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An Overview of Progress and New Developments in FTIR Lubricant Condition Monitoring Methodology

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ABSTRACT: Fourier transform infrared (FTIR) spectroscopy has found an important analytical niche in the field of condition monitoring (CM) of lubricants, lubricant quality being a primary determinant of the wear and operational efficiency of engines and machinery. The ability to track a wide range of functional groups associated with chemical changes in lubricants by FTIR spectroscopy allows the overall quality of lubricants to be assessed and informed decisions made as to whether a lubricant needs to be replaced or not. Newer automated FTIR systems in centralized laboratories are now capable of analyzing oil samples at rates of >120 samples/h, providing trending information on soot, moisture, glycol, oxidative status, anti-wear additives, and nitration, amongst other measures. The current FTIR CM methodology is based on ASTM Standard Practice E2412-10 and is restricted primarily to petroleum or mineral oils; however, the ability to spectrally classify oils could overcome this limitation and broaden the scope of the methodology substantially. Quantitative FTIR methods have come to the fore to carry out more specific measures related to oil condition, specifically the determination of acid content and base content, as well as moisture. These methods have been designed to overcome some key limitations associated with the corresponding ASTM titrimetric procedures and expand the overall utility of FTIR instrumentation in centralized lubricant analysis laboratories. This paper provides an overview of FTIR CM, how it has been and can be further improved, and discusses the recent advances in the newer quantitative FTIR CM methods as well as the issues that need to be addressed to further enhance the utility of FTIR spectroscopy in relation to lubricant analysis.

KEYWORDS: lubricant analysis, FTIR spectroscopy, acid number, base number, moisture content, spectral reconstruction

Introduction

Lubricants undergo complex chemical changes when in-service as a result of thermal, physical, and oxidative stresses imposed on them as they lubricate moving surfaces. Whether they perform their task adequately depends on their formulation and their "condition" as a function of time. Although the term condition is rather nebulous, it implies a measure of changes in the quality of the lubricant relative to its original formulation and its ability to perform the lubrication task for which it was originally designed. Depending on the application, the loss of lubricant performance may range from problematic to catastrophic—in the case of a bicycle chain, lubricant failure may make pedaling harder, whereas a bearing malfunction due to poor lubrication in a jet engine clearly has more serious consequences. Lubricant condition monitoring (CM) tends to focus on factors known to affect equipment performance and reliability and aims to enable informed decisions to be made as to whether there is a need to replace the lubricant or in some instances to re-additize [1]. Although time- or mileage-based criteria can be and often are used to schedule lubricant changes, CM affords the possibility of optimizing lubricant use by avoiding unnecessary changes while simultaneously safeguarding against premature lubrication degradation and consequent machinery failure. Typical examples of sectors where CM is a cost-effective and useful diagnostic tool include the military, the transportation sector, and various industrial sectors operating heavy equipment that is expensive and requires organized ongoing service and maintenance.

Lubricant CM can involve a wide variety of measures, including wear metals, magnetic metal debris, oil particle counts, viscosity, acid number (AN) or base number (BN), soot, levels of specific additives (e.g., anti-wear, antioxidants) and specific contaminants (e.g., moisture and glycol), as well as the lubricant's overall oxidative status [2,3]. Fourier transform infrared (FTIR) spectroscopy has emerged as a CM

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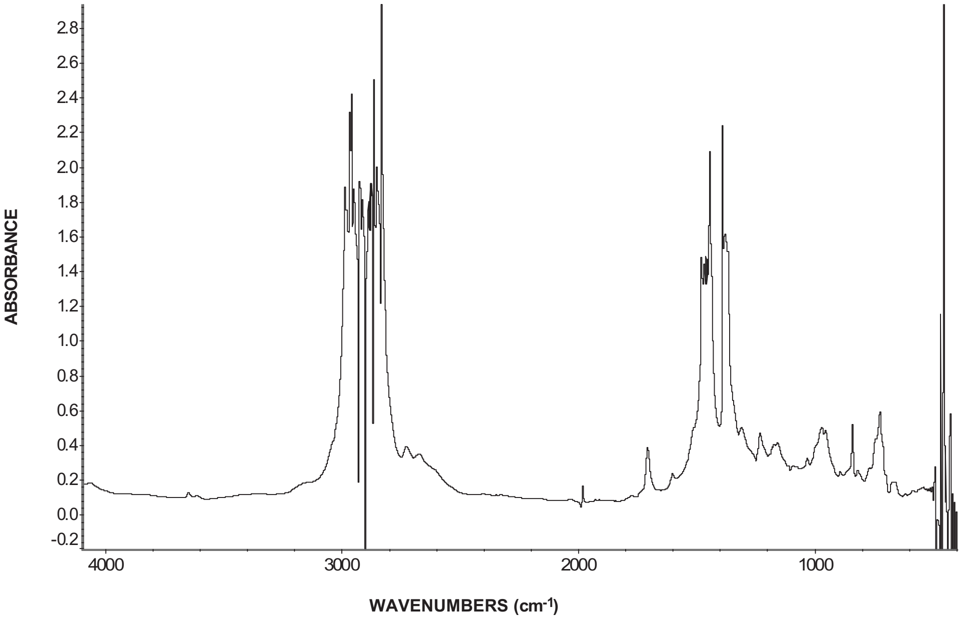

FIG. 1—*Spectrum of a typical new mineral oil based commercial motor oil formulation.*

tool of choice because it provides a simple means of screening lubricants for a wide range of important lubricant quality parameters, yielding a wealth of information in a matter of minutes [4,5]. Because most oil constituents and contaminants have fairly distinct infrared (IR) signatures, FTIR spectroscopy can provide much of the basic oil condition information required to make a determination as to whether the oil is potentially problematic, either by comparing its FTIR spectrum with that of a reference oil or by trending the in-service oil over time without using a reference oil. Beyond this essentially *qualitative* approach, FTIR spectroscopy has also been developed as a *quantitative* analytical tool that can be applied to determine acid content (AC), base content (BC), and moisture content in lubricants [6]. These quantitative FTIR methods provide laboratories with rapid, automated, and high-throughput alternatives to conventional ASTM titrimetric procedures. In this paper, we examine the benefits of FTIR CM, its limitations and enhancements, as well as the newer quantitative methods and their more recent enhancements.

