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Automated Acid Content Determination in Lubricants by FTIR Spectroscopy as an Alternative to Acid Number Determination

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ABSTRACT: A new instrumental method for the quantitative measurement of acid content (AC) in mineral-based lubricants was devised by employing FTIR spectroscopy, with AC serving as an alternative to traditional acid number (AN) measures commonly made to assess lubricant quality. The method involves the addition of an oil-immiscible ethanolic solution of the base sodium hydrogen cyanamide (NaHN–C≡N) to the lubricant to extract and react with the acids present. After separation of the phases, the FTIR spectrum of the ethanol layer is recorded, and a differential spectrum is generated by subtracting out the spectrum of the reagent solution. AC is determined by measuring the absorbance of NaHN–C≡N at 2109 cm^{-1} (νC≡N) in the differential spectrum, which is proportional to the extent to which the reagent has been consumed by reaction with acidic constituents in the oil. Calibration standards were prepared by direct addition of oleic acid to the NaHN–C≡N/ethanol solution, and a calibration equation for the determination of AC was obtained by a quadratic fit of the concentration data to the FTIR νC≡N absorbance data. The equivalent response of the νC≡N band to strong inorganic acids and oleic acid demonstrated that NaHN–C≡N, a somewhat weaker base than KOH, fully ionizes organic acids. Comparison between FTIR AC values and titrimetric AN values (obtained by ASTM D664-89) for a set of used oils spanning an AN range of 0.3–5 mg KOH/g showed a reasonably good linear relationship ($R=0.985$), with the FTIR method generally producing lower values. This tendency was attributed to the presence of weakly acidic species, which would be less extensively ionized by NaHN–C≡N than by KOH. Implementation of the FTIR AC method on an autosampler-equipped spectrometer allows for the automated analysis of up to 120 preprepared samples/h, representing a significant increase in analytical throughput relative to traditional titrimetric procedures as well as substantive reductions in consumables and waste oil.

KEYWORDS: FTIR spectroscopic analysis, lubricant analysis, condition monitoring, automated analysis, titration, extraction, carboxylic acids, mineral acids, sodium hydrogen cyanamide, sodium carbodiimide

Introduction

Fourier transform infrared (FTIR) spectroscopy has found extensive application as an automated, qualitative analytical technique for condition monitoring (CM) of in-service lubricants of machinery, vehicles, and equipment. It is based on monitoring changes in the spectral signature of a lubricant at periodic sampling intervals, with the objective of screening lubricant quality so that oils are replaced only when their functionality is clearly compromised. An overview of CM analyses by FTIR has been presented in a recent publication [1], in which we described a technique termed spectral reconstitution that facilitates a substantial increase in sample throughput (>100 samples/h), and which represents an important advance for centralized laboratories that routinely perform CM analyses on hundreds of samples per day [2]. We have also worked toward enhancing the general utility of FTIR spectroscopy as a tool for lubricant analysis through the development of new, automated *quantitative* methods to assess critical lubricant parameters such as acid number (AN), base number (BN) and moisture content [3,4]. These FTIR methods help to amortize the investment in CM FTIR instrumentation as well as providing substantive cost reductions and production benefits relative to the slow and reagent-intensive ASTM titrimetric methods traditionally employed for the determination of these quality parameters.

The present study extends our previous work on acidity determination by FTIR spectroscopy by simplifying the procedure and thus increasing sample throughput by a factor of >2, relative to earlier

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TABLE 1—*Tabulation of acids that may accumulate in lubricants as a function of their lubrication application.*

Acid Type	Source	Lube Application
COOH	Oil oxidation	All severe lubricant environments
HCl/HF	Refrigerant breakdown	Chillers
H_2SO_4	H_2S contamination in diesel fuel and water, breakdown of antiwear and extreme-pressure additives	Diesel engines, NG compressors, hydraulic systems
HNO_3	Nitration and nitric oxides	Gas engines, gasoline engines
H_3PO_4	By-product of phosphate ester degradation	Mobile equipment, especially hydraulics

FTIR methodology [3]. AN determinations are important in tracking lubricant quality, as acidity is of concern from the standpoint of oil functionality and is associated with equipment corrosion. Table 1 lists the predominant acids that may accumulate in various types of lubricants. In combustion engines, these include organic acids (COOH) produced over time as a result of oxidative processes as well as strong inorganic acids that may be incorporated into oils as a result of blow-by or due to inherent acidity in fuels. In refrigeration compressor systems, refrigerant breakdown can lead to the accumulation of HCl or HF in the lubricants used. Given that H^+ itself is not IR-active, a key obstacle to the determination of acidity by FTIR spectroscopy would appear to be the need to measure the specific IR absorptions of each of the acids listed in Table 1, which is problematic as monatomic anions (i.e., Cl^-. F^-) do not give rise to IR absorption bands. This obstacle, however, has been surmounted by developing the concept of *signal transduction,* whereby the acids in the sample are reacted with a base whose conjugate acid has a readily measurable IR absorption [3]. In an earlier method developed on the basis of this concept, two spectra are acquired for each sample, one before and one after addition of the base. The first spectrum is subtracted from the second in order to isolate the spectral changes associated with the acid-base reaction and to eliminate spectral interferences arising from the oil matrix by differential spectroscopy [3]. This approach provides an overall measure of all acid contributions, and extensive experience with this approach has indicated that the results track the AN values determined by the ASTM D664-89 potentiometric titration fairly well [5], producing similar trends, but not directly comparable results in terms of absolute magnitude. Approximately 60 samples/h can be analyzed by this method on an FTIR system equipped with an autosampler [6], a good throughput relative to that of automated titrimetric procedures; however, the requirement of two analyses to obtain a single result is clearly a drawback of this method.

