# Determination of Acid Number and Base Number in Lubricants by Fourier Transform Infrared Spectroscopy

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This paper describes the development of practical Fourier transform infrared (FT-IR) methods for the determination of acid number (AN) and base number (BN) in lubricants through the combined use of signal transduction via stoichiometric reactions and differential spectroscopy to circumvent matrix effects. Trifluoroacetic acid and potassium phthalimide were used as stoichiometric reactants to provide infrared (IR) signals proportional to the basic and acidic constituents present in oils. Samples were initially diluted with 1-propanol, then split, with one half treated with the stoichiometric reactant and the other half with a blank reagent, their spectra collected, and a differential spectrum obtained to ratio out the invariant spectral contributions from the sample. Quantitation for AN and BN was based on measurement of the peak height of the $\nu(C{=}O)$ or $\nu(COO^-)$ absorptions, respectively, of the products of the corresponding stoichiometric reactions, yielding a standard error of calibration of <0.1 mg KOH/g oil. The AN/BN FT-IR methods were validated by the analysis of a wide range of new and used oils supplied by third parties, which had been analyzed by ASTM methods. Good correlations were obtained between the chemical and FT-IR methods, indicating that the measures are on the whole comparable. From a practical perspective, these new FT-IR methods have significant advantages over ASTM titrimetric methods in terms of environmental considerations, sample size, and speed of analysis, as well as the variety of oil types that can be handled. FT-IR analysis combining stoichiometric signal transduction with differential spectroscopy may be of wider utility as an alternative to titration in the determination of acid or basic constituents in complex nonaqueous systems.

Index Headings: Fourier transform infrared; FT-IR; Oil analysis; Acid/base reactions; Signal transduction.

## INTRODUCTION

Acid number (AN) and base number (BN) are fundamental measures of lubricant quality that are routinely used both to characterize new oils and to monitor relative changes in acidity or reserve alkalinity over time. Most lubricants contain performance additives, many of which tend to have acidic or basic characteristics, with one of these characteristics usually predominating in new oil formulations. In the case of gasoline and diesel motor oils, basic characteristics tend to predominate, largely due to the presence of detergents and dispersants incorporated to assist in reducing carbon and sludge deposits and to neutralize corrosive acids formed as by-products of combustion and oil oxidation. Most industrial oils such as insulating (transformer), turbine, hydraulic, and other specialty oils exhibit acidic or neutral characteristics. Hence, lubricating oil formulations commonly have an AN or BN specification, and changes in these values may be monitored during the lubricant's service life and re-lated to lubricant functionality and mechanical wear for a particular machine or component. As such, AN and BN determinations are a cornerstone of any condition monitoring program. The American Society for Testing and Materials (ASTM) has standardized colorimetric and potentiometric methods for AN and BN determinations, all titers being expressed as mg KOH/g oil. In practice, potentiometric methods are the most widely employed as they are not susceptible to interference by soot or colored additives in the oils. However, even with the use of an autotitrator, potentiometric methods are problematic, and the availability of an alternative, simple instrumental method that minimizes solvent use would be a distinct improvement.

Infrared spectroscopy has long had a place in lubricant analysis, being used to characterize various constituents in oils, and, in recent years, the use of Fourier transform infrared (FT-IR) analyzers to track changes in lubricating oils over time as part of condition monitoring programs has become commonplace. However, a fundamental difficulty precluding the direct determination of oil quality parameters such as AN and BN from the FT-IR spectra of lubricants is the ''structural specificity'' of infrared analysis as opposed to the ''chemical specificity'' of the titrimetric methods traditionally used to measure these parameters. In other words, whereas the response of a titrimetric method is not affected by the nature of the acid or base, beyond its dependence on the $pK_a$ value of the analyte in relation to the titrimetric endpoint employed, the prediction of AN or BN by FT-IR spectroscopy would require the development of calibrations that model all the molecular species, many of them undefined, contributing to the acidic/basic characteristics of lubricating oils. This difficulty is compounded by matrix effects due to the wide variety of additives used in oil formulations as well as the complex chemical changes taking place during a lubricant's service life. These matrix effects can be so unpredictable that modeling them by chemometric techniques such as partial least-squares regression (PLS) is difficult, and thus FT-IR lubricant analysis is usually limited to trending, as opposed to accurate quantitation, except for well-defined systems. Differential spectroscopy has been used successfully to minimize matrix effects by measuring changes relative to a reference oil;[1] however, the drawbacks of this approach include the impracticality of keeping a reference oil on hand for each brand/formulation and the possibility of oil formulation mismatches, either through use of the incorrect reference oil or as a result of batch-to-batch formulation variability.