IR Spectroscopy

All organic molecules absorb IR energy at specific wavelengths that match the frequencies of their molecular vibrations. Indeed, a pure compound has a unique IR spectrum that represents a “fingerprint” from which it can be definitively identified. Similarly, a well-defined mixture of compounds, such as a new lubricant, has its own characteristic spectrum, representing the overlap of the spectral contributions of all the individual components making up the mixture (Fig. 1).

One of the strengths of IR spectroscopy derives from the fact that specific functional groups, such as CH_3, CH_2, OH, COOH, NH_2, etc., each absorb in defined wavelength regions, allowing one to ascertain their presence in a sample and, to some degree, the relative proportions of each. This capability to provide functional-group information is one of the underlying principles of FTIR CM analysis, in that many of the chemical changes occurring in in-service oils over time are associated with the formation or loss of particular functional groups. Similarly, the quantitative lubricant analysis methods described in this paper have all been designed around the concept of functional-group absorptions and their adherence to Beer’s law (i.e., the direct proportionality between the concentration of the functional group in the sample and the intensity of its absorption in the sample’s IR spectrum).

Qualitative FTIR CM

Owing to the variability and the complexity of the IR spectra of lubricants, FTIR CM of in-service lubricants is usually a comparative trending procedure. The basic premise is to track spectral changes over time and associate these changes with well-defined and known quality changes or objective measures thereof. Although it was recognized early on that IR spectroscopy had potential as a screening tool for assessing in-service lubricant quality [3,5], the concept was not developed in a structured manner until the backing of the U.S. military establishment was placed behind the effort. In the mid-1990s, FTIR CM protocols were elaborated for the Joint Oil Analysis Program (JOAP) of the U.S. military, with much of this fundamental development work being carried out by Toms [7–10] at the JOAP Technology Support Center. The basic premise underlying the JOAP initiative was that routine FTIR examination of in-service oils could be employed to monitor their condition so as to minimize mechanical failures in the field and lead to improved use of lubricant resources. The development work conducted by Toms involved an extensive study of the typical spectral changes taking place in in-service mil-spec oils over time, supplemented by experiments in which components were spiked into the oils to simulate various types/levels of contamination. This seminal work focused on relating specific spectral changes to well-known deteriorative processes, such as the loss of anti-wear additives, ingress of moisture, oxidation, soot accumulation, and glycol contamination, amongst others, which will be referred to in this paper as CM parameters, and ultimately led to the development of ASTM E2412-10, Standard Practice for Condition Monitoring of Used Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry [11]. The rapid and centralized analysis of in-service lubricants was also facilitated by the commercialization of automated FTIR analyzers for lubricant CM [12,13], which CM laboratories commonly link to a laboratory information management system (LIMS) to produce concise reports on lubricant quality specific to the equipment from which the oil was sampled [13]. If trend lines derived from the FTIR CM parameters as a function of time/mileage have been developed for the equipment in question and correlated with oil quality, FTIR CM analysis can serve to trigger an objective "treat oil" or "change oil" action, as discussed in ASTM E2412-10. Although maximizing the effectiveness of FTIR CM in this manner can be a fairly sophisticated undertaking, it has real benefits, in terms of both lowering lubricant costs and reducing mechanical failures, for organizations that have large equipment inventories or fleets. However, even in the absence of such an experiential database, equipment operators can still benefit from general assessments made by experienced commercial laboratories based on FTIR CM data.

Current FTIR CM Procedures

Typically, representative oil samples are taken periodically from the equipment of interest and sent to a laboratory for FTIR analysis. As in all types of CM, sampling intervals are scheduled on the basis of the type of equipment, its operating conditions, the type of oil, and available historical data. At the laboratory end, samples are typically loaded into an auto-sampler tray, one of the strengths of FTIR spectroscopy being its ability to automatically analyze an oil sample "as is." The sample is pumped from the sample bottle, usually via a peristaltic or syringe-pump, into a 100 μm ZnSe transmission cell, and its IR spectrum is then collected in <1 min. Under software control, the specific absorbance or peak area measurements that have been defined for the various CM parameters [11] are then made, and the resulting information is exported to LIMS for reporting. The cell is subsequently rinsed with an oil-miscible solvent and re-loaded with the next oil sample and the process is repeated.

It should be noted that FTIR CM results are not necessarily comparable from one laboratory to another when ASTM Standard Practice E2412-10 is followed, as the latter allows for a certain amount of latitude in the instrument settings. For this reason, ASTM Sub-committee D02.96-03 has developed a new Standard Practice (ASTM D7418–07, Standard Practice for Setup and Operation of Fourier Transform Infrared (FTIR) Spectrometers for In-Service Oil Condition Monitoring [14]), which standardizes the instrument configuration and data collection protocol so that the spectral information collected for the same sample in different laboratories should be comparable. In addition, depending on the instrument manufacturer and its software, the algorithms (regions and baselines) used to measure the various FTIR CM parameters are not necessarily identical, and thus Sub-committee D02.96-03 has developed Refs 15–18 and is continuing to develop test methods associated with the practice to standardize these individual measures.

