Quantitative Determination of Moisture in Lubricants by Fourier Transform Infrared Spectroscopy

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This paper describes the development of a practical Fourier transform infrared (FT-IR) method for the determination of moisture in lubricants through the combined use of signal transduction and differential spectroscopy to circumvent matrix effects. The acid-catalyzed stoichiometric reaction of 2,2-dimethoxypropane (DMP) with moisture to produce acetone was used to provide IR signals proportional to the amount of moisture present in oils. Calibration standards were prepared by spiking polyalphaolefin (PAO) gravimetrically with water using dioxane as a carrier. For FT-IR analysis, standards and samples were diluted with acidified isooctane and then split, with one aliquot treated with DMP and the other with a blank reagent. The spectra of the two aliquots were collected, and a differential spectrum was obtained so as to ratio out the invariant spectral contributions from the sample. Quantitation for moisture was based on measurement of the peak height of the $\nu(C=O)$ absorption of acetone at 1717 cm^{-1}, yielding a standard error of calibration of $\sim$40 ppm H$_2$O. The method was validated by standard addition of water in dioxane to PAO containing added base as well as to new and used oils. In all cases the method responded quantitatively to standard addition, the average standard error of prediction being $\sim$80 ppm, with the results showing only a minor dependence on the oil formulation. From an analytical perspective, the FT-IR method is both more reproducible and more accurate than Karl Fischer methods and has advantages in terms of environmental considerations, sample size, and speed of analysis as well as the variety of oil types that can be handled. Signal transduction/differential spectroscopy may have broader utility as an alternative means for the determination of low levels of moisture in complex matrices.

Index Headings: Fourier transform infrared; FT-IR; Oil analysis; Karl Fischer; Signal transduction; Calibration standards; Differential spectroscopy.

INTRODUCTION

The determination of moisture in lubricants is an important condition monitoring analysis that is routinely carried out, as the presence of water affects lubricant efficiency and facilitates corrosion and other detrimental reactions that can degrade machinery efficiency and performance.[1] There are a variety of standard American Society for Testing and Materials (ASTM) methods for the determination of water in petroleum and related products, based on either distillation or Karl Fischer (KF) procedures, many specific to particular product types.[2] The ASTM D4006 distillation procedure is onerous, requires large samples, has limited sensitivity, and is not suited to high-volume laboratory testing.[3] KF titrimetric procedures (manual, potentiometric, or coulometric) are usu-

ally the methods of choice and have proved to work well in "clean" oil matrices but are problematic when new and used oils containing undefined additives and breakdown products are analyzed.[4] Aside from physical sources of error such as electrode fouling, moisture in glassware, sample contamination, and separation of water during sample storage, there are many chemical interferences, including condensation or redox reactions caused by aldehydes, amines, ammonia, ketones, halogens, mercaptans, metallic O/OH compounds, oxidizers, and sulfides. Other causes of variation include differing formulations of pyridine-free KF reagent packages sold by various vendors. These and other reasons are commonly cited for the generally poor reproducibility obtained for ASTM inter-laboratory crosschecks. Specific chemical interferences, when known to be present, can be suppressed to some degree by use of additional reagents or alternatively through the use of a vaporizer to remove water from the oil matrix and distilling it over into the KF cell and then titrating. Of the ASTM KF methods, the D6304 coulometric method is considered to be the most comprehensive automated procedure applicable to the general analysis of petroleum products and lubricants, covering lube additives, lube oils, base oils, automatic transmission fluids, and other petroleum products.[5] The method is considered capable of measuring 10–25 000 ppm water and allows for the use of an auxiliary vaporizer to minimize chemical interferences and improve the reproducibility of analyses of viscous oils, which are difficult to disperse in the KF reagents. Although the KF methodology works well for simple, defined lubricants, it is largely considered to provide relative rather than absolute moisture data for formulated new or used oils. With few, if any, alternative methods on the horizon, KF-based procedures remain the only practical means of carrying out automated, high sample volume analysis of moisture in lubricants.

Fourier transform infrared (FT-IR) spectroscopy is an alternative means by which moisture can readily be measured in oils,[6] as water exhibits strong absorption bands due to the O–H stretching ($\sim$3400 cm^{-1}) and bending vibrations ($\sim$1642 cm^{-1}). Although the method is simple and highly sensitive for certain types of samples, such as simple mineral oils containing few additives, FT-IR moisture analysis of formulated and in-service oils is complicated by undefined spectral interferences from other OH-containing constituents such as alcohols, phenols, and hydroperoxides, and the modeling of these interferences is further confounded by hydrogen bonding effects. These "matrix effects" are a spectroscopic parallel to the problems associated with the KF method and have hindered

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the development of a generalized FT-IR based moisture analysis method. Such matrix effects in lubricants have recently been circumvented in a new FT-IR method developed for the determination of acid number (AN) and base number (BN) through the combined use of signal transduction and differential spectroscopy.[7] This paper describes the development of a generalized FT-IR method for the analysis of moisture in lubricants based on this approach and its validation by standard addition.