The McGill IR Group has worked extensively on the development of quantitative FT-IR methods for the anal-

ysis of edible fats and oils[2,3] and foresees substantial analytical and environmental benefits if this methodology could be applied in the lubricant sector. One of the concepts developed in our work is the use of reagents that react stoichiometrically and specifically with the analyte of interest to form a product that can be more readily quantitated by FT-IR spectroscopy, a process that may be termed *signal transduction*. For example, although hydroperoxides, which are the primary products in lipid autoxidation, can, in principle, be quantified by measurement of their O–H stretching absorption band at 3444 $cm^{-1}$, this measurement is subject to spectral interferences from a wide variety of other OH-containing species that may be present in fats and oils, such as alcohols, mono- and diglycerides, free fatty acids, and water, making it difficult to develop a robust PLS calibration model.[4] Thus, we employed signal transduction by taking advantage of the stoichiometric reaction of hydroperoxide groups with triphenylphosphine to form triphenylphosphine oxide, which has an intense and easily measured infrared (IR) absorption band at 542 $cm^{-1}$ that allowed for its accurate quantitation.[5] In the present work, the concept of signal transduction via stoichiometric reactions was applied to the determination of acid number (AN) and base number (BN) of lubricants. The analytical approach developed has made it possible for the first time to determine these key oil quality parameters by FT-IR spectroscopy as well as to address the problem of matrix effects through differential spectroscopy without the necessity to keep a reference oil on hand. This paper outlines the principles of this approach, describes its practical implementation, and compares the AN and BN results obtained for a wide variety of new and used lubricating oils to those obtained by ASTM titrimetric procedures.

## EXPERIMENTAL

**Reagents and Samples.** All reagents used for methodology development were obtained from Aldrich (Milwaukee, WI), including 4-nitrophenol (4-NP, 99%), dodecylamine (DDA, 99+%), trifluoroacetic acid (TFA), potassium phthalimide (KPhthal), and 1-propanol (1-PrOH). Additive-free polyalphaolefin (PAO) base oil as well as samples of a wide variety of new brand-name engine lubricants were supplied by Thermal Lube Inc. (Pointe-Claire, PQ, Canada). A wide range of pre-analyzed new and used oils were supplied by Hewitt Equipment Ltd. (Pointe-Claire, PQ, Canada), Quality Engineering Test Establishment of the Department of National Defense (Ottawa, ON, Canada), the Naval Engineering Test Establishment (Lachine, PQ, Canada), and the Engine System Development Center (ESDC, Lachine, PQ, Canada). These included marine engine oils (naval vessels), locomotive oils, truck and bus oils, jet engine oils, compressor oils, and agricultural machinery oils. Most were mineral-based oils, but some ester-based synthetic oils and mineral/ester blends were also included in this sample set. All these oils had been analyzed in the respective laboratories supplying them by ASTM potentiometric methods,[6] BN data being obtained primarily by perchloric acid titration (ASTM D2896-92), with some data available from the HCl titration method (ASTM

D4739-92), and AN data being obtained by KOH titration (ASTM D664-89).

**Fourier Transform Infrared Spectroscopy.** *Instrumentation.* The instrument used for this study was a Bomem WorkIR spectrometer (Bomem, Quebec, PQ, Canada) equipped with a DTGS detector and purged with dry air from a Balston dryer (Balston, Lexington, MA). Samples were aspirated into a 230-$\mu$m $CaF_2$ transmission flow cell mounted on a sample shuttle (Dwight Analytical, Toronto, ON, Canada). The spectrometer was controlled by an IBM-compatible Pentium 150-MHz PC running under proprietary Windows-based UMPIRE® (Universal Method Platform for InfraRed Evaluation) software (Thermal-Lube, Pointe-Claire, PQ, Canada). All spectra were collected by coadding 4 scans at a resolution of 8 $cm^{-1}$ and a gain of 1.0.

*Preparation of Standards.* Six AN and six BN standards were prepared by gravimetric addition of 4-NP and DDA, respectively, to PAO to produce standards covering an AN range of 0–5 mg KOH/g and a BN range of 0–20 mg KOH/g.

*Analytical Protocol.* *Sample Preparation.* A 4.50-g sample of the oil was mixed with 6 mL of 1-PrOH, and 4-mL aliquots of the diluted oil were placed in two centrifuge tubes, labeled BR (blank reagent) and RR (reactive reagent). Six milliliters of 1-PrOH, serving as the "blank reagent" for both AN and BN analysis, was added to the BR tube, and 6 mL of a solution of KPhthal in 1-PrOH (20 g/L; AN reactive reagent) or TFA in 1-PrOH (50 mL/L; BN reactive reagent) was added to the RR tube. It should be noted that KPhthal has limited solubility in 1-PrOH and was dispensed via bottle re-pipette as a fine dispersion that was maintained by continuous and vigorous agitation. After addition of the blank and reactive reagents, the samples were centrifuged in a clinical centrifuge for 5 min to remove any turbidity.