Analytical Issues

A major complicating factor associated with FTIR CM analyses is that data interpretation can be heavily dependent on the oil formulation because IR absorption bands of the oil may interfere with measurement of the spectral changes that are to be monitored in in-service oils over time. An illustrative example is provided by ASTM D7414-09, Standard Test Method for Condition Monitoring of Oxidation in In-Service Petroleum and Hydrocarbon Based Lubricants by Trend Analysis [16]. This method makes measurements in the carbonyl absorption region of the spectrum where organic esters and acids absorb. In terms of monitoring oxidation, such a measurement is valid in the spectra of purely hydrocarbon-based oils, but meaningless in the spectra of ester-based oils because the carbonyl absorption band of the ester linkage will swamp that of any organic acids and esters produced by oxidation. It is for this reason that the scope of the above ASTM method is restricted to "petroleum and hydrocarbon-based lubricants," as its title indicates. For similar reasons, ASTM E2412-10 addresses three lubricant categories individually [i.e., petroleum-based (crankcase) lubricants, extreme-pressure (EP) fluids, and polyol ester fluids] in relation to which CM parameters are meaningful and how spectral measurements (region and baseline) are to be made for these parameters. However, within any such category, there will be a wide range of proprietary formulations marketed by various lubricant suppliers as well as unique formulations designed for specialized applications, and these formulation differences will manifest themselves in the FTIR spectra of the oils, again complicating the interpretation of FTIR CM data. Within this context, two FTIR CM analytical approaches have evolved: Direct trend analysis and differential trend analysis, both of which have merits and limitations. Direct trend analysis works on the assumption that spectral changes over time that are superimposed on the spectrum characteristic of the oil in question can be tracked to develop an oil degradation profile and intervention criteria. Differential trend analysis is a more rigorous procedure that involves collecting the spectrum of an in-service oil sample and subtracting from it the spectrum of the corresponding "fresh" oil or other appropriate reference oil, such that the net spectral changes that have taken place are isolated in the difference spectrum [19]. This approach works well if the oil is well-defined and one can be assured that it has not been topped up with some other oil. Direct trend analysis is more practical, but less rigorous, good for the routine monitoring of, for example, oils obtained from a truck fleet, where the oils employed are generally similar. Differential trend analysis is more exacting and is more attuned to examining gear or compressor oils, where the oil formulation is quite specific, the same oil is expected to stay in use for long periods of time, and changes in moisture, oxidative status, and additives are important degradation indicators. However, this approach requires that the spectrum of the appropriate reference oil be available in a spectral database or recorded as part of the sample analysis protocol. Ultimately, neither the direct nor the differential approach is entirely satisfactory, the first from the standpoint of formulation dependence and the second from the standpoint of practicality. It should be noted that both these approaches are encompassed within ASTM E2412-10 [11] and ASTM D7418–07 [14] as well as in the associated test methods [15–18].

Broadening the Analytical Scope of CM

In light of the issues discussed above, it would be useful to devise a general spectral classification system for oils so that the selection of appropriate CM parameters and associated spectral measurements can be made solely on the basis of the spectral characteristics of the oil formulation. Although spectral searching and matching routines are addressed in general terms by ASTM E2310-04 [20], several challenges will have to be addressed in developing this concept. One of the major challenges is to achieve correct classification of in-service oils that have undergone chemical changes (e.g., oxidation, additive depletion, soot buildup, etc.), given that the corresponding spectral changes represent confounding factors for the classification. A potential means of addressing this challenge investigated by the present authors involves the use of region selection algorithms to optimize classifiers at each branch of a "decision tree;" however, further research will be required to validate this approach. If successful, oils could not only be grouped on the basis of their spectral similarities and categorized accordingly, but appropriate FTIR CM analytical protocols could be developed for each oil "category" and validated in terms of spectral regions where measurements could best be made for the appropriate parameters of interest. As noted above, ASTM E2412-10 specifies FTIR CM measurement parameters for only three classes of lubricants (petroleum lubricants, EP petroleum lubricants, and polyol esters), and although the possibility of encompassing other lubricant types as data becomes available is mentioned in ASTM E2412-10, it has yet to come to fruition. If a generalized oil classification system were to be devised for existing commercial formulations and updated as new ones come on stream, efforts to broaden the scope of FTIR CM to encompass a wider range of oils would be facilitated. Although it will be difficult to demonstrate the universal reliability of this approach to FTIR CM, given the very large number of lubricant products currently on the market, the use of a spectrally based classification system should provide safeguards against sample misclassification that are lacking in present-day FTIR CM. In addition, such a system could overcome the general confusion associated with trade names and "end-use" lubricant designations (e.g., ester versus mineral versus synthetic versus EP fluid versus compressor oil, etc.). Trade names and end-use nomenclature are used interchangeably in the industry but the products do not necessarily have a common denominator in terms of the base oil or additive package, which often leads to confusion as well as analytical anomalies. A spectral classification system encompassing a wide range of oil formulations from mineral to ester-based, and combinations thereof, as well as other oil types (e.g., phosphate esters, polyalkylene glycol oils, etc.) could ultimately provide a simplified cross-referenced chemical/functional categorization scheme for thousands of brand-name lubricants, providing lubricant purchasers with a useful means of identifying and selecting among alternative products for a given application.