EXPERIMENTAL

Reagents and Samples. All reagents and solvents were obtained from Aldrich (Milwaukee, WI), including 2,2-dimethoxypropane (DMP, 98%), trifluoroacetic acid (TFA, 99%), dodecylamine (DDA, 98%), triethylamine (TEA, 99.5%), 1,4-dioxane (spectrophotometric grade), and isooctane (spectrophotometric grade). Additive-free polyalphaolefin (PAO) base oil and new and used lubricating oils were supplied by Thermal Lube Inc. (Pointe-Claire, PQ, Canada). An acidification reagent (AR) was prepared by adding 7% (w/w) TFA to dry dioxane and storing it over dry $CaCl_2$ for a minimum of 72 h prior to mixing it 1:1 with isooctane, this solution serving as a diluent for oil samples. All oils, solvents, and solutions (except AR) that were required to be dry were stored over a mixture of oven-dried molecular sieves and $CaCl_2$.

Preparation of Standards and Standard Addition. Six primary moisture standards covering a range of 0–20 000 ppm (0–2% w/w) were prepared by gravimetric addition of water to dry dioxane. Subsequently, six secondary calibration standards, covering a range of 0–2000 ppm, were prepared by gravimetrically adding the primary standards to dry PAO in a ratio of 1:9. Pseudo-standards were prepared by spiking PAO with a 1:2 molar mixture of acetone/methanol in amounts corresponding to those that would be produced by the stoichiometric reaction of DMP with 0–2000 ppm water. Standard addition experiments were carried out by adding the primary or pseudo-standards to PAO as well as to new and used oils of various types.

Sample Preparation. The secondary calibration standards as well as all samples were taken through the analytical protocol presented in Fig. 1. A 10.0-g sample of the oil was mixed with 8 mL of the diluent (1:1 AR/isooctane). Two 9-mL aliquots of the diluted oil were taken and placed in separate 15-mL centrifuge tubes, one labeled BR (blank reagent) and the other RR (reactive reagent), to which were added 0.4 mL of isooctane and 0.4 mL of DMP, respectively. The tubes were shaken and left to stand for 10 min to allow the reaction of DMP with the moisture in the sample to go to completion. Residual acidity was then quenched by adding 1 mL of TEA in isooctane (3.02 g/mL) to both test tubes. Tubes were than capped and centrifuged for 5 min to remove any turbidity.

Fourier Transform Infrared Spectroscopy. The spectrometer used for this study was a Bomem WorkIR (Bomem, Quebec, PQ, Canada) equipped with a DTGS detector and purged with dry air from a Balston dryer (Balston, Lexington, MA). Samples were analyzed by aspirating them into a 230-μm CaF_2 transmission flow cell mounted on a sample shuttle (Dwight Analytical, Toron-
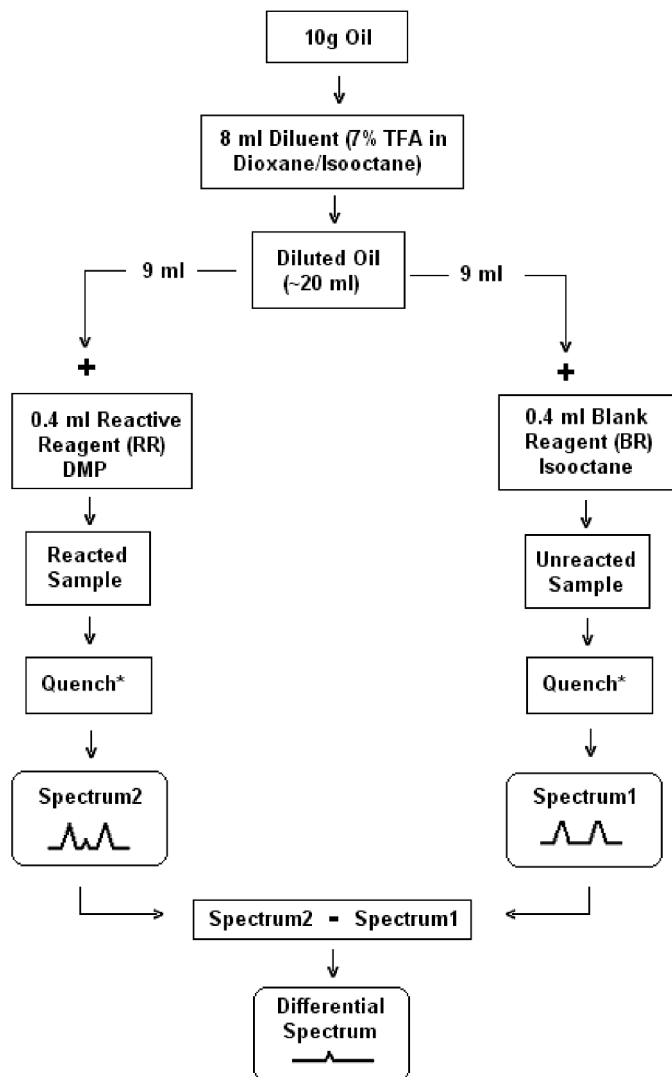