In this paper, we present a means by which to overcome this limitation through the use of a combined extraction/signal-transduction approach. While having its roots in the previous AN methodology, this approach has also evolved from the development of FTIR methods for the determination of free fatty acid (FFA) content in edible oils. Specifically, "indirect" methods for this analysis, whereby the oil is extracted with a basic methanolic solution to convert the FFAs to their carboxylate salts, which are then quantitated by FTIR spectroscopy, have provided a simple yet effective means of eliminating oil spectral interferences [7]. While this methodology should be equally applicable to the determination of organic (i.e., carboxylic) acids in lubricants, the determination of total acidity requires a base that has suitable spectral characteristics for use in signal transduction. Among the bases that have been successfully employed for effecting the $COOH \rightarrow COO^-$ conversion in FFA analysis, sodium hydrogen cyanamide ($NaHN-C\equiv N$) is potentially ideal in this regard, by virtue of its intense and fairly well isolated $\nu C\equiv N$ absorption band [8]. Although a methanolic solution of this base is unsuitable as a "signal-transducing" reagent for reasons that will be described later in this paper, the use of ethanol as solvent restores the signal-transducing capability of $NaHN-C\equiv N$ and hence also provides a means of differentiating between organic and inorganic acidic constituents. Thus, this paper describes the determination of acidity in lubricants by extraction/signal transduction using ethanolic $NaHN-C\equiv N$.

As a final note at the outset, an issue of terminology merits discussion. Given the potential advantages of replacing traditional titrimetric AN methods by FTIR methods, as outlined above, an important question that arises concerns the extent to which these two types of methods can be expected to concur. In this regard, it may be noted that ASTM has several official methods for the determination of AN in lubricants that differ in the titrant used, the titration endpoint, and the analytical procedure and hence effectively differ in their "definition" of acidity. Thus, the variable AN contributions of weakly acidic substances that may be present in lubricants, such as phenolics, lactones, resins, salts of heavy metals or ammonia, as well as acid salts of polybasic acids and certain additives, are considered the main cause of the non-concurrence between the results obtained by various titrimetric AN methods. As such, there are clear warnings in the various ASTM AN methods that the values from different methods are in effect not directly comparable. This caveat is equally applicable to FTIR methods based on signal transduction, which effectively mimic titrimetric procedures but use a unique, spectrally active base, such as potassium phthalimide or $NaHN{-}C{\equiv}N$, whose pK_a in effect determines the spectral “endpoint.” As will be seen below, it is our contention that the FTIR method described in the present paper satisfactorily measures all acids of concern from an oil quality or corrosion standpoint and thus serves the same purpose as most AN analyses of in-service lubricants. However, because it is both conceptually and procedurally different from conventional titration procedures, we have accepted a recommendation that the values obtained by this FTIR method be referred to as acid content (AC), reported in the same units as AN (i.e., mg KOH/g oil). Throughout the remainder of this paper, only results obtained by official ASTM AN methods or equivalent titrimetric procedures are designated as AN values; data obtained by alternative titrimetric methods for the purpose of comparison with FTIR AC results are considered to be AC rather than AN values.

Materials and Methods

Reagents and Sample Preparation

Sodium hydrogen cyanamide ($NaHN{-}C{\equiv}N$), also known as sodium carbodiimide, oleic acid, and anhydrous ethanol were obtained from Sigma-Aldrich and were all of reagent grade. The anhydrous ethanol was kept over 3A molecular sieves, 8–12 mesh (also from Sigma-Aldrich). Additive-free mineral oil (P-032) as well as a variety of new and used oils was obtained from Thermal-Lube Inc. (Pointe Claire, QC, Canada), a lubricant formulator. The reagent solution employed in the FTIR AC methodology was prepared by dissolving $NaHN{-}C{\equiv}N$ in anhydrous ethanol at a concentration of ~2.5 g/L. The resulting solution was filtered through Whatman #1 filter paper to remove any turbidity resulting from insolubles and was then stored at −18°C (freezer). Sample preparation for FTIR analysis involved weighing 8 g of oil into a 30-mL screw-capped vial and adding 18 mL of the $NaHN{-}C{\equiv}N$/ethanol reagent solution. After capping, the vials were subjected to 5 min of horizontal shaking on an Eberbach (Ann Arbor, MI) reciprocal shaker operated at four cycles/s and then left to stand for up to 30 min to allow for complete phase separation prior to FTIR analysis of the upper ethanol layer. For direct FTIR–titrimetric comparisons, the sample preparation/extraction procedures were scaled up to provide sufficient sample for analysis by both techniques.

FTIR Spectroscopy

The instrument used in this study was a COAT (Continuous Oil Analysis and Treatment) FTIR analyzer (Thermal-Lube Inc., Pointe Claire, QC, Canada), which integrates a Bomem WorkIR FTIR spectrometer, an autosampler, and a micro-pump to facilitate automated sample analysis. The instrument was controlled by UMPIRE (Universal Method Platform for Infra Red Evaluation), a proprietary software package developed by Thermal-Lube. The spectrometer was equipped with either a 100- or a 300-μm CaF_2 transmission flow cell, depending on the AC range to be covered (0–5 or 0−2 mg KOH/g oil, respectively). For method development work, the sample (upper ethanol layer in the sample vial) was manually aspirated into the cell using vacuum. Once the methodology was automated, samples were pumped into the cell automatically from vials loaded into the autosampler rack [9]. All spectra were collected by co-addition of 16 scans at a resolution of 4 cm^{-1} and ratioed against an open-beam background spectrum. To correct for displacement effects due to the slight, but variable miscibility of oils with the reagent solution, the spectrum of each sample was multiplied by a displacement correction factor (DCF), determined by dividing the height of the ethanol overtone band at 1925 cm^{-1} in the spectrum of the reagent solution by the height of this band in the spectrum of the sample extract. Following multiplication of the latter spectrum by DCF, the spectrum of the reagent solution was subtracted from it to produce a differential spectrum, from which the AC was determined using the calibration equation devised. In the case of automated analysis, the first two vials in the autosampler tray were reserved for ethanol (used to condition the cell) and the reagent solution, with the spectrum of the latter serving as the reference spectrum employed by the software for the determination of DCF for all samples subsequently analyzed. In both manual and automated modes of analysis, the spectra of the reagent solution and the sample extract(s) were recorded within 2 h after addition of the reagent solution to the sample(s) to minimize errors resulting from the slow conversion of sodium hydrogen cyanamide to its breakdown products.