CM Improvements

The comments above indicate that FTIR CM, although used extensively and cost effective, is still a technology that has significant room for improvement to make it a more utilitarian analytical tool. Aside from these considerations, a recent advance in FTIR CM has been the implementation of *spectral reconstitution*, a technique that has a major impact on sample throughput and solvent use. With this technique, the viscosity of the oil sample is reduced by diluting it with low-cost kerosene or odorless mineral spirits (OMS) containing a unique spectral marker, thus allowing the sample to be pumped more rapidly into the IR transmission cell and eliminating the need for a solvent rinse between samples [21]. The presence of the spectral marker in the diluent then allows the spectrum of the original neat oil sample to be obtained via spectral reconstitution by quantitatively stripping out the spectrum of the diluent; Figure 2 presents a schematic diagram of how spectral reconstitution works.

The spectral reconstitution technique has been implemented on Thermal-Lube's continuous oil analysis and treatment (COAT) System, an integrated auto-sampler and FTIR analyzer (Fig. 3) that uses a single low-dead-volume pump to load diluted samples into the IR transmission cell, with each sample being rinsed out by flowing the next sample through the cell. The fact that a spectral marker is present also allows the dilution to be approximate, the marker measure determining the precise dilution. Aside from the substantial analytical speed benefits conferred (up to 180 samples/h versus 20–30 samples/h with conventional peristaltic- or syringe-pump-based FTIR auto-sampler systems [22]), spectral reconstitution also minimizes cell wear, allows the use of low-cost KCl cell windows (versus ZnSe), and requires less sample and solvent, thus minimizing the environmental impact associated with the oil and solvent waste generated. All the procedural elements of FTIR CM in accordance with ASTM D7418–07 are followed except that the neat oil spectrum is not measured directly but is instead reconstituted from the spectrum of a diluted sample. Extensive comparisons of CM data obtained under standardized conditions by the spectral reconstitution technique and by conventional FTIR analysis of the corresponding neat oil samples indicate that the two procedures effectively provide identical data [21].

Quantitative FTIR Analysis

As noted earlier, FTIR spectroscopy is not restricted to providing CM trending data but is also capable of delivering quantitative analytical data for key oil quality parameters, specifically AN, BN, and moisture (H_2O). For in-service oils, these three parameters are all important oil quality indicators that are routinely analyzed for and quantified, usually after CM screening procedures point to a potential problem with the oil. Depending on the application, lubricants in most non-combustion-related applications tend to acidify largely as a result of oxidative processes producing relatively weak organic acids while in most combustion applications, the acidity is contributed by both oxidation and blow-by gases, the latter producing strong acids (nitric, sulfuric). AN analysis tends to be restricted to low-ash oils, which do not contain acid-neutralizing base additive packages (e.g., compressor oils) as they slowly accumulate acidity by oxidation. BN analysis is associated with high-ash oils containing base additive packages (commonly known as detergents) to counteract more rapidly accumulating stronger acids. Thus, the formation of acids in these types of oils does not result in acid accumulation but rather in the loss of the reserve alkalinity, and it is this loss that is measured in BN analysis. Closely related to both of these measures is moisture, which, being both a reactant and a reaction medium, is closely linked to acidity-related corrosion as well as a