*Spectral Analysis.* The transmission flow cell was loaded with ~2 mL of the BR-treated sample and its single-beam spectrum was recorded. After flushing the cell with isopropanol, ~2 mL of the RR-treated sample was loaded into the cell and its single-beam spectrum was recorded and ratioed against the spectrum of its BR-treated counterpart. For quantitation of BN, the peak height at 1679 $cm^{-1}$ was measured relative to a single baseline point at 2150 $cm^{-1}$. For quantitation of AN, the peak height at 1727 or 1774 $cm^{-1}$ was measured relative to a single baseline point at 1850 $cm^{-1}$.

## RESULTS

**Analytical Approach.** In the approach employed in the present work, the lack of "chemical specificity" that precludes the direct determination of AN and BN by FT-IR spectroscopy is overcome by signal transduction via the stoichiometric reaction of the various acids or bases present in the sample with a specific reagent to yield a single product that can be readily quantitated by FT-IR spectroscopy. This signal transduction approach is depicted schematically in Fig. 1, which illustrates the determination of AN by the addition of KPhthal to an oil containing undefined acidic constituents (AH).

In the implementation of this approach, the selection of the signal-transducing reagents was primarily based on
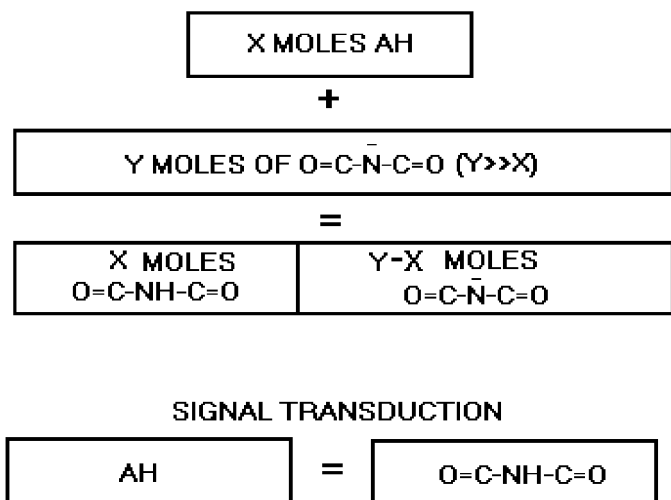
FIG. 1. Schematic diagram illustrating the concept of signal transduction in relation to the determination of AN by FT-IR spectroscopy using potassium phthalimide (represented as O=C–N̄–C=O for simplicity) as the signal-transducing reagent.



FIG. 2. Analytical protocol for the determination of AN by FT-IR spectroscopy.

two criteria that must be met in order for signal transduction to operate effectively: (1) the reagents should react quantitatively with not only the strong but also the weak acids or bases present in lubricating oils, and (2) the acid/base reaction must produce a readily measurable spectral change. The second criterion suggested the potential suitability of organic carbonyl-containing acids and bases, which exhibit strong $\nu(C=O)$ and $\nu(COO^-)$ absorption bands in a region of the spectrum (1800–1550 cm$^{-1}$) where most hydrocarbon-based lubricants do not absorb strongly, whereas the first required that the acid and base selected be as strong as possible. On this basis, the potassium salt of the weak acid phthalimide (pK$_a$ = 9.9) and the strong acid TFA (pK$_a$ = 0.50) were ultimately chosen for use as signal-transducing reagents in the AN and BN methods, respectively, with 1-PrOH found to be suitable as a carrier of the reagents and for dilution of oil samples.

Signal transduction, while providing an avenue to quantitation of AN and BN, does not entirely address the problem of matrix effects, as oil compositional variability commonly results in undefined spectral interferences that could affect the measurement of the $\nu(C=O)$ and $\nu(COO^-)$ signals. In particular, mineral oils often contain synthetic esters as a significant component of their formulation, and many synthetic oils are ester based (e.g., jet engine lubricants). These oils thus exhibit $\nu(C=O)$ absorptions in the region between 1750 and 1700 cm$^{-1}$, which may interfere with AN and BN measurements. It was envisioned that differential spectroscopy could be used to minimize such matrix effects. This would involve an additional step of splitting the oil sample into two equal parts and treating one aliquot with a solution containing the reactive reagent (KPhthal or TFA) and the other aliquot with a blank reagent solution and then collecting their respective spectra. By taking the differential spectrum of these two spectra, the invariant spectral contributions of the oil sample would be eliminated, leaving only the spectral information related to the signal transduction reaction, assuming that the treatment of the sam-
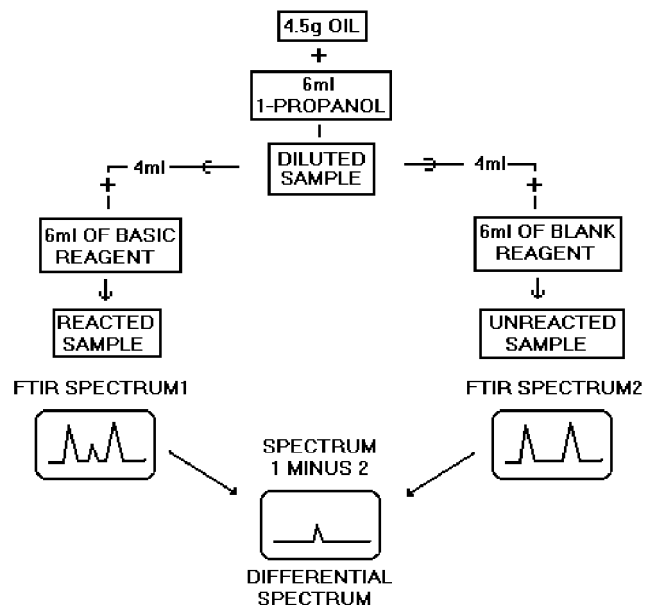
ple with the reactive reagent does not significantly perturb the absorption bands of the oil. In this manner, the spectral features associated with the oil matrix are eliminated without the need for a reference oil, since the sample effectively serves as its own reference. Hence, a combination of signal transduction and differential spectroscopy could provide a potential avenue for quantifying the amount of acids or bases in an oil. Work was thus undertaken to implement this approach in a practical fashion and to assess its analytical performance.

**Acid Number and Base Number Protocols.** The analytical protocol developed for the FT-IR AN method is illustrated in Fig. 2; the BN procedure parallels the AN protocol except for the use of a different reactive reagent. The oil is diluted in the first step, and the diluted sample is subsequently split, with one aliquot being reacted with the appropriate reactive reagent (RR; KPhthal or TFA in 1-PrOH), while the other aliquot is diluted with the blank reagent (BR; 1-PrOH). The spectrum of the RR-treated sample is then ratioed against that of the BR-treated sample to produce a differential spectrum. Figure 3 illustrates typical differential spectra obtained for a series of PAO samples spiked with 4-NP and analyzed according to the protocol illustrated in Fig. 2. The acid–base reaction between 4-NP and the signal-transducing reagent, KPhthal, produces the two $\nu(C=O)$ bands of phthalimide (1727 and 1774 cm$^{-1}$, designated $\nu(C=O)_1$ and $\nu(C=O)_2$, respectively), which rise proportionately as the AN increases, a corresponding loss of 4-NP and formation of its anion being seen in the 1600–1550 cm$^{-1}$ region. Figure 4 presents a typical standard curve derived from the differential spectra shown in Fig. 3 for the $\nu(C=O)_1$ band referenced to a single baseline point at 1850 cm$^{-1}$. The linear regression equations obtained for the $\nu(C=O)_1$ and $\nu(C=O)_2$ bands were:
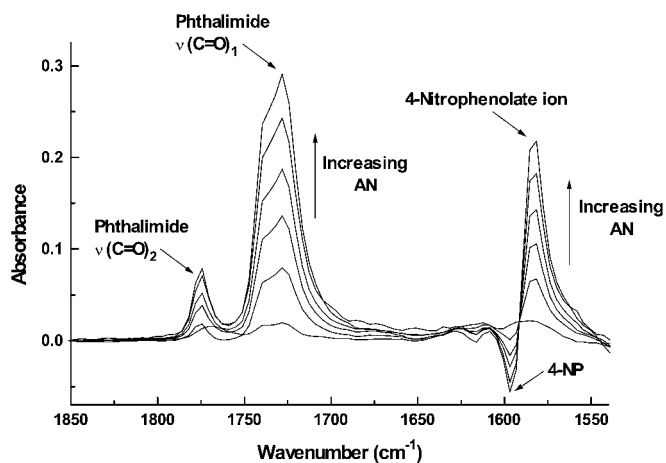
FIG. 3. Differential spectra obtained for PAO spiked with 4-NP (AN = 0–5 mg KOH/g oil) and analyzed by the protocol outlined in Fig. 2, using KPhthal as the signal-transducing reagent, illustrating the increase in the phthalimide $\nu(C=O)_1$ (1727 cm$^{-1}$) and $\nu(C=O)_2$ (1774 cm$^{-1}$) bands with increasing AN.
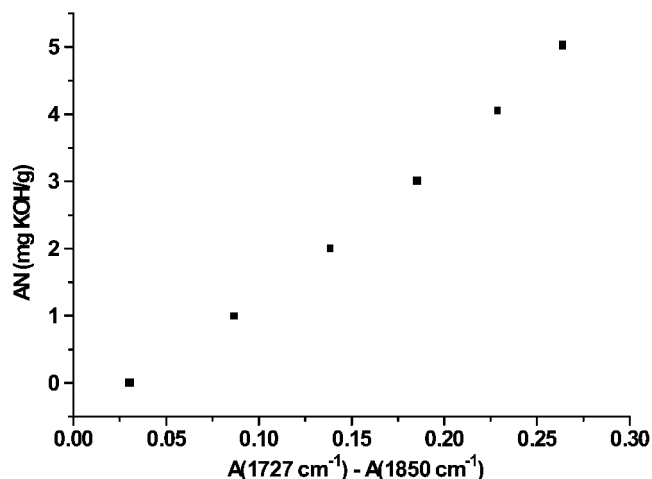


FIG. 4. AN calibration curve obtained using PAO samples spiked with varying amounts of 4-nitrophenol as calibration standards and KPhthal as the signal-transducing reagent. The calculated AN of the standards is plotted vs. the height of the $\nu(C=O)_1$ band of phthalimide (1727 cm$^{-1}$) referenced to a single baseline point at 1850 cm$^{-1}$.

$$AN = -0.8186 + 21.34Abs_{(1727/1850\ cm^{-1})}$$

$$R = 0.997 \qquad SD = 0.17 \tag{1}$$

$$AN = -1.2488 + 81.61Abs_{(1774/1850\ cm^{-1})}$$

$$R = 0.996 \qquad SD = 0.23 \tag{2}$$

Figure 5 illustrates the differential spectra obtained for BN standards prepared by spiking PAO with DDA and using TFA as the signal-transducing reagent. In this case, the COOH band of TFA (which is off scale) drops while the COO$^-$ band rises as BN increases. The calibration equation based on measurement of the COO$^-$ absorbance (measured at 1679 cm$^{-1}$) referenced to a single-point baseline at 2150 cm$^{-1}$ was:

$$BN = -2.76 + 20.60Abs_{(1679/2150\ cm^{-1})}$$

$$R = 0.996 \qquad SD = 0.33 \tag{3}$$

Although the above calibration equations were developed for mineral oils, their applicability to the analysis of synthetic ester-based oils was verified. For AN determinations, the $\nu(C=O)_1$ band (1727 cm$^{-1}$) was obscured by off-scale ester absorptions, but AN analysis was still possible, albeit with somewhat less sensitivity, with the use of the weaker $\nu(C=O)_2$ band (1774 cm$^{-1}$) (Fig. 6a). The trifluoroacetate $\nu(COO^-)$ band used in the determination of BN was unaffected by the ester absorption band (Fig. 6b), owing to its lower frequency (1679 cm$^{-1}$).

**Validation of the Fourier Transform Infrared Acid Number and Base Number Methods.** *Theoretical Considerations.* The extent to which the AN or BN values obtained by the FT-IR and the standard ASTM methods can be expected to agree depends on the relative responses of these methods to acids and bases of different strength. To illustrate the relative responses expected on a theoretical basis, Fig. 7 presents idealized acid/base titration curves for the ASTM potentiometric KOH (D664) and HCl (D4739) titration methods, with their respective pH endpoints demarcated together with the pK$_a$ values of the signal-transducing reagents employed in the FT-IR

AN and BN methods, as well as those of the acid and base used to prepare FT-IR calibration standards.

For the ASTM methods, the fractions of acid (AH) and base (B:) titrated at the respective titrimetric endpoints are given by the Henderson–Hasselbalch equation:

$$\log([A^-]/[AH]) = 11.0 - pK_a(AH) \tag{4}$$

$$\log([BH^+]/[B:]) = pK_a(BH^+) - 4.0 \tag{5}$$

In the case of the FT-IR methods, the BN and AN "endpoints" are related to the pK$_a$ values of the signal-transducing reagents. Thus, when TFA (represented below as RCOOH) is added in excess to react with the basic constituents in an oil, the following equilibria are established:

$$B: + RCOOH \rightleftharpoons BH^+ + RCOO^- \tag{6}$$
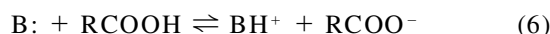
Assuming that the sample initially contains a single weakly basic species, the equilibrium constant for the above reaction is given by:
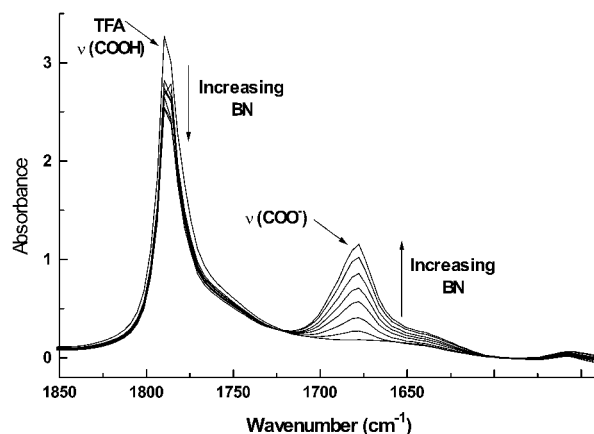


FIG. 5. Differential spectra generated for a series of samples prepared by spiking PAO with DDA (BN = 0–20 mg KOH/g oil), illustrating the relative changes produced in the COOH (1788 cm$^{-1}$) and COO$^-$ (1679 cm$^{-1}$) absorptions of the signal-transducing reagent TFA and its anion.
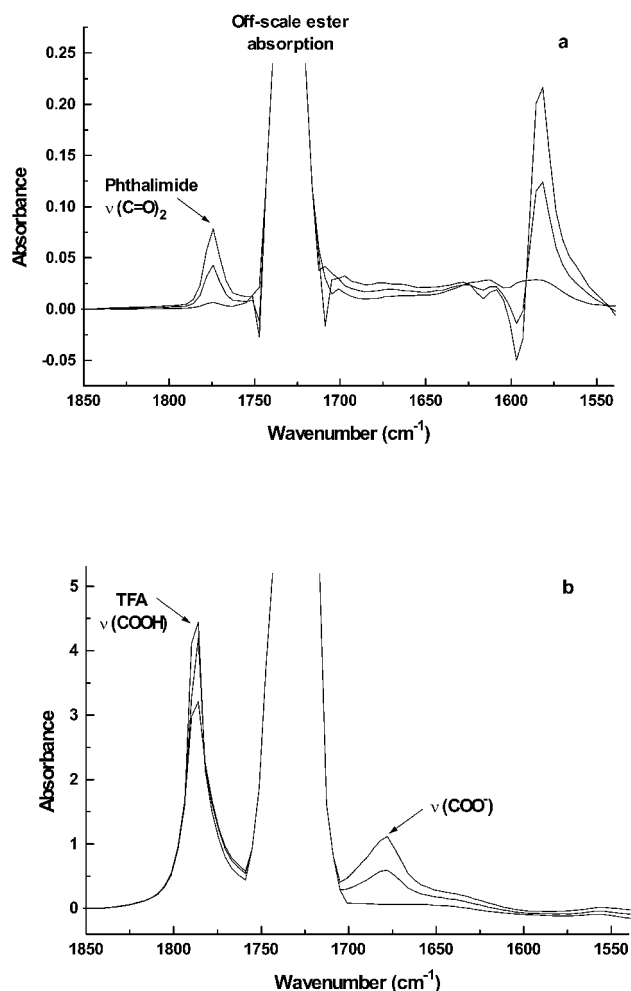
FIG. 6. Overlaid spectra of ester-based oils spiked with (**a**) acid (4-NP) and (**b**) base (DDA) and analyzed by the AN and BN protocols, illustrating that AN and BN are measurable in the presence of off-scale ester absorptions (1750–1700 cm$^{-1}$). Owing to the masking of the phthalimide $\nu(C=O)_1$ band, only the weaker $\nu(C=O)_2$ band is available for the determination of AN.

$$K_{eq} = K_a(TFA)/K_a(BH^+) \qquad (7)$$

Thus, at equilibrium:

$$\log([BH^+]/[B{:}]) = pK_a(BH^+) - pK_a(TFA)$$
$$+ \log([RCOOH]/[RCOO^-]) \qquad (8)$$

Similarly, for the AN method, using KPhthal as the signal-transducing reagent:

$$\log([A^-]/[AH]) = pK_a(Phthal) - pK_a(AH)$$
$$+ \log([KPhthal]/[Phthal]) \qquad (9)$$

Comparison of Eqs. 5 and 8 shows that the FT-IR method should respond to weaker bases than the D664 titrimetric method because the "pH endpoint" of the FT-IR method, determined by the pK$_a$ of the signal-transducing reagent (TFA, pK$_a$ = 0.5), is more than 3 log units lower than the titrimetric endpoint. However, the relationship between the two methods is complicated by the contribution of the final term on the right-hand side of Eq. 8. On the other hand, in the case of the AN method, the corresponding term in Eq. 9 makes a negligible contribution owing
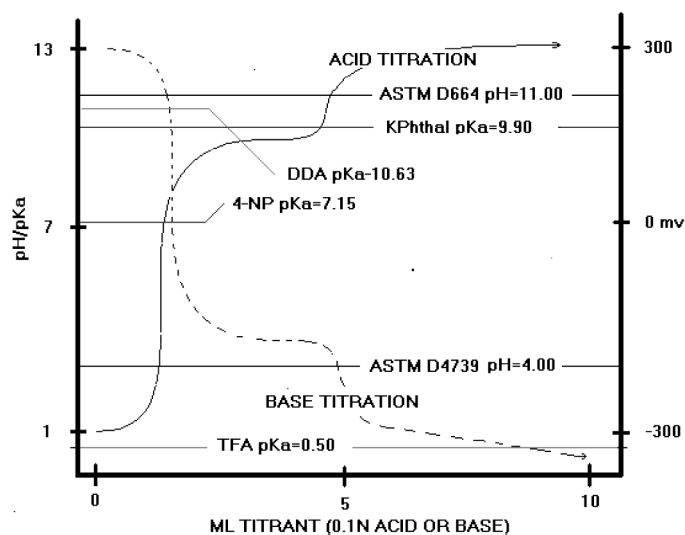


