FTIR Acid and Base Number Analyses: Their Potential to Replace ASTM Methods

F.R. van de Voort
McGill IR Group, McGill University 21,111 Lakehore Road, St. Anne de Bellevue, Quebec, Canada H9X 3V9,
vandevoort@macdonald.mcgill.ca

D. Pinchuk
Thermal-Lube Inc., 255 Avenue Labrosse, Pointe Claire, Quebec, Canada H9R 1A3
dave@thermal-lube.com

M. Davies
Naval Engineering Test Establishment, La Salle Quebec, Canada H6R 1Z2
daviesm@nete.dnd.ca

A. Taghizadeh
Engine System Development Centre, 155 Montreal-Toronto Highway, Lachine, Quebec, Canada H8S 1B4
a.taghizadeh@esdc.com

Abstract: The ASTM Acid Number (AN) and Base Number (BN) analyses provide two of the most fundamental condition monitoring measures associated with lubricant quality, providing status information on oil oxidation and/or reserve alkalinity, respectively. Although a crucial measure, the various ASTM titrimetric methods are expensive and problematic to carry out as well as being difficult to compare and interpret given their differing protocols. Novel *quantitative* Fourier transform infrared (FTIR) based AN and BN spectroscopic methods have been developed utilizing acid/base reactions as per ASTM methods. These FTIR methods use a single step back titration in conjunction with *signal transduction* to allow the wide variety of acids and bases in the oil to be quantitated by a single FTIR protocol. By splitting the sample to be analyzed and treating half with a reactive reagent and the other half with a blank reagent and using *differential spectroscopy*, the need for a reference oil is eliminated. This new FTIR methodology provides for speed of analysis, simplicity, minimal reagent use and disposal and gives data with which the industry is familiar. These new methods have been validated by standard addition as well as compared to ASTM potentiometric and colorimetric methods. In their packaged form the new FTIR AN and BN methods are a significant advance over the traditional ASTM methods without sacrificing scientific rigor, reproducibility or accuracy and they should be considered by the condition monitoring community and ASTM for standardization and generalized testing.

Key Words: Condition monitoring, Acid Number, Base Number, FTIR Spectroscopy, lubricant analysis, automation.

Introduction: Fourier transform infrared (FTIR) spectrometers are considered valuable multifunctional analytical tools for condition monitoring because of their ability to provide a composite molecular fingerprint of an oil. Each organic constituent in the oil has its own fingerprint, and many key constituents and contaminants (antioxidants, water, soot, etc.) give rise to unique spectral features that can be measured and tracked. This is the basis for the FTIR oil analysis protocols established by the Joint Oil Analysis Program (JOAP), which allow the tracking of a wide range of parameters indicative of oil condition and contamination, ranging from soot to nitration. The objective of condition monitoring is to replace a lubricant only when its functionality is compromised, a practice that is cost-effective for fleets, the military and critical systems. Although the FTIR oil analysis protocols that have been developed provide valuable information for condition monitoring purposes, the results are expressed in *qualitative* and rather arbitrary terms related to absorbance values of the constituents. The ability to express these results in more quantitative terms is compromised by the impracticality of having to rely on the availability of a reference oil relative to which changes can be compared.

ASTM AN/BN : Acid Number (AN) and Base Number (BN) represent two of the most fundamental quantitative measures common to the assessment of lubricant quality for both new and used oils. In simple terms, AN represents acidic constituents in an oil (additives or acids formed by oxidation/fuel combustion) and BN represents basic constituents usually added to neutralize acids accumulating in an oil. These two measurements are commonly used to characterize new and used oils in terms of formulation, oxidative status or reserve alkalinity. The ASTM methods for AN and BN determination are tedious and problematic titrimetric methods, which can be subdivided into colorimetric and potentiometric methods. The colorimetric method is simple but is limited to colorless oils, which prevents most formulated and used oils from being analyzed. The potentiometric methods, of which there are several, are more versatile overall, as they can handle most oils and can be automated using an autotitrator. The various ASTM potentiometric methods differ in their procedural details, and the results can be quite different. One of the main problems with all AN and BN analyses is the variety of endpoints, their interpretation and terminology (i.e., acid number, base number, total acid number, total base number, strong acid number, strong base number, and neutralization number) all expressed as mg KOH/g oil. Figure 1 illustrates this problem by providing some examples of “titration” curves and the AN and BN values one would obtain depending on the method.