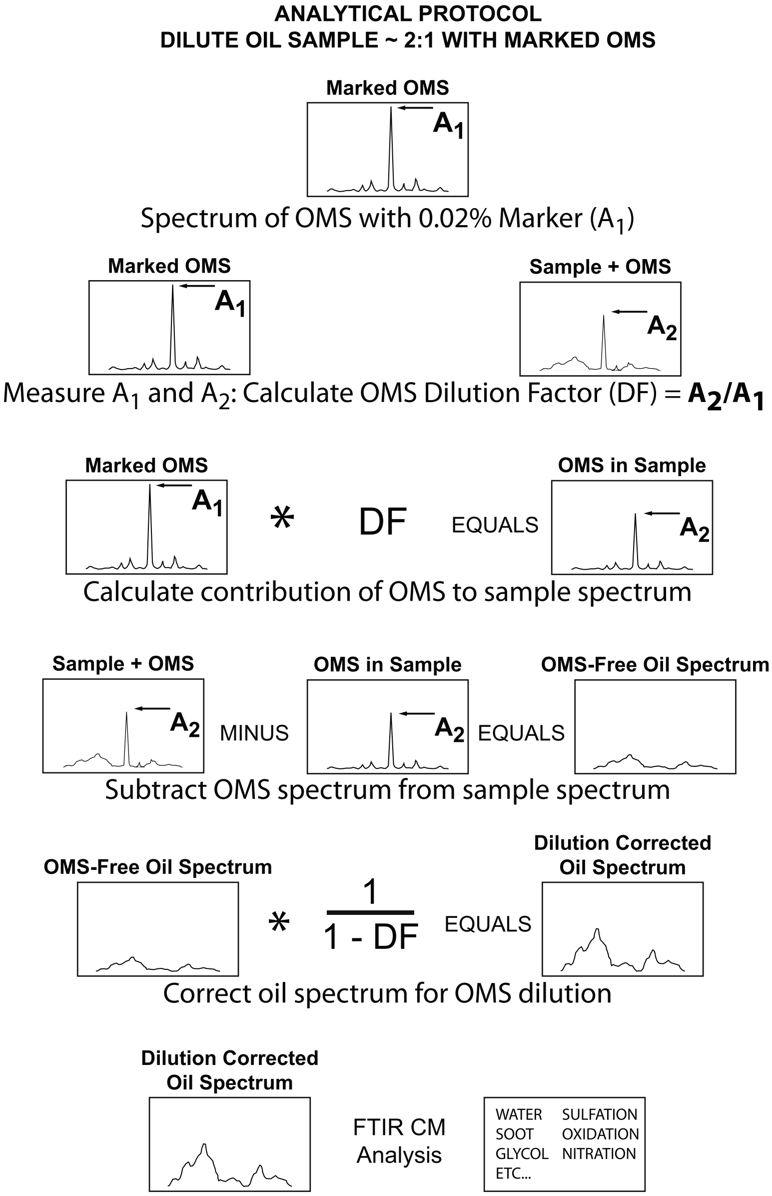

FIG. 2—*Schematic diagram showing the spectral manipulations required so that an oil sample that has been diluted with OMS or kerosene containing a unique spectral marker is mathematically transformed back into the spectrum of the original neat sample.*

variety of other detrimental changes that can take place in oils when it is present.

The ASTM methods for AN and BN and for moisture determinations, utilizing acid-base and Karl Fischer titration, respectively, are generally acknowledged to be problematic, of limited accuracy and reproducibility, and relatively expensive to carry out from the standpoint of equipment and reagents. For these reasons, substantial efforts have been employed to develop automated FTIR methods for these analyses that are simpler, less costly, and more reliable than the ASTM titrimetric procedures. As described more fully in the following paragraphs, this methodology development work has been an iterative process, aimed at simplifying the workable methods originally developed [23,24] as well as increasing sample throughput rates. In addition, measures of acidity and reserve alkalinity obtained by the FTIR procedures have been differentiated from the traditional AN and BN measures by being recast as AC (AC_{pK_a}) and BC (BC_{pK_a}), respectively, where the subscript represents the pK_a of the spectrally active base or acid employed in the FTIR determinations. AC and BC data are expressed in units of mEq acid/g oil and mEq base/g oil, respectively, but can be readily converted to the units of AN and BN (mg KOH/g oil); however, the values obtained will generally not match those obtained by ASTM titrimetric methods owing to the differences in the pK_a values of the "titrants" employed in the FTIR and ASTM methods

FIG. 3—*The COAT system, an integrated auto-sampler and FTIR analyzer designed for lubricant analysis, capable of carrying out qualitative FTIR CM as well as analyzing oils quantitatively for AN, BN, or* H_2O *at throughput rates of up to 180 samples/h.*

Acid Content

The ASTM methods for the determination of AN, such as the widely employed ASTM D664-09a [25], are designed to measure acidity accumulation in a range of oil and lubricant products, such as the accumulation of acidic combustion by-products and acids formed by oxidation, or to measure corrosive naphthenic acids commonly found in crude oils [26]. For FTIR AN determinations, the original method [23] was based on the stoichiometric reaction of a spectrally active base, potassium phthalimide, dispersed in oil-miscible 1-propanol, with acids present in the oil. The calibration was developed by reacting the potassium phthalimide reagent solution with 4-nitrophenol and measuring the absorbance of the product (neutral phthalimide), which exhibits an intense band at 1727 cm^{-1}. In the analysis of oils, any interfering oil absorptions were accounted for by preparing two samples: One with the active reagent (potassium phthalimide in *n*-propanol) and one with a blank reagent (1-propanol). Although workable, this dual-sample procedure is clearly cumbersome, and consequently subsequent work focused on eliminating the requirement to prepare sample blanks. This objective was met by selecting sodium hydrogen cyanamide (NaHNCN) as the spectrally active base [27]. Because NaHNCN, unlike potassium phthalimide, could be solubilized in a solvent (ethanol) that is immiscible with most oils, the need to prepare a sample blank to compensate for spectral interferences associated with the oil matrix was eliminated for most types of samples. NaHNCN (pK_a of ~9.5) is basic enough to react fully with all organic (carboxylic) acids and stronger acids that may be present in oil samples. As a result of the acid-base reaction, the $\nu\text{C}{\equiv}\text{N}$ band of NaHNCN, which is observed at 2109 cm^{-1}, is lost in proportion to the total amount of acid present. Any organic acids present are converted into their carboxylate salts (COO^-) and measured separately at 1570 cm^{-1}. Accordingly, this FTIR method not only measures acidity but also differentiates between the types of acidity present, providing additional information that may be useful in assessing the corrosion