FIG. 7. Idealized ASTM titration curves for oils containing acidic (———) or basic (– – –) constituents illustrating the respective ASTM D664 and D4739 potentiometric endpoints and their relationship to the FT-IR "endpoints", defined as the pK$_a$ values of the signal-transducing reagents, and pK$_a$ values of the acid and base used for calibration of the FT-IR AN and BN methods.

to the very limited solubility of KPhthal in the 1-PrOH-diluted oil samples. In addition, the AN FT-IR endpoint (9.90) is much closer to the potentiometric pH endpoint (11) than in the case of the BN method, and thus a good correspondence between the results obtained by the FT-IR and potentiometric AN methods would be expected on theoretical grounds.

***Validation Results*** . A wide variety of new and used oils representing a broad range of lubricant applications were obtained from well-established oil analysis laboratories. After FT-IR analyses of these samples were carried out and the results submitted, the corresponding titrimetric results were provided. Among these samples, 32 had been analyzed for AN by ASTM D664 (KOH potentiometric titration) and 17 had been analyzed for BN by ASTM D4739 (HCl potentiometric titration). To obtain an unambiguous comparison between the FT-IR and potentiometric AN and BN results, zero regression (Z-reg) was used to eliminate the contribution of the intercept to the regression slope. The FT-IR data were also assessed in terms of mean differences (MD$_a$) and standard deviations of the differences (SDD$_a$) for accuracy, considering the chemical results to be the reference data.

$$AN_{FT\text{-}IR} = 0.984 AN_{ASTM\,D664} \qquad R = 0.953$$
$$SD = 0.46 \qquad\qquad N = 32$$
$$MD_a = -0.03 \qquad\qquad SDD_a = 0.46 \qquad (10)$$
$$BN_{FT\text{-}IR} = 1.030 BN_{ASTM\,D4739} \qquad R = 0.731$$
$$SD = 0.69 \qquad\qquad N = 17$$
$$MD_a = 0.23 \qquad\qquad SDD_a = 0.67 \qquad (11)$$

These results clearly indicate that the use of a stoichiometric reaction to effect signal transduction combined with the use of differential FT-IR spectroscopy to circumvent matrix effects provides an effective means of tracking AN and BN changes. The regression data indicate
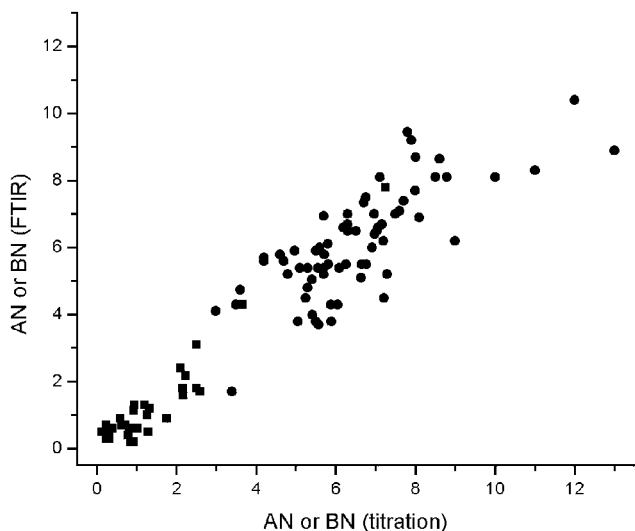
FIG. 8.   Composite plot of AN (■) and BN (●) FT-IR results for samples supplied by third parties plotted against the corresponding chemical analysis data.

that there is close to a 1:1 correspondence between the FT-IR and ASTM results, and the $MD_a$ values confirm that the FT-IR data have no statistically significant bias. The stated reproducibility of ASTM D664 is 28% and 44% of the mean of two results for fresh and used oils, respectively, whereas that of ASTM D4739 is 21.1% of the mean of two results.[7] For the AN and BN values spanned by the validation samples, these percentages would correspond to a mean AN reproducibility of 0.37 mg KOH/g and a mean BN reproducibility of 1.43 mg KOH/g. On this basis, the $SDD_a$ values presented in Eqs. 10 and 11 are within the errors of the reference data. This analysis effectively represents a worst-case scenario given that the chemical data was obtained from various laboratories. A reproducibility assessment for the FT-IR methods was carried out by analyzing five replicates of each of twenty used bus oils for AN and BN. The average SD was on the order of ±0.40 mg KOH/g for both methods.