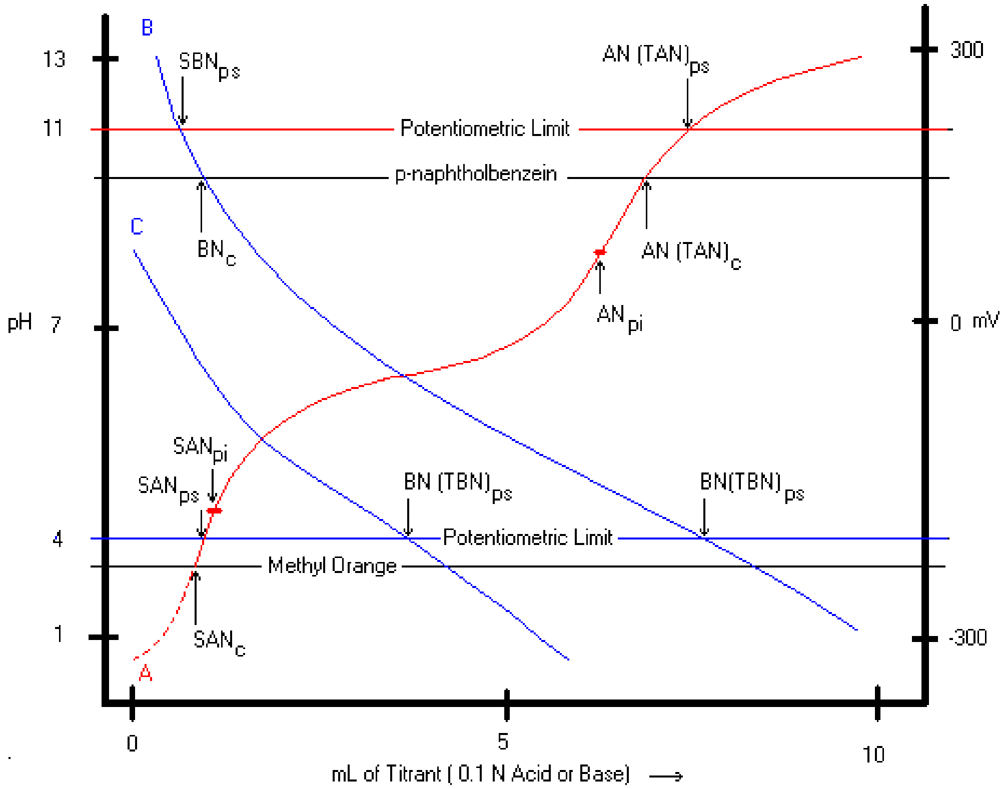

Figure 1. Idealized titration curves for the titration of oils with acid (curve A) or base (curves B and C) in accordance with the respective ASTM methods indicating their endpoints and associated terminology, with the subscript "c" referring to a colorimetric endpoint and subscripts "ps" and "pi" representing standardized and inflection-based potentiometric endpoints, respectively.

It is understandable that there is substantial confusion in the industry as to what reported AN or BN values mean, and practitioners have now recommended that the terminology be restricted to simply AN and BN. However, the answers obtained from the various methods will still differ. Moreover, industrial laboratories often deviate from strict ASTM protocols to facilitate more rapid analyses or make the methods more convenient in terms of solvent or electrode use, and this further confounds the situation. Despite these problems, the ASTM methods are the only fundamentally sound methods available for the determination of AN and BN. Based on our own extensive analysis, the limitations of the ASTM methods boil down to a combination of procedure (titration) and mode of detection (potentiometric/colorimetric), but no better alternatives have been developed.

AN/BN by FTIR?: It has taken several years of research to develop quantitative FTIR-based AN and BN methods, but practical and readily implemented methods are now available. The methods took some time to evolve because there were some substantive hurdles that had to be overcome. The two key problems that had to be addressed were:

(a) (a) How and what to measure
(b) (b) How to eliminate spectral interferences, taking into account the inherent variability/complexity of the oil matrix (reference oil issue)

A solution was devised by maintaining the fundamental tenets of the ASTM methods and combining the concept of *signal transduction* with *differential spectroscopy*. The concept of signal transduction is illustrated in Figure 2 in relation to the determination of the AN of an oil containing various undefined acidic components. In step 1, a fixed amount of strong base is added to convert the acids into their salts, the amount of base consumed being proportionate to the AN of the oil.

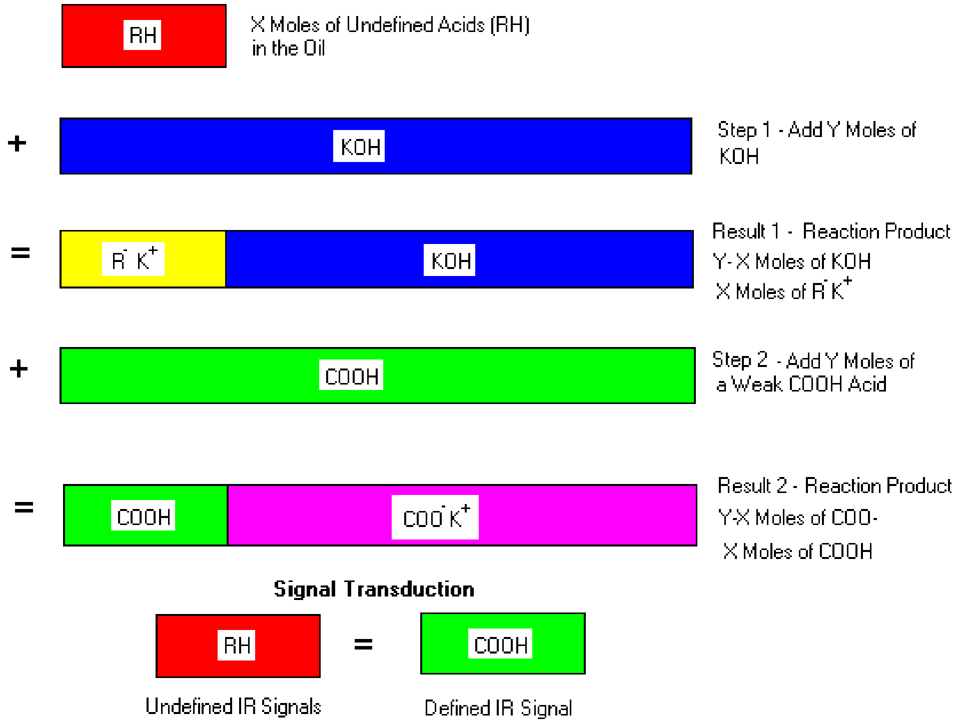

Figure 2. Schematic diagram illustrating the concept of signal transduction in relation to the determination of AN by FTIR spectroscopy. The process for BN analysis uses a strong acid and a weak base to achieve the same result.

In step 2, a fixed amount of a weak carboxylic acid is added to react with the residual base to produce a proportionate amount of the carboxylate salt, with the amount of unreacted carboxylic acid being proportionate to the initial AN of the sample. Because both steps 1 and 2 involve a very strong base, the reactions go rapidly to completion. The carboxylic acids and salts present at the end of this sequence of reactions absorb strongly in the mid-IR portion of the spectrum over the 1800-1500 cm^{-1} range. Accordingly, this process yields distinct, accurately measurable IR signals that can be used to determine AN, eliminating the need for stepwise titration. However, since the composition (and hence the spectral features) of oils is unpredictable and variable, there is every chance that absorption bands due to the oil and its constituents will interfere with the COOH/COO^- signals generated. Thus, these so-called “matrix” effects have to be taken care of, which can be achieved through the use of differential spectroscopy. This is done by splitting the oil sample after step 1 and adding a solution of the weak carboxylic acid reagent to one half while the other half has a “blank reagent” (i.e., pure solvent) added to it, after which the spectrum of each half is recorded. The spectrum of the blank is then subtracted from that of the acid-treated sample to produce a differential spectrum – in this process, the common spectral contributions of the oil are subtracted out, leaving only the spectrum of the reaction products (COOH/COO^-). The complete procedure from preparing the sample to obtaining the differential spectrum is illustrated in Figure 3.

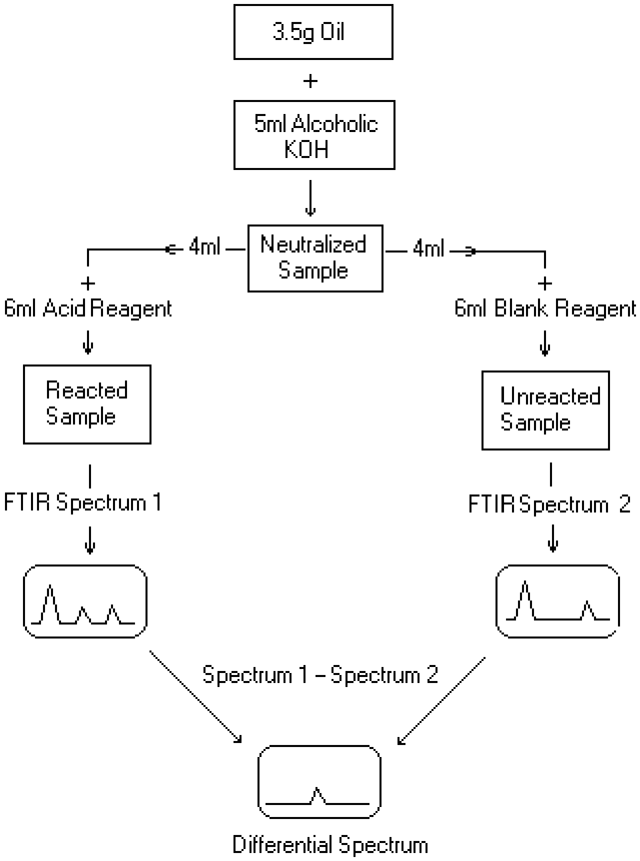

Figure 3. Analytical protocol for the determination of AN by FTIR spectroscopy. The BN protocol is identical except for the reagents.

Figure 4 illustrates the transduced COOH and COO^- IR signals one obtains when polyalphaolefin (PAO) is spiked with known amounts of a non-carboxylic acid (p-toluenesulfonic acid) and taken through the AN FTIR analytical protocol. These spectra are free of matrix absorptions, and plots of either the COOH or COO^- peak heights vs. AN are linear and can be used as calibration plots. The slopes of these plots are independent of the acid type or acid mixture present in the oil. Thus, PAO spiked with a pure acid is used to calibrate the FTIR spectrometer, and the linear regression equations obtained are programmed so that the instrument outputs AN values directly.

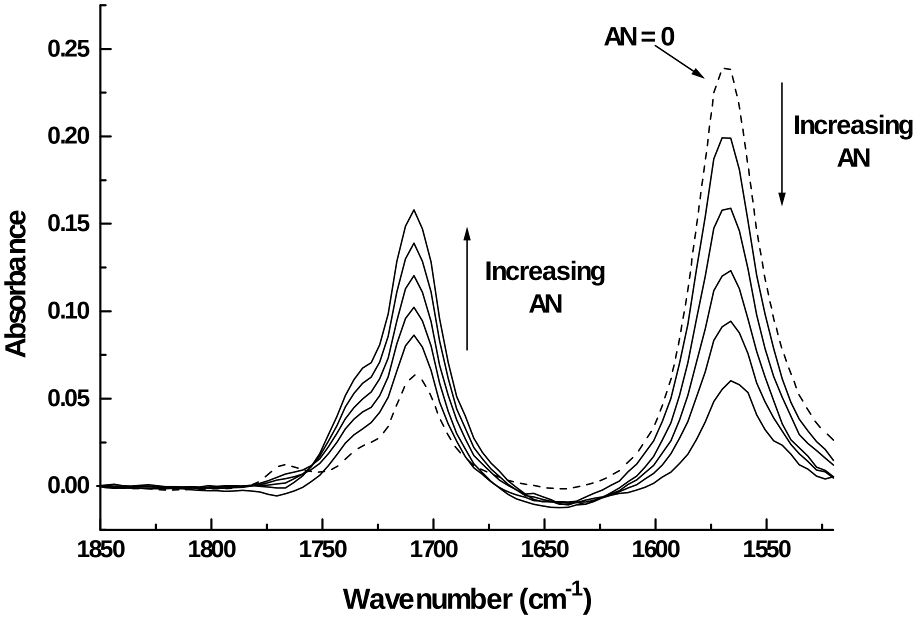

Figure 4. Differential spectra generated for a series of standards prepared by spiking PAO with p-toluenesulfonic acid and analyzed according to the protocol illustrated in Figure 3.

Utility and Performance: The FTIR procedure is simple and robust. Of particular importance is that it is based on the same analytical principles as the ASTM methods, giving the methodology a degree of credibility most alternative AN/BN methods lack. From Figure 3 it is apparent that the sample size as well as reagent volumes are minimal, reducing solvent costs and minimizing disposal problems. If the oils do not contain esters, the samples remain stable indefinitely after preparation. Such samples can be batched for FTIR analysis using an integrated autosampler, making the method well suited to high-volume commercial and industrial laboratories. Table 1 summarizes the basic analytical performance specifications of the AN and BN methods.

Table 1. Performance specifications for the FTIR AN/BN methods.

ACID NUMBER	**SPECIFICATIONS**
Range	1-6 mg KOH/g
Reproducibility	+/- 0.10 mg KOH/g
Analytical Time	5 min
BASE NUMBER	**SPECIFICATIONS**
Range	1-201-20mg KOH/g
Reproducibility	+/- 0.10 mg KOH/g
Analytical Time	5 min

The FTIR AN/BN methods have been evaluated using standard addition of defined amounts of acid and/or base to a wide variety of new and used oils. The FTIR method has responded well in a bi-directional manner and is thus able to measure both AN and BN when acids and bases coexist in oils. Figure 5 illustrates typical BN results for three new oils and one used oil spiked with dodecylamine. Overall, although the numerical FTIR AN/BN values are not directly comparable to those of the ASTM methods (for reasons illustrated in Figure 1), the potentiometric method also tracked standard addition changes in a 1:1 manner much like the FTIR method, within the errors of measurement.

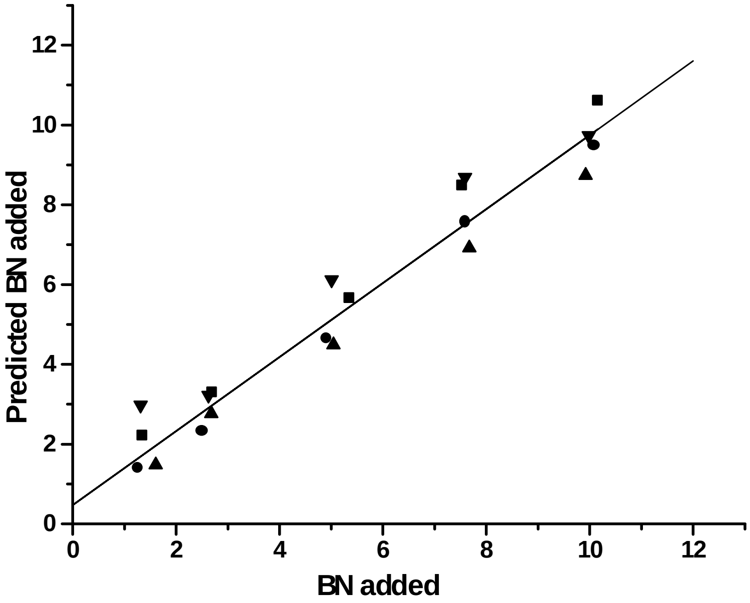

Figure 5. Response of FTIR BN method to standard addition of dodecylamine to three new motor oils and one used oil.

COAT® AN/BN Analysis System: The AN and BN methods described above have been implemented on a Thermal-Lube Continuous Oil Analysis and Treatment (COAT) system, which uses a ruggedized Bomem spectrometer operated under Thermal-Lube's Umpire® software. The instrument is equipped with a 200 um CaF_2 transmission flow cell which is loaded manually under vacuum; an automated version of the system has an integrated autosampler. The same instrument configuration can be employed to measure the parameters included in the JOAP FTIR oil analysis protocols (except for fuel contamination, which requires measurements at wave numbers below the transmission cut-off of the CaF_2 window material). The AN and BN methods use identical analytical protocols, and the Umpire® operating software provides onscreen instructions for performing the methods. The simple user interface, with operator and manager access levels, allows analyses to be performed by untrained personnel, and AN and BN results are presented onscreen and automatically archived.

Conclusion: The COAT® FTIR AN/BN Analysis system represents the first tangible advance for AN or BN methods since the first potentiometric method was introduced. This new methodology has been tested extensively in the development laboratory; however, its capabilities and limitations will be defined only when it is in the hands of daily practitioners. This will depend to a large degree on the interest the condition monitoring community shows in trying this new technology**. Given that the methodology is based on well-understood chemical principles and has some distinct advantages over present standard methods, it may behove the condition monitoring community and the ASTM to examine quantitative FTIR analysis as an alternative procedure for the determination of AN and BN.

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**Contact D. Pinchuk, President, Thermal-Lube Inc. dave@thermal-lube.com