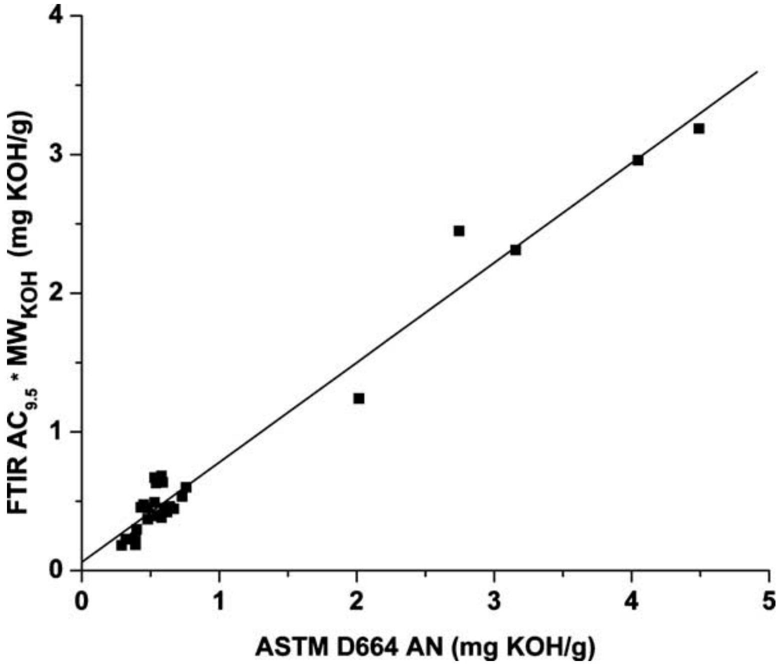

FIG. 4—*Plot of FTIR AC results for 32 in-service oils versus AN data obtained by ASTM D664-09a potentiometric titration. A plot of the same data was previously published in Ref 27 (note: In the latter publication, FTIR AC values were reported in units of mg KOH/g rather than mEq acid/g).*

potential associated with the acidity in the oil. Oleic acid, a carboxylic acid and hence considered representative of the weakest acids found in in-service oils that are of significance from a quality standpoint, is used for calibration, standards being prepared by direct addition of this acid to the NaHNCN/ethanol reagent solution. The calibration equations are formulated in terms of unit acidity (mEq acid/mL of reagent solution) to make them universally applicable (i.e., independent of the sample preparation protocol); in the analysis of oils, the values of total and organic unit acidity obtained from the FTIR analysis are each multiplied by the volume of reagent solution added to the oil sample and divided by the weight of the oil sample to yield total AC and organic acid content (OAC) in units of mEq acid/g oil, with any difference between AC and OAC being considered to be the inorganic acid content.

Implementation of the FTIR AC method on an auto-sampler-equipped spectrometer allowed for the automated analysis (after sample preparation) of up to 180 samples/h, representing a significant increase in analytical throughput relative to autotitrators. A comparison between the FTIR results (multiplied by the molecular weight of KOH to express them in the same units as AN) determined for 32 in-service oils and their AN values, determined by ASTM D664-09a, is shown in Fig. 4 and yielded the following linear regression relationship:

$$(AC_{9.5} \cdot MW_{\mathrm{KOH}}) = 0.06 + 0.72 \cdot AN_{\mathrm{titration}} \quad SD = 0.14 \quad R = 0.985$$

These results indicate that although the FTIR method produces lower values than KOH titration, which is attributable to its use of the weaker base NaHNCN, there is a good correlation between the FTIR and titrimetric results.

A somewhat similar FTIR AC method is being developed specifically for phosphate esters, commonly used as fire-retardant hydraulic fluids in power-plant compressor hydraulic speed control systems [28] and other high-temperature applications. These esters develop acidity predominantly via hydrolysis. There is great interest in differentiating between the more weakly acidic partial hydrolysis products and the stronger and more corrosive phosphoric acid. Acid formation is the primary contamination parameter for this type of fluid. By using carefully selected IR-active bases of known pK_a, the FTIR AC method is capable of differentiating between these hydrolysis products (F. R. van de Voort and T. Yuan, manuscript in preparation [29]). Thus, in general terms, FTIR AC methodologies are not only rapid and automated procedures but are also capable of providing more specific information in terms of the nature of the acidity.

Base Content

As noted earlier, BN measurements are designed to measure the reserve alkalinity in lubricants. Overbased detergents are common additives in oil formulations destined for combustion engines, with the amount of base (usually metal carbonates) incorporated being a function of the acidity the lubricant is expected to encounter. Thus, marine engines, burning high-sulfur bunker C crude, require high levels of base formulated in their crankcase oils to counter the acidity generated as the fuel is burned, while for truck diesel engines burning low-sulfur diesel, the base requirement is much more modest. In addition to detergents, dispersants also tend to have basic characteristics and these may also contribute to the measured BN of an oil, depending on the BN method used. ASTM D2896-07a [30], which uses perchloric acid, is considered to measure all basic materials present whereas ASTM D4739-08e1 [31], which uses HCl, is considered to predominantly measure the metal carbonates in the detergents, but little, if any, of the dispersant contribution. This distinction is not necessarily adhered to, such that in-service oils are often analyzed by either method, leading to some confusion in relation to inter-laboratory results obtained for the same sample analyzed by different methods. For the FTIR analysis, trifluoroacetic acid (TFA) in 1-propanol has been selected as the spectrally active acid employed to react with the bases present in oils [23]. Because TFA has a pK_a of $\sim$0.5, it is strong enough to react with metal carbonates (e.g., $CaCO_3$), but not with weaker basic dispersants. Like the FTIR AN method, the original FTIR BN method [23] required the preparation of two samples to obtain a single BN measure. This method has recently been upgraded to a single-sample procedure (S. Ehsan, J. Sedman, F. R. van de Voort, E. Akochi-Koblé. T. Yuan, and D. Takouk, manuscript submitted for publication [32]) with its measurement being recast as BC to differentiate it from the traditional BN measure. The base employed for calibration has been changed from dodecylamine to 1-methylimidazole, which is a liquid and therefore easier to handle. As in the original method, the reagent solution employed is TFA in *n*-propanol. The use of a more polar solvent such as ethanol caused detergents present in the fluid to coalesce and form a gel, preventing the acid-base reaction from going to completion. Even with the 1-propanol reagent solution, this problem was highly prevalent with new high-BN oils and additives but was overcome by diluting the oil sample with heptane. In contrast to the AC method, in which matrix effects are minimized owing to the immiscibility of most oil samples with the reagent solution, the BC method relies on the use of second derivative spectra computed using a gap-segment algorithm to minimize spectral interferences. The latter algorithm, which has been extensively employed in near-IR spectroscopy [33], incorporates smoothing into the derivative calculation and therefore provides second derivative spectra with superior signal-to-noise ratios compared to conventional second derivative spectra (computed by the simple first-difference approach). In addition, because quantitation of BC is based on a universal calibration in terms of unit basicity (mEq base/mL of reagent solution), the spectra collected for samples are mathematically corrected to compensate for oil miscibility with the reagent solution by employing a spectrally determined dilution factor. Validation studies of this single-sample BC method conducted to date have indicated that the use of a universal calibration in combination with a spectral dilution correction and a gap-segment second derivative is a viable means of obtaining quantitative results, without necessarily having to resort to the use of an oil-immiscible solvent to aid in minimizing oil spectral interferences. Figure 5 presents typical results of these ongoing validation studies, yielding the following relationship between the FTIR $BC_{0.5}$ results (multiplied by the molecular weight of KOH) and BN values obtained by ASTM D2896-07a (perchloric acid titration) for a set of 18 in-service oils