Among the set of validation samples, 52 samples had been analyzed for BN by ASTM D2896, which is an alternative potentiometric titration method that appears to have largely supplanted ASTM D4739. Because this method uses an anhydrous solvent system, with perchloric acid serving as the titrant, it does not yield results directly comparable to those provided by ASTM D4739, producing higher BN values for oils containing strongly over-based additives and nitrogenous polymeric compounds.[7] This trend was also reflected by the slope of the Z-reg equation relating the FT-IR BN data to those obtained by ASTM D2896 and the larger values of the regression SD, $MD_a$, and $SDD_a$:

$$BN_{FT-IR} = 0.897BN_{ASTM\ D2896} \qquad R = 0.781$$

$$SD = 1.17 \qquad\qquad N = 52$$

$$MD_a = -0.60 \qquad\qquad SDD_a = 1.25 \qquad (12)$$

An overall summary of the AN and BN validation results is provided by the composite plot presented in Fig. 8. Given the differences in the "endpoints" employed in the

FT-IR and ASTM methods, compounded by the use of an anhydrous solvent system in ASTM D2896, the correlation between the chemical and FT-IR data is surprisingly good. In this regard, it may be noted that the FT-IR and ASTM methods would be expected to respond similarly to the major acidic constituents of interest in used oils, i.e., carboxylic acids produced by oil oxidation ($pK_as$ ~4–5), as well as stronger combustion acids (sulfuric and nitric), and to most of the stronger basic detergents and neutralizing agents.

## DISCUSSION

The new FT-IR lubricant analysis methods developed in this work afford an alternative to the ASTM titrimetric methods for the determination of AN and BN, bringing with them environmental benefits (minimal solvent/reagent use and disposal) and simplicity of analysis. Like the ASTM methods, the FT-IR methodology is based on simple acid/base reactions; however, the pH electrode, which has poor response and reproducibility in predominantly nonaqueous systems, has effectively been replaced by a spectrophotometric detection system. This substitution eliminates titration procedures, providing for a marked increase in speed of analysis as well as improved reproducibility. The validation results obtained in this study for a wide variety of new and used oils, including both hydrocarbon- and ester-based oils, trended titrimetric AN and BN values relatively well. This concurrence obviates any radical shift in the analytical frame of reference for those accustomed to interpreting AN and BN data for quality control or condition monitoring purposes.

In terms of methodology, the FT-IR procedure is straightforward and has the advantage that both the AN and BN protocols are identical, only differing in the reactive reagent employed. Sample-handing difficulties due to oil viscosity and light scattering by the soot present in used oils are addressed by dilution and centrifugation, respectively. Although the downside to this FT-IR method is the need for sample preparation, the sample preparation procedure is rapid with the use of bottle pipette dispensers and re-pipettes (~3 min/sample), and samples can be analyzed immediately (centrifugation recommended) or after a time lapse of >3 h, allowing one to bypass the centrifugation step. Once prepared, >60 samples can be analyzed per hour with the use of an autosampler.

## CONCLUSION

The FT-IR AN/BN methods developed have significant advantages over ASTM titrimetric methods in terms of environmental considerations, speed of analysis, reagent/solvent use, and flexibility in the variety of base oils and formulations that can be handled. Signal transduction using a dicarbonyl salt and a carboxylic acid has been demonstrated to provide a means for the accurate measurement of undefined acids and bases, respectively, in lubricating oils, with matrix effects being circumvented through the use of differential spectroscopy. This approach makes use of the same principles as titrimetric methods but without their attendant problems, and it is likely that FT-IR spectroscopy could have wider utility

as an alternative to titrimetric analysis of non-aqueous samples.

1. M. C. Garry and J. Bowman, Thermo Nicolet Technical Note 9698, Thermo Nicolet Corp., Madison, WI (2001).
2. F. R. van de Voort, J. Sedman, and T. Russin, Eur. J. Lipid Sci. Technol. **103,** 875 (2001).
3. F. R. van de Voort and J. Sedman, Inform **11,** 614 (2000).
4. F. R. van de Voort, J. Sedman, A. A. Ismail, J. Dubois, and A. Nicodemo, J. Am. Oil Chem. Soc. **71,** 921 (1994).
5. K. Ma, F. R. van de Voort, J. Sedman, and A. A. Ismail, J. Am. Oil Chem. Soc. **74,** 897 (1997).
6. Annual Book of ASTM Standards, Vol. 5.01, Philadelphia (1990).
7. R. A. Kishore Nadkarni, *Guide to ASTM Test Methods for the Analysis of Petroleum Products and Lubricants* (ASTM, West Conshohocken, PA, 2000), p. 45.