent-free Solvent-Diluent added to one portion and a Reagent-Diluent containing NaPhenolate, the IR active base, added to the other and spectrally analysed as a pair; hence the term split-paired analysis. These are scanned sequentially, first as a background scan (I_{on}) followed by a sample scan (I_n); producing a differential spectrum -Log (I_n/I_{on}) = ΔAbs_n. This contrasts to the automated method, where a representative sample of the oil-type undergoing analysis (e.g., mineral based turbine oils) is used as a common reference spectrum

and treated with the Solvent-Diluent serving as I_o for all subsequent oils of that type (I_n). Here the differential spectra are ΔAbs_n = -Log (I_n/I_o), with all oils being ratioed against a common reference oil rather than the same oil as per the manual method. Thus, in the manual method, each oil serves as its own reference, ratioing out all the common spectral features of the oil, while in the automated analytical procedure, the less rigorous use of a common representative oil is a necessity to facilitate automation. As a consequence, one requires a secondary PLS-based chemometric calibration to support the primary oleic acid calibration to account for the additional variability associated with the oil-type spectra being analysed (e.g., all mineral-based diesel engine oils). This additional PLS requirement is a substantive undertaking (2) but rewarded by high sample throughputs (>100/h) providing titrimetric quality AN results.

Analytical Benefits

Although the manual method brings compromises in terms of sample handling and analytical speed, one gains three significant benefits; (a) elimination for the need to develop a secondary PLS-based chemometric calibration, (b) independence of oil-type (e.g., universality) and (c) the ability to differentiate between weak and strong acids. These benefits all arise from the splitting the analytical samples ratioing out their common spectral features and leaving the spectral contributions of the acid-base reaction to be measured in the ΔAbs spectrum. Splitting the calibration samples also provides additional oleic acid spectral response information in relation to Carboxylic acid (COOH) concentration (Figure 1) dependence. Thus, one obtains access to both the primary response of NaPhenolate representative of the total acidity (~AN) as well as weak acids (COOH) from the oleic acid response. As such, with a sample undergoing analysis, any weak acid (COOH) measurably present can be quantified along with the total acidity or AN of an oil when mixed acid-types are present; their difference allows one to calculate the strong acid contribution:

$$Acidity_{STRONG} = Acidity_{TOTAL} - Acidity_{COOH} \quad [1]$$

Such acid differentiation could prove useful in assessing the corrosion potential and reactivity of acids present in an oil, particularly if combined with moisture content information, moisture being a catalyst in terms of acid reactivity.

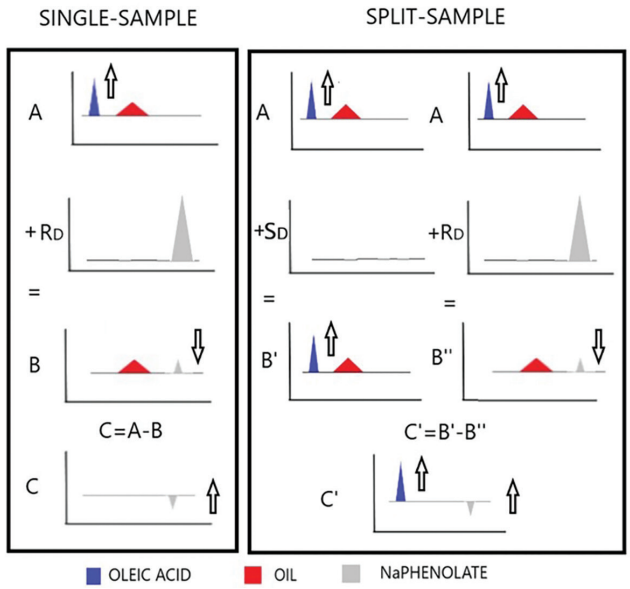

Figure 1: *Automated single-sample vs. the manual split-paired sample procedure modelled in spectral terms. Reagent-Diluent (RD) and/or Solvent-Diluent (SD) is added to calibration standard A to produce spectra B. Spectra C and C' are the final Δ spectra produced by each procedure. Note spectrum C' contains both components, while spectrum C only one. The arrows indicate the direction of absorbance change for each component as acidity rises.*

Generic AN Implementation

Even with clear benefits, the general implementation of the manual stoichiometric AN method is constrained as many FTIR CM systems rely on proprietary instrumentation and software, a common problem in the spectroscopy domain. One way in which this issue has been addressed has been provided by Dr. Friedrich Menges, the developer of SpectraGryph, generic post-spectral processing software that allows the examination, processing and automatic extraction of data from spectra collected on virtually any spectrometer (10). Available as an internet download, SpectraGryph is free for

trial use with site licenses available to commercial and institutional users, a means for eliminating the constraints and incompatibilities to implementing new methods. The software is intuitive and most operations (measuring areas, peak heights, baseline correct, smooth, take derivatives etc.) are available and sequenced as macros from a list of selectable processes. The final output is a simple comma separated (.csv) file which can be passed on to Excel® and when combined with the macro capability within Excel®, one can readily calibrate, predict, and report/print analytical results in lieu of a laboratory information management system (LIMS).