Calibration

Calibration standards were gravimetrically prepared by adding oleic acid to the NaHN–C≡N/ethanol reagent solution. The concentrations of acid in these calibration standards were converted to "oil" AC values, expressed in units of mg KOH/g oil and calculated on the basis of the sample preparation protocol (18 mL of reagent/8 g oil). Thus to prepare a calibration standard with an AC equal to *Z* mg KOH/g oil, the amount of oleic acid to be weighed out and added to 18 mL of reagent was calculated as follows: Oleic $\text{acid}_{\text{mg}} = 8 \times Z \times \text{Mw}_{\text{oleic acid}} / \text{Mw}_{\text{KOH}} = 8 \times Z \times 5.03$. The spectra of the calibration standards were collected by co-addition of 16 scans at a resolution of 4 cm^{-1} and ratioed against an open-beam background spectrum. Following subtraction of the spectrum of the reagent solution from the spectra of the standards, the (negative) intensity of the $\nu\text{C}{\equiv}\text{N}$ band at 2109 cm^{-1} was measured relative to a single-point baseline at 1859 cm^{-1}. A calibration equation was derived by least-squares regression of AC against $\text{Abs}_{2109/1859\ \text{cm}^{-1}}$ using a quadratic fit.

Assessment and Validation of the Methodology

A preliminary assessment of the methodology involved standard addition of oleic acid to an unformulated base mineral oil, P-032. These spiked oils were analyzed for acid content (AC) by the FTIR analytical protocol described and by potentiometric titration using a Mettler-Toledo DL58 auto-titrator equipped with a DGi114 solvent electrode. To make the FTIR and titrimetric procedures directly comparable, the spiked P-032 oils were extracted with a NaOH/ethanol solution (isomolar with the NaHN–C≡N/ethanol reagent solution) and back-titrated with 0.1 N HCl, the endpoint being determined from the inflection point of the titration curve. A second study entailed extraction of used-oil samples with NaHN–C≡N/ethanol followed by FTIR analysis as well as back-titration of the extracts. For validation, 27 used-oil samples were provided by Hewitt Equipment (Pointe-Claire, QC, Canada) along with their corresponding AN data obtained by potentiometric titration in accordance with ASTM D664-89. This validation set was supplemented with five compressor oils obtained from Thermal-Lube Inc., for which AN values were obtained in our laboratory by extraction with ethanolic NaOH followed by back-titration with HCl as described above.

Results and Discussion

Principles of the FTIR Acid Content Method

The FTIR method for the determination of acid content in lubricants developed in this work is based on the extraction of the acids present in the lubricant into an ethanolic solution of the base NaHN–C≡N, which serves as a "signal-transducing" reagent. As mentioned at the outset, an analogous signal-transduction approach was developed in our previous work on the determination of AN as well as BN by FTIR spectroscopy [3], but the lack of an extraction step led to certain drawbacks. In this earlier methodology, the acid content of an oil was determined by adding a solution of potassium phthalimide in *n*-propanol (the signal-transducing reagent) to the oil and measuring the $\nu(\text{C}{=}\text{O})$ absorption of phthalimide produced by the acid-base reaction. To eliminate spectral interferences from the oil, a two-step analytical protocol was required, whereby the oil sample was split into two halves, one-half was mixed with the signal-transducing reagent and the other with an equal volume of *n*-propanol, and the spectrum of the latter was subtracted from that of the former to produce a differential spectrum representing the spectral changes associated with the acid-base reaction. The objective of the present work was to simplify the methodology by extracting the acids present in an oil sample into an oil-immiscible signal-transducing reagent, thereby eliminating spectral interferences from the oil rather than compensating for them by differential spectroscopy. Beyond halving the sample preparation and spectral acquisition time, this combined extraction/signal-transduction approach can provide substantial additional gains in sample throughput owing to the reduction in sample viscosity.

In developing this approach, an alternative signal-transducing reagent was sought because phthalimide would undergo partitioning in a two-phase system. Sodium hydrogen cyanamide ($NaHN{-}C{\equiv}N$) was identified as a potential candidate on the basis of its fairly strong basicity and the suitable IR absorption characteristics of the $C{\equiv}N$ functional group. Initial work with this base concerned its use in FTIR methodology for the determination of free fatty acid (FFA) content (effectively AN) in edible oils (triacylglycerols) [8]. Because the $\nu C{=}O$ absorption of FFAs overlaps with the intense ester $\nu C{=}O$ absorption of triacylglycerols, FFAs are more readily quantitated if converted to their carboxylate salts by extraction into alcoholic KOH [7]. However, errors due to saponification of triacylglycerols by this strongly basic solution have been reported. Thus, our initial work focused primarily on the use of a methanolic $NaHN{-}C{\equiv}N$ solution as an alternative to alcoholic KOH rather than as a signal-transducing reagent. However, it became evident during this investigation that the latter (but not the former) possibility was precluded by the instability of $NaHN{-}C{\equiv}N$ in methanol, as evidenced by the progressive decrease of its $\nu C{\equiv}N$ band over time, resulting in complete disappearance of this band approximately four days after preparation of the solution, with the concomitant appearance of two new bands at 1650 and 1610 cm^{-1}. These spectral changes are postulated to arise from tautomerization of $NaH{-}N{-}C{\equiv}N$ to an unstable carbodiimide ($NaN{=}C{=}NH$) and subsequent reaction of this species with methanol to form methyl isourea ($H_2N{-}C(OCH_3){=}NH$). Although the nature of the basic species present in an "aged" reagent (i.e., a solution that no longer exhibits any $\nu C{\equiv}N$ absorption) remains under investigation, extraction of edible oils with such a solution deprotonates all the FFAs without saponifying triacylglycerols, and hence this "aged" reagent worked well as an alternative to alcoholic KOH for the FTIR determination of FFAs by measurement of their carboxylate salts [8].

Although the above FFA methodology could be used to measure carboxylic acids in mineral and synthetic lubricants, the results would have to be qualified as "oxidative" acidity values [10] rather than acid content *per se*, as inorganic acids would not contribute to this form of FTIR-determined acidity. Thus, the concept of employing $NaHN{-}C{\equiv}N$ in FTIR analysis of lubricants had to be abandoned. However, efforts to adapt the FFA methodology for use with a variable-filter-array IR spectrometer [11] led to the serendipitous discovery that the stability of $NaHN{-}C{\equiv}N$ in ethanol is surprisingly different from that observed in methanol. Although the $\nu C{\equiv}N$ band in the spectrum of an ethanolic $NaHN{-}C{\equiv}N$ solution shows a gradual decrease over time, the rate at which $NaHN{-}C{\equiv}N$ is depleted is much slower than in methanol, taking ~60 days to reach completion. Furthermore, the solution has been found to be indefinitely stable when stored at freezer temperatures. Consequently, the stability of ethanolic $NaHN{-}C{\equiv}N$ is sufficient to warrant its consideration as a signal-transducing reagent for the determination of acidity in lubricants. The principle of this approach is illustrated in Fig. 1, which shows the strong $\nu C{\equiv}N$ band observed at 2109 cm^{-1} in the spectrum of an ethanolic solution of $NaHN{-}C{\equiv}N$ (Fig. 1(*a*)) and the shift of this band by >100 cm^{-1} upon formation of cyanamide ($H_2N{-}C{\equiv}N$) by addition of excess acid to the basic solution (Fig. 1(*b*)). The differential spectrum obtained by subtraction of Fig. 1(*a*) from 1(*b*), shown in Fig. 1(*c*), exhibits a well-isolated and easily measurable negative $NaHN{-}C{\equiv}N$ band that represents the amount of base consumed by the acid-base reaction. Thus, the acid content of an oil sample can, in principle, be determined by extraction of the oil with an ethanolic $NaHN{-}C{\equiv}N$ solution of appropriate concentration (dependent on the amount of acid in the oil) followed by measurement of the decrease of the $\nu C{\equiv}N$ band in the spectrum of this reagent solution resulting from reaction of $NaHN{-}C{\equiv}N$ with the extracted acids.

Another important consideration in relation to the suitability of ethanolic $NaHN{-}C{\equiv}N$ as a reagent for a lubricant FTIR AC analysis is its basicity. As the only pK_b data available for $NaHN{-}C{\equiv}N$ is a value determined in DMSO, we obtained relative pK_b data by titrating isomolar ethanolic solutions of $NaHN{-}C{\equiv}N$ and NaOH with 0.1 N HCl. The results indicated that the pK_b values differed by ~1.45 units, with $NaHN{-}C{\equiv}N$ being the weaker base. Thus, in principle, an FTIR AC method using ethanolic $NaHN{-}C{\equiv}N$ as a base should fully measure the weakest acids of concern from an oil quality standpoint, namely, carboxylic acids, as well as all acids stronger than carboxylic acids.

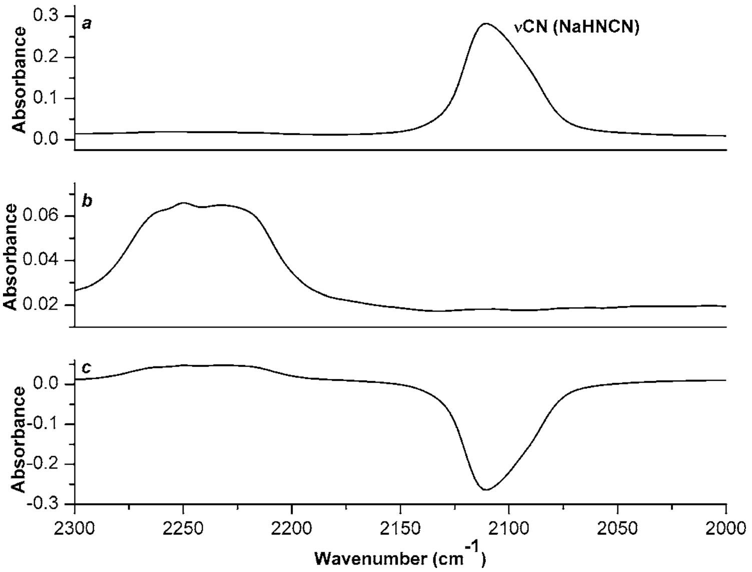

FIG. 1—*The $\nu C{\equiv}N$ band in the FTIR spectrum of NaHN–C≡N in ethanol (a) and in the spectrum obtained after addition of excess acid (b). The spectrum of ethanol has been subtracted out. The differential spectrum (c), produced by subtraction of (a) from (b), shows the spectral changes associated with the acid-base reaction.*

Calibration

The relationship between AC and the intensity of the $\nu C{\equiv}N$ band was established by the quantitative addition of varying amounts of acids to a ~2.5 g/L NaHN–C≡N/ethanol solution. The acids selected were strong inorganic acids (HCl, HNO_3, and H_2SO_4) and oleic acid ($C_{18}H_{35}COOH$), the latter considered representative of organic acids in general. Figure 2 illustrates a series of differential spectra obtained by subtracting the spectrum of the reagent solution from the spectra recorded after spiking this solution with varying amounts of oleic acid to produce "oil" AC values in the range of 1–5 mg KOH/g oil. In these spectra, the increasingly negative intensity of the $\nu C{\equiv}N$ band is paralleled by an increase in the intensity of the νCOO^- band of the salt of oleic acid at 1569 cm^{-1}. Figure 3(*a*) presents calibration plots of AC versus the absolute value of the absorbance at 2109 ($\nu C{\equiv}N$) and 1569 cm^{-1} (νCOO^-), both measured relative to a single-point baseline at 1859 cm^{-1}. These plots illustrate that the relationship for the $\nu C{\equiv}N$ band is distinctly curvilinear, while that for the νCOO^- band is linear. Data for both these bands were assessed by least-squares regressions using both first- and second-order equations:

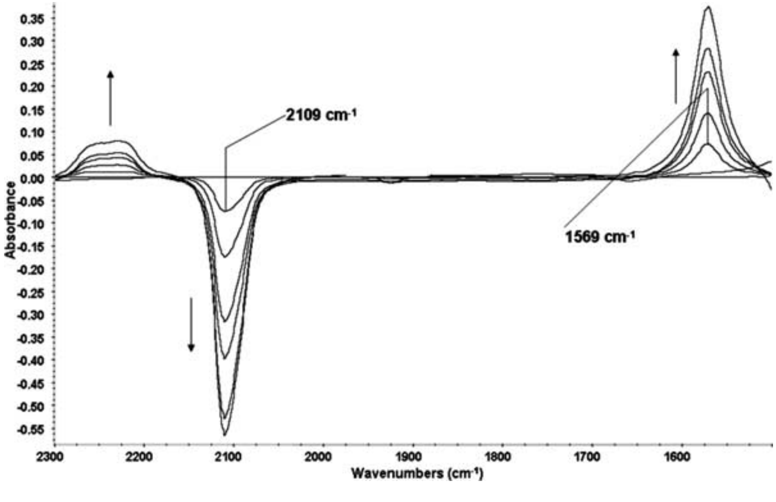

FIG. 2—*Series of differential spectra obtained upon addition of increasing amounts of oleic acid to the NaHNCN/ethanol reagent solution, showing the decrease of the $\nu C{\equiv}N$ band and the growth of the νCOO^- band of the oleate salt produced by the acid-base reaction.*

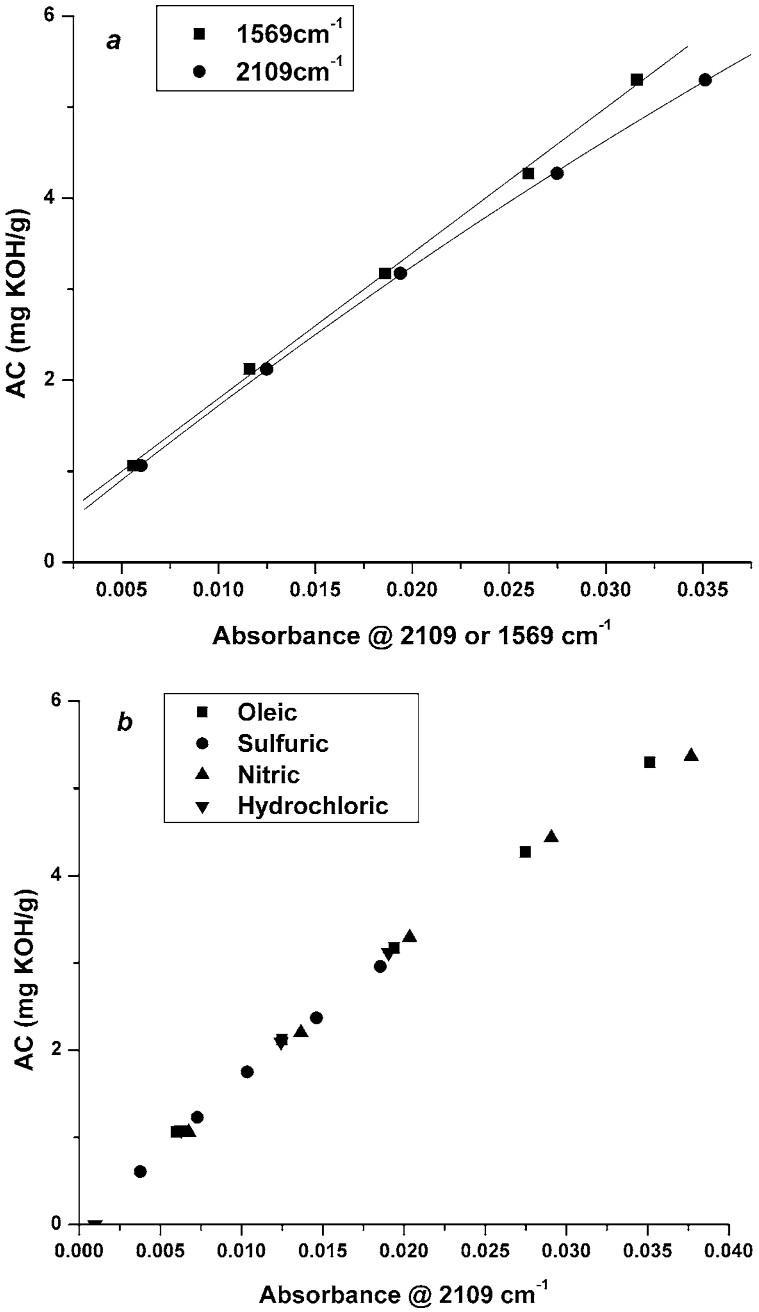

FIG. 3—*(a) AC versus absorbance plots for the* $\nu C{\equiv}N$ *band at 2109* cm^{-1} *and the* νCOO^- *band at 1569* cm^{-1} *in the differential spectra obtained after addition of various amounts of oleic acid to the reagent solution. (b) Composite plot of AC versus absorbance at 2109* cm^{-1} *for addition of HCl,* H_2SO_4*,* HNO_3*, and oleic acid to the reagent solution. The absorbance values of the* $\nu C{\equiv}N$ *band have been multiplied by −1 to facilitate comparison of the plots.*

$$AC_{(2109\ cm^{-1})} = 0.27 - 144.71 * Abs \quad R = -0.999 \quad SD = 0.08 \tag{1}$$

$$AC_{(2109\ cm^{-1})} = 0.05 - 174.27 * Abs - 716.2 * Abs^2 \quad R = 0.999 \quad SD = 0.02 \tag{2}$$

$$AC_{(1569\ cm^{-1})} = 0.20 + 159.72 * Abs \quad R = 0.999 \quad SD = 0.07 \tag{3}$$

$$AC_{(1569\ cm^{-1})} = 0.21 + 157.6 * Abs + 56.7 * Abs^2 \quad R = 0.998 \quad SD = 0.08 \tag{4}$$

As can be seen, for the $\nu C{\equiv}N$ band the quadratic fit (Eq 2) results in a fourfold decrease in the regression SD by comparison with the linear fit (Eq 1), whereas for the νCOO^- band no improvement is obtained with a quadratic fit. Figure 3(*b*) shows that the responses of the $\nu\mathrm{C{\equiv}N}$ band upon addition of strong inorganic acids (HCl, HNO_3, and H_2SO_4) to the reagent solution were all similar to those obtained with oleic acid, confirming that the NaHN–C≡N/ethanol solution is sufficiently basic to fully ionize the relatively weak organic acid. Combining all the acid responses presented in Fig. 3(*b*) yielded the following first- and second-order regression relationships:

$$\mathrm{AC}_{(\mathrm{All\ Acids})} = 0.16 - 146.83 * \mathrm{Abs} \quad R = -0.996 \quad SD = 0.13 \tag{5}$$

$$\mathrm{AC}_{(\mathrm{All\ Acids})} = -0.10 - 189.09 * \mathrm{Abs} - 1109.7 * \mathrm{Abs}^2 \quad R = -0.998 \quad SD = 0.06 \tag{6}$$

The similarity of Eqs 5 and 6 to Eqs 1 and 2 indicates that a calibration equation based only on oleic acid standards can serve for the determination of carboxylic acids and all acids stronger than carboxylic acids in lubricants, yielding a value designated as AC. Oleic acid is a convenient standard, being easier to handle than strong acids and readily dissolving in hydrophobic media. In addition, although not explicitly considered in this work, the use of oleic acid as a calibration standard affords a potential means of independently measuring the contributions of organic acids to AC via a calibration based on the $\nu\mathrm{COO^-}$ band. This additional capability may be of diagnostic value, given the different routes by which inorganic and organic acids accumulate in lubricants as well as their differing effects on oil quality and corrosivity (see Table 1).

In calibrating the FTIR AC method with standards prepared by direct addition of oleic acid to the NaHN–C≡N/ethanol reagent solution, the scaling factor required to adjust the AC values by the oil:reagent-solution ratio employed in the extraction step, standardized at 1:2.25 w/v, is effectively built into the calibration equation. Accordingly, use of this calibration equation not only requires that this standardized ratio be strictly adhered to but also rests on the assumption that the lubricant is completely immiscible with the ethanolic reagent solution into which any acids present in the oil are extracted. This assumption may not be entirely valid and would lead to overestimation of AC because dilution of the ethanol phase by oil will lead to an increase in the (negative) intensity of the $\nu\mathrm{C{\equiv}N}$ band in the differential spectrum. Accordingly, it was necessary to devise a means of compensating for the normally slight, but variable, miscibility of oils with the reagent solution. The procedure developed involves the use of the ethanol overtone absorption at 1925 $\mathrm{cm^{-1}}$ to measure the extent of dilution of the reagent solution by oil dissolved in it. This band is suitable for this purpose because there are rarely interfering absorptions in this region of the IR spectrum. Thus, prior to generating the differential spectrum, a displacement correction factor (DCF) is calculated by measuring the ratio of the absorbance at 1925 $\mathrm{cm^{-1}}$ in the spectrum of the reagent solution to that in the spectrum of the sample extract, and the latter spectrum is then multiplied by the DCF. The differential spectrum produced after this step mathematically corresponds to the spectrum that would have been obtained in the absence of any displacement effect, allowing the AC value of the sample to be determined directly from the original calibration equation.

A final consideration in relation to the validity of the calibration is the need to safeguard against the possibility of errors resulting from instability of NaHN–C≡N and its conversion to other products. While the NaHN–C≡N/ethanol reagent solution appears to be stable indefinitely when stored at −18 °C, slow conversion does occur at room temperature, resulting in a significant drop in the intensity (~8 %) of the $\nu\mathrm{C{\equiv}N}$ band within 24 h. A small change in intensity is not of concern *per se* because AC determination is based on the intensity of the $\nu\mathrm{C{\equiv}N}$ band in the differential spectrum obtained by subtraction of the spectrum of the reagent solution from that of the sample extract. Thus, provided that these two spectra are collected within a reasonable time (<2 h) after addition of the reagent solution to the sample, the effect of the slow conversion of NaHN–C≡N will be negligible. However, given that a methanolic solution of NaHN–C≡N remains capable of deprotonating carboxylic acids after complete disappearance of the $\nu\mathrm{C{\equiv}N}$ band, it is likely that the slow depletion of NaHN–C≡N in ethanol is accompanied by the formation of basic species that will react with acids extracted from the oil and will thus lead to errors in the determination of AC, since the ionization of these acids will not produce any change in the $\nu\mathrm{C{\equiv}N}$ band. As such, if the extent of depletion of NaHN–C≡N in the reagent solution becomes significant, as measured by spectroscopic changes, then the calibration developed ceases to be valid. Thus, it is important to verify that the spectrum of the reagent solution that is about to be employed for sample analysis matches that of the original zero-AC calibration standard. If the height of the $\nu\mathrm{C{\equiv}N}$ band has decreased by >1 %, then recalibration with oleic acid is required to account for the altered response of the $\nu\mathrm{C{\equiv}N}$ band to

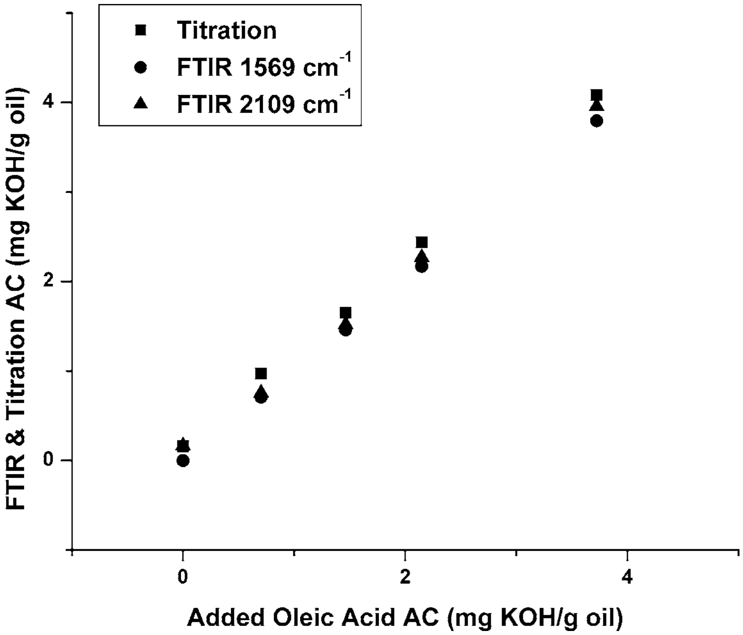

FIG. 4—*Plots of FTIR and titrimetric AC results for a mineral oil spiked with various amounts of oleic acid versus AC values calculated from the spiked amounts. The FTIR results were obtained from measurements of the* ν*C*$\equiv$*N (2109 cm*$^{-1}$*) or the* ν*COO*$^{-}$ *(1569 cm*$^{-1}$*) band in the spectra of ethanolic sodium hydrogen cyanamide extracts of the spiked oils, with the use of Eqs 2 and 3, respectively. The titrimetric data were obtained by extracting the same oils with ethanolic NaOH and back-titrating with HCl.*

changes in AC. Together with storing the reagent solution at −18 °C, this technique provides a means by which the reagent solution can be used for extended periods of time. However, the applicability of this recalibration approach beyond a 10 % decrease in the height of the νC$\equiv$N band has not been tested.

Validation

Table 1 indicates that the acids of concern in in-service oils are primarily organic acids associated with the oxidative breakdown of lubricants or ester additives as well as any strong inorganic acids, although, as noted earlier, many other substances that may be present in oils have some acid character and could contribute variably to FTIR AC values on the one hand and titrimetric AN values on the other. Because the acidity of acids weaker than carboxylic acids is generally not significant in terms of contributing to corrosion, oil quality and impaired functionality, our initial assessments of the FTIR-based AC methodology were carried out using acid-free P-032 mineral oil spiked with defined but varying amounts of oleic acid, serving as a representative carboxylic acid. Each of these samples was split into two halves, which were then extracted with isomolar solutions of ethanolic NaHN−C$\equiv$N and ethanolic NaOH for AC determinations by the FTIR method and by back-titration (inflection endpoint), respectively. In Fig. 4, the FTIR results obtained using the νC$\equiv$N and νCOO^{-} calibration equations (Eqs 2 and 3, respectively), as well as the titrimetric results, are plotted against the actual AC values, calculated from the amounts of oleic acid added to the oil. The corresponding linear regression relationships are presented below:

$$\text{FTIR AC}_{(2109\ \text{cm}^{-1})} = 0.08 + 1.028 * \text{AC}_{\text{spiked}} \quad R = 0.999 \quad SD = 0.07 \tag{7}$$

$$\text{FTIR AC}_{(1569\ \text{cm}^{-1})} = -0.01 + 1.019 * \text{AC}_{\text{spiked}} \quad R = 0.999 \quad SD = 0.02 \tag{8}$$

$$\text{Titration AC} = 0.17 + 1.047 * \text{AC}_{\text{spiked}} \quad R = 0.999 \quad SD = 0.05 \tag{9}$$

Figure 4 graphically illustrates the correspondence between the two sets of FTIR AC measurements as well as between the FTIR and titrimetric results. Furthermore, all three regression equations (Eqs 7–9) have no appreciable intercept and a slope close to unity, indicating that NaHN−C$\equiv$N/ethanol as well as NaOH/ethanol completely extracted the oleic acid spiked into the mineral oil and converted it to its carboxylate salt.

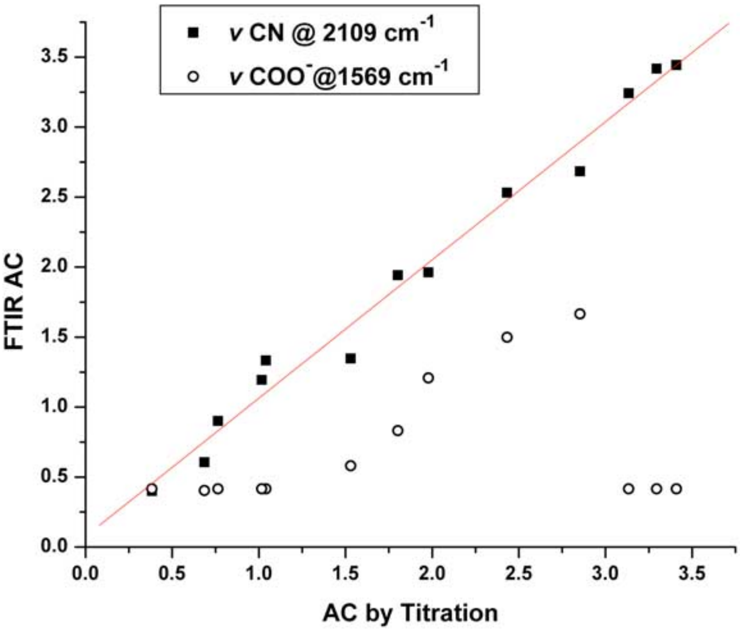

FIG. 5—*AC results obtained for 13 used oils extracted with ethanolic sodium hydrogen cyanamide and measured by HCl back-titration and FTIR analysis. FTIR results based on measurement of the* ν*C≡N band (2109* cm^{-1}*) represent the total acidity whereas the 1569* cm^{-1} *band is specific to organic acids.*

Having demonstrated that the FTIR AC method can accurately measure all acids as strong as or stronger than carboxylic acids, we undertook validation studies using real lubricants. To assess the repeatability and reproducibility of the method, a set of 22 used engine oils of unknown AC was analyzed in duplicate in a single day and reanalyzed several weeks later. The results indicated that the FTIR analyses were repeatable to within ±0.06 mg KOH/g oil and reproducible to within ±0.19 mg KOH/g oil over an FTIR-determined AC range of 0–~2.5 mg KOH/g oil.

The accuracy of the FTIR method was then assessed by extracting 13 of these used oils with the NaHN–C≡N/ethanol reagent solution, with half of each extract being analyzed by the FTIR method and the other half back-titrated with HCl. Figure 5 illustrates the correspondence between the titrimetric results and the FTIR AC results obtained using both the νC≡N and νCOO^- measurements. It is clear that the νC≡N measurement tracks the titrimetric data well, as shown by the following regression equation:

$$AC_{FTIR} = -0.07 + 1.013 * AC_{titration} \quad SD = 0.14 \quad R = 0.991 \tag{10}$$

On the other hand, the νCOO^- measurement does not provide correct AC values, indicating that acids other than carboxylic acids are present in this set of samples; in fact, several of the samples with the highest titrimetric AC values did not exhibit any νCOO^- absorption at all. However, this measurement may be useful diagnostically as it allows the carboxylic acids produced by oil degradation (e.g., oxidation, ester breakdown processes) to be differentiated from other sources of acidity in oils (e.g., combustion blow-by).

Although Eq 10 demonstrates that the FTIR and titration results concur when the base employed in both methods is NaHN–C≡N, it does not necessarily imply concurrence with ASTM titrimetric data obtained using KOH, a stronger base. Thus, a second experiment was carried out by analyzing 27 used-oil samples independently preanalyzed by a commercial laboratory using ASTM D664-89. Figure 6(*a*) presents a plot of the FTIR data versus the commercial laboratory results for this series, which yielded the following linear regression equation:

$$AC_{FTIR} = 0.035 + 0.767 * AN_{titration} \quad SD = 0.11 \quad R = 0.622 \tag{11}$$

Overall, the FTIR-determined AC is ~25 % lower than the AN determined by titration, indicating that these samples contain some weakly acidic substances that are more reactive with KOH than with NaHN–C≡N. The relationship appears quite poor from a correlational standpoint (R=0.62), largely owing to the narrow AN range spanned by these samples. Thus, in Fig. 6(*b*) these data are combined with

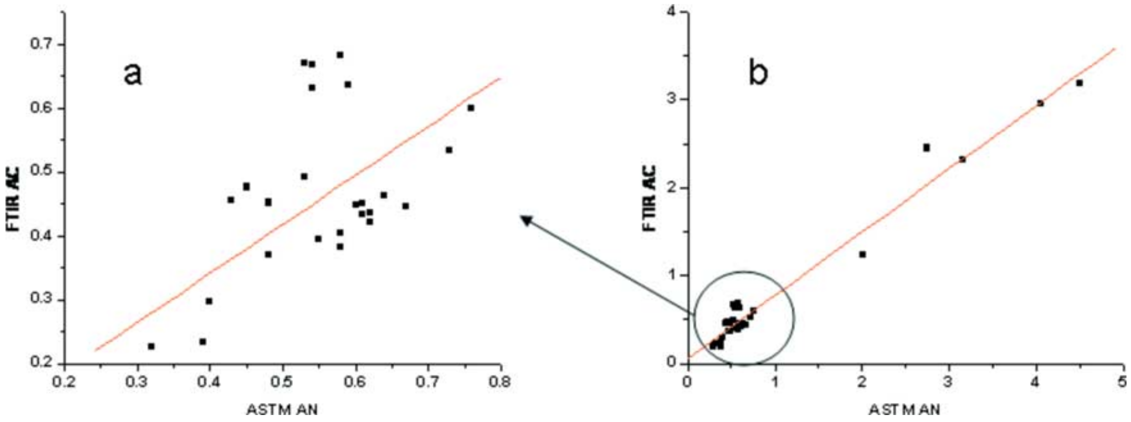

FIG. 6—*(a) Plot of FTIR AC results for 27 used oils versus AN data obtained in a commercial analytical laboratory by ASTM D664-89 potentiometric titration. (b) Combined plot for the 27 used-oil samples and five compressor oil samples spanning a broader AN range.*

those obtained for five compressor oils spanning a much broader AN range, for which the titrimetric data were obtained in our laboratory by extracting the oils with ethanolic NaOH and back-titrating the extracts with HCl. Linear regression of the data for this enlarged sample set yielded the following relationship:

$$AC_{\mathrm{FTIR}} = 0.060 + 0.718 * AN_{\mathrm{titration}} \quad SD = 0.14 \quad R = 0.985 \tag{12}$$

Although the SD of the new relationship is slightly greater, there is a substantial drop in the coefficient of variation (from ~12 % to ~3 %), simply owing to the broadening of the AN range. Given that the FTIR and titrimetric procedures are completely different and use two different bases, their results are surprisingly well correlated. Clearly, more extensive validation studies will be required with a much wider variety of oils before any definitive conclusions can be reached as to the overall performance of this FTIR method relative to titrimetric ASTM methods. Even if there is a reasonable correlation, it is best to clearly differentiate these measures (AC as opposed to AN). In this context, it is our contention that only organic and stronger acids are of concern from an oil quality or corrosion standpoint, and thus for in-service oils AC values will be just as meaningful as (or possibly more meaningful than) AN values obtained by established ASTM methods using stronger bases.

Potential Benefits of the FTIR AC Method

FTIR AC determination is similar in principle to the ASTM titrimetric AN methods but very different in procedure, and, as such, its advantages are manifold. These include simplicity, a traceable and defined calibration, no issues of variable and poorly defined endpoints to contend with, as well as economic and environmental benefits associated with the very substantive reduction in consumables and waste oil/solvent disposal. In its automated form, implemented on a COAT (Continuous Oil Analysis and Treatment) system, as described in Materials and Methods, the software-controlled system has the capability to analyze ~120 pre-extracted samples per hour, a very substantive speed advantage over any automated titrimetric AN systems currently available. In this context, most lubricant analysis laboratories already have automated or semi-automated FTIR systems dedicated to qualitative condition monitoring of lubricants, the utility of which can be enhanced by implementation of the FTIR AC analysis. In addition, the functional-group information inherent to the AC method allows differentiation between organic and other acids contributing to the acidity of lubricants, data that may be of additional diagnostic value.

Conclusion

The objective of this study has been to lay the groundwork for a simple and readily automatable FTIR-based procedure for determining AC of lubricating oils. Based on the results of this development study, the indications are that this AC method could be a viable alternative to titration-based AN determinations, producing accurate and reproducible results that are comparable within the method and which roughly correlate with ASTM titrimetric methods. However, careful and extensive validation work will be required to solidify this conclusion, bearing in mind that comparison of the results from different AN methods is problematic in its own right as the magnitude of the values is strongly method-dependent. For these reasons as well as its ability to differentiate between organic acid and inorganic acid contributions, the FTIR measure has been designated AC so as to avoid its confusion with the various ASTM titrimetric AN methods.

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