$$(BC_{0.5} \cdot MW_{\mathrm{KOH}}) = 0.79 \cdot BN_{\mathrm{D2896}}; \quad SD = 0.52; \quad R = 0.978$$

Given the use of a much weaker acid in the FTIR method, the fact that the slope of the regression line (forced through the origin) is <1 is to be expected for samples that contain weak bases, while the correlation between the FTIR and titrimetric results is surprisingly good. In this regard, it may be noted that the correlation coefficient is only reduced slightly (to 0.966) when the two samples falling below the BN range of 6–10 mg KOH/g are excluded from the regression.

Moisture

The third FTIR method of consequence is the measurement of moisture in lubricants based on a simple acetonitrile extraction procedure [34]. The premise is that most hydrophobic lubricants are largely immiscible with polar acetonitrile. The water can be extracted from the oil and readily be measured spectrally

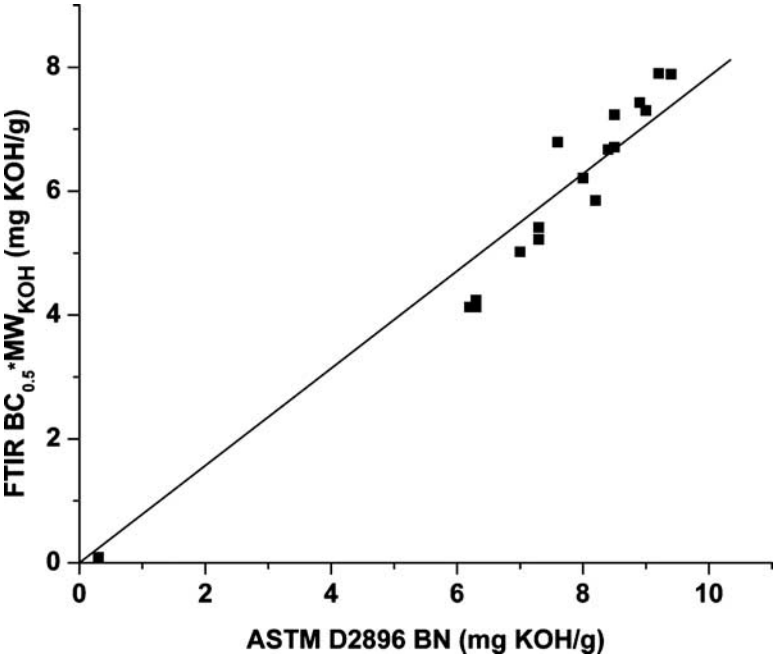

FIG. 5—*Plot of FTIR $BC_{0.5}$ results for 18 in-service oils versus BN data obtained by ASTM D2896-07a potentiometric titration.*

from a differential spectrum obtained by subtracting the spectrum of dry acetonitrile from that of the acetonitrile extract obtained from the oil. It was been found that this simple extraction procedure tracks Karl Fischer moisture determinations very well and is reproducible and adequately sensitive. Like AN and BN analyses, this procedure, in its automated form and implemented on the COAT system, can attain FTIR throughput rates of up to 180 samples/h after sample preparation. A moisture calibration is developed simply by adding defined amounts of water to dry acetonitrile. Since its development, this methodology has been generalized and improved significantly, in particular from the standpoint of the determination of the absolute moisture content of acetonitrile through the addition of D_2O. The use of D_2O is workable because acetonitrile is an aprotic solvent and hence does not undergo any H–D exchange. Thus, any H_2O present in the acetonitrile will fully exchange with an excess of added D_2O to produce HOD, quantitatively, thereby eliminating the 1630 cm^{-1} band arising from the H–O–H bending vibration. Thus, measurement of this band in a differential spectrum obtained by subtracting the spectrum of the D_2O-treated acetonitrile from that of the acetonitrile prior to D_2O addition provides an absolute measure of the moisture present in the acetonitrile. Not only does this provide knowledge of the moisture content of the extracting solvent, but this concept can be taken further to provide absolute moisture contents in oils. Further generalization of the method includes the ability to work with samples that are partially miscible with acetonitrile, using measurements of the intensity of an acetonitrile overtone band to compensate for density and/or dilution effects and, as in the BC method, employing the gap-segment second derivative to minimize spectral interferences.

Principles of Quantitation

There are some common denominators associated with how quantitation is achieved in the FTIR methods for the determination of AC, BC, and moisture, albeit with some differences in the details, which will not be elaborated on here.

One of the key principles is that the calibrations are all simply based on adding various known amounts of the component of interest [i.e., a representative acid (oleic acid), a representative base (1-methylimidazole), or H_2O] to a reagent solution (AC and BC calibrations) or a pure solvent (moisture calibration) and obtaining a linear regression equation relating the parameter in question (AC, BC, or moisture) to a spectral response at a single wavelength in the absorbance or second derivative spectra of these calibration solutions. Such calibrations are very easy to develop and understand and independent of sample characteristics. Critical to the application of these calibrations in the analysis of oil samples is the capability to correct for any dilution or change in density of the reagent solution/solvent, the extent of which will depend on the degree of miscibility of the sample in question, or particular components therein, with the solvent employed. Thus, while the correction for a predominantly immiscible sample would be negligible, a miscible sample would displace a very significant portion of the solvent and hence a substantial correction must be made to compensate. This correction is accomplished by employing a weak solvent overtone band as a measure of the "amount" of reagent solution/solvent in the cell and determining the correction factor (spectral multiplier) that will make the intensity of this band equal to its intensity in the spectrum of the reagent solution/solvent employed in the calibration procedure; when this correction factor is then applied to the spectrum, one is effectively "filling" the IR cell with the reagent solution/solvent. This procedure facilitates the use of these simple universal calibrations, devoid of sample spectral contributions. Of course, any miscibility brings with it some potential spectral contributions from the sample, especially if the sample is highly miscible; however, even in the latter case, the sample spectral contributions can be minimized through the use of a gap-segment second derivative rather than relying on the conventional differential spectrum used in the dual-sample FTIR methods. In general terms, one can be confident in the results of the rapid single-sample procedures for AC, BC, and moisture content when the miscibility of the sample with the reagent solution or extraction solvent is low, which is generally the case, and employ the dual-sample procedures when very precise data are required for samples that are significantly miscible with the reagent solution or extraction solvent, which can make spectral interferences problematic.

Methodology Summary

A unifying principle associated with the FTIR AC, BC, and moisture content methods is sample viscosity reduction, either through sample dilution or by partitioning the component of interest into a low-viscosity solvent. This facilitates rapid sample throughput without the need for cell rinsing between samples. All methods are based on simple spectral measurements directly related to changes associated with the component(s) in question. UMPIRE-PRO (Universal Method Platform for Infra Red Evaluation) software executes all spectral data manipulation, analyzes the data, and exports the results in various compatible formats. The use of universal calibrations renders all the quantitative methods straight-forward to calibrate and implement, drawing on simple Beer's Law principles rather than often poorly understood black-box inputs and outputs associated with more advanced chemometric procedures. In the case of spectral reconstitution procedures used for CM, the accurate assessment of the diluent and spectral marker concentration allows one to obtain a facsimile of the neat oil spectrum without having to pump a viscous sample through the IR cell, therefore facilitating higher speeds and minimizing the wear and tear on the IR cell windows. In addition, all these novel FTIR methods confer the benefits of automation and high sample throughput, while minimizing reagent use and oil waste.

Role of ASTM

As a voluntary organization, the ASTM is driven by the mutual interests of the parties involved to have available peer-reviewed methods that are reliable and workable in the hands of the users. FTIR CM analysis of lubricants, pioneered by the JOAP, is still in the process of being standardized and validated by the D02.96-03 IR and FTIR sub-committee. Long-standing ASTM wet-chemical methods for the determination of AN, BN, and H_2O have seen only minor changes over the past 30 years. Thus, the FTIR methods discussed in this paper represent a significant innovation, and bringing them to fruition by formulating them as standardized ASTM methods is the next challenge. These methods must then undergo interlaboratory testing to determine whether consistent and valid results can be obtained and to ensure that they will perform reliably in the hands of many users and under a wide range of conditions. Given that FTIR spectrometers are ubiquitous in modern CM laboratories worldwide, the infrastructure is available for the implementation and testing of the methods in independent laboratories following simple, rigorous, and manual protocols. Once the methods have been tested and proven, automation can be implemented to attain the higher throughputs already available on systems like Thermal-Lube's COAT System, which has been designed using the concepts presented here.

Conclusion

FTIR spectroscopy is an important automated qualitative CM screening tool for in-service lubricant analysis. This screening methodology has been advanced in terms of sample throughput through the use of spectral reconstitution, allowing up to 180 pre-prepared samples to be analyzed per hour. Although CM is presently limited largely to mineral based oils, it is foreseen that direct trending can be broadened to a much wider range of basestocks and formulated oils by bringing to bear new oil identification/classification capabilities and adjusting the measurement regions and parameters accordingly. More importantly, the most common quantitative follow-up analyses, AN, BN, and moisture content, have also been developed into viable automatable FTIR methods, significantly extending the utility and analytical role of FTIR spectroscopy in relation to lubricant analysis. AN and moisture analyses, specifically, may well have wider application beyond lubricants per se, and will likely prove to be applicable to a wide range of hydrophobic materials, including fuels (diesel, gasoline, and biodiesel), biodiesel feedstocks, and crude oils. Whether FTIR quantitative methodology will be accepted by the broader lubricant analytical community and the ASTM will depend to a large degree on the desire of commercial CM laboratories to take advantage of the economies of scale offered by this technology.

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