Implementation

SpectraGryph was used to implement AN analysis for an on-site FTIR (Agilent 5500) equipped with a convenient and simple-to-use TumblIR® (Figure 2) open architecture accessory. The instrument was destined for on-site use at a remote mining operation in Papua New Guinea for manual CM analysis as well as carrying out deterministic AN analyses of oils in lieu of titration. Titration was not an option and direct-PLS AN determinations were considered inadequate in terms of accuracy or oil-type flexibility. SpectraGryph was bundled with Excel to make a viable AN Analytical Package linked by a coordinating file structure to obtain on-site quantitative AN results. Paired samples were prepared and scanned by FTIR (Figure 3) with SpectraGryph macros run post-spectrally and the .csv file passed onto Excel to calculate and report the results.

Figure 2: *TumblIR® open architecture accessory ideally suited for oil analysis.*

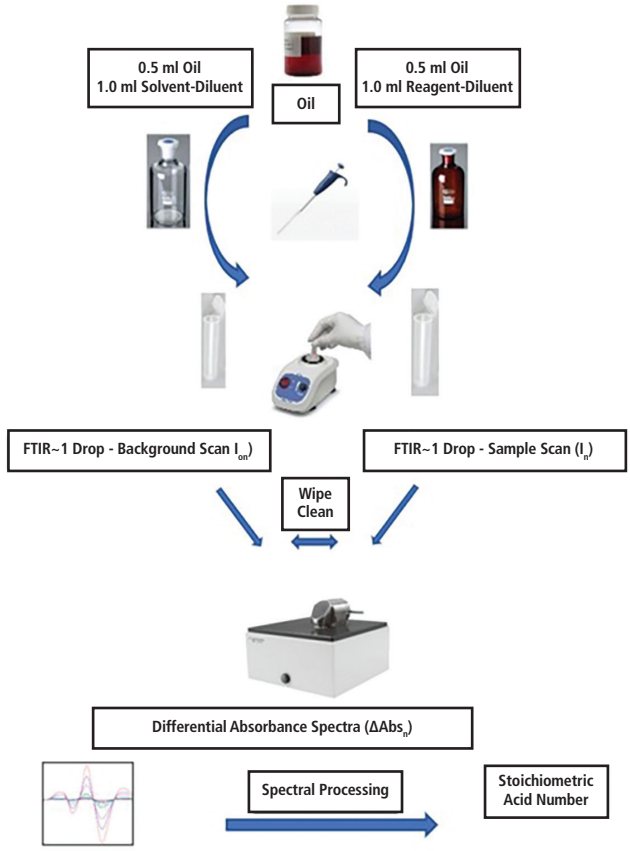

Figure 3: *Basic analytical protocol used for paired-split sample calibration and analysis.*

Calibration

Calibration simply involves the volumetric addition of pure oleic acid to a neutral hydrocarbon matrix (e.g., low viscosity neutral mineral oil or lamp oil), to produce a series of calibration standards covering an effective range of ~0-4 AN. These are split, treated with their respective diluents, scanned and the second derivative of the differential spectra measured for the NaPhenolate and Oleic acid absorptions at 1589 and 1710 cm^{-1}. The absorptions are related by linear regression to the oleic acid concentration expressed as mg Oleic Acid/ml (Figure 4); the calibration precision being < ± 0.10 AN. Samples are analysed in a similar manner, processed via the respective regression equations, and using the known (or assumed) density of the oil, converting the acidity determined into AN_{TOTAL} and AN_{COOH}, the difference being AN_{STRONG}.

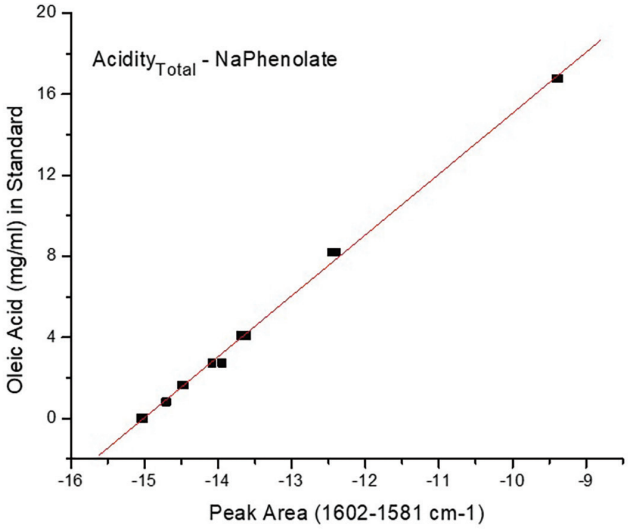

Figure 4: *NaPhenolate absorption response to addition of acidity in the form of Oleic Acid to develop a predictive relationship to determine AN.*

Performance

The manual AN methods' unique capabilities are summarised by the analytical results presented in Figure 5. Here an oxidised mineral oil containing both weak and strong acids was serially diluted with an acid-free ester-based oil with AN analysed for and tracked as a function of dilution. AN$_{TOTAL}$ and AN$_{COOH}$ each track linearly even as the spectral signature of the oil continuously varies as a result of blending the two oils. Any instrument relying on a chemometric calibration would fail this test as it would not be able to account for the spectral variations induced by dilution of one oil type with another that is spectrally different. This artificial process mimics topping-up with the wrong oil or selecting the wrong oil-type on a direct read instrument, occurrences that are not that unusual but can significantly confound analytical predictions. The manual AN method succeeds because each sample serves as its own reference and all oil matrix changes are accounted for and ratioed out, thus correctly tracking the expected changes. The corollary is that any oil-type (e.g., mineral, ester, hydraulic, etc.) can be analysed for AN in any sequence without having to rely on restrictive correlational chemometric models, proper oil selection or mis-predictions due to the analysis of non-representative samples.

Relevance and Conclusion

The standard ASTM titrimetric AN and BN methods are slow, expensive, and environmentally problematic, with no reliable, viable deterministic alternatives available. Current FTIR/IR PLS-based direct read AN methods are of questionable value for critical deterministic purposes, their accuracy being reliant on the manufacturers' claims rather than objective measures or performance validations. The generic stoichiometric AN method developed provides for a robust FTIR-based primary calibration, an objective means of validation, the ability to differentiate between weak and strong acids as well as providing a means for wider implementation via SpectraGryph and Excel®. Even at ~20 samples/h its performance characteristics should be attractive to most CM and on-site FTIR users wishing to obtain deterministic AN data in lieu of titration. Given that a generic approach is available for implementation, this approach may be more readily adopted by standards associations like the ISO and ASTM for interlaboratory assessments and performance evaluations and open the door to related methods (e.g., BN and H_2O) which have been developed along similar lines.

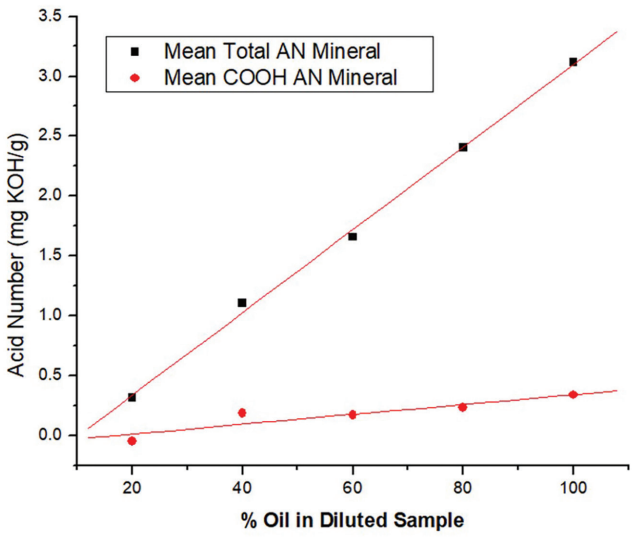

Figure 5: *Serial dilution of mineral oil spiked with oleic acid and p-toluene sulfonic acid diluted with a neutral ester-based oil. AN tracks linearly even as spectral characteristics of the oil change with dilution.*

About the Authors

Dr. Frederik van de Voort is Emeritus Professor at McGill University in Montreal, QC Canada and has published extensively and developed a range of quantitative FTIR analytical methods for lubricants and edible oils, with several patents to his credit.

Michael Viset is a Hydrocarbon Consultant located in Australia and was instrumental in initiating the development and testing of the manual FTIR AN method and its implementation for on-site analysis at the Ok Tedi mine in Papua New Guinea.

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