Fig. 1. Schematic diagram of the analytical protocol used to obtain a differential spectrum reflecting the amount of water present in the original oil sample. See text for elaboration regarding the quench step.

to, ON, Canada). The spectrometer was controlled by an IBM-compatible Pentium 150-MHz PC running proprietary Windows-based UMPIRE® (Universal Method Platform for InfraRed Evaluation) software (Thermal-Lube, Pointe-Claire, PQ, Canada), which provided an operator interface to facilitate routine analysis of samples. All spectra were collected by coadding 4 scans at a resolution of 8 cm⁻¹ using a gain of 1.0.

For both calibration and sample analysis, the transmission flow cell was loaded with ~2 mL of the BR-treated aliquot and a single-beam spectrum (BR spectrum) was recorded. After flushing the cell with isooctane, ~2 mL of the RR-treated aliquot was loaded into the cell and a single-beam spectrum (RR spectrum) was recorded. The RR spectrum was then ratioed against the BR spectrum to produce the differential spectrum used for quantitation. A calibration equation was derived by simple linear regression of the calculated moisture contents of the calibration standards against peak height at 1717 cm⁻¹, corresponding to the $\nu(C=O)$ absorption maximum of the acetone produced by the water/DMP reaction, relative to a single-point baseline at 2150 cm⁻¹. The operation of

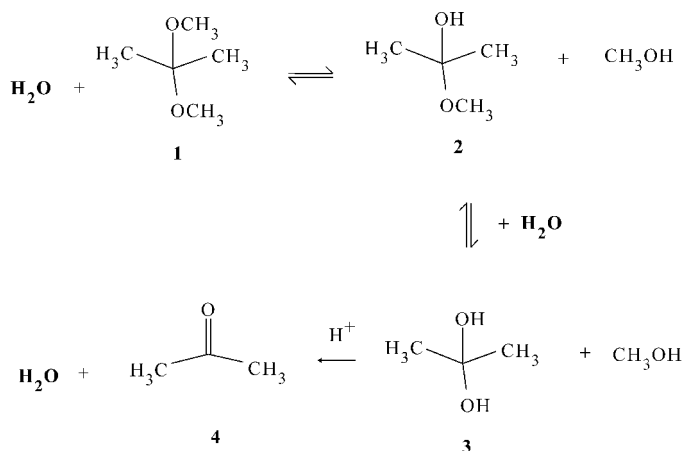Fig. 2. Reaction scheme for the conversion of 2,2-dimethoxypropane (DMP) to acetone in the presence of moisture.

Fig. 3. Spectra of primary water/dioxane standards (0–20000 ppm) after the spectral contributions of dioxane have been subtracted out.

the spectrometer, spectral manipulations, and quantitation were automated using UMPIRE® routines, including a routine to measure and automatically correct for any moisture present in the diluent and reagents.

RESULTS

Analytical Context and Calibration Issues. The reaction of DMP with water under acidic conditions to produce acetone (Fig. 2) has been successfully used to determine trace levels (15 ppm) of moisture in organic solvents, the acetone produced normally being measured by capillary gas chromatography (GC).[8,9] This reaction was investigated in our earlier work as a means of determining moisture in lubricants by FT-IR spectroscopy.[10] However, in that method, quantitation was based on the ν(OH) absorption at 3690 cm^{-1} of the gem-diol (**3** in Fig. 2) formed in the absence of acid. Although workable, this approach was complicated by oil-dependent spectral interferences and the equilibrium between species **2** and **3**, requiring the use of partial least squares (PLS) regression to develop calibrations. With the experience gained in developing FT-IR methods for the determination of AN and BN in lubricants,[7] the DMP/water reaction was revisited to determine whether driving the reaction to completion through the addition of acid to form acetone (**4**) would allow for the development of a simpler and more robust FT-IR moisture analysis method.

In order to proceed with the development of this methodology, the ability to incorporate known amounts of moisture into oils to prepare calibration standards and to validate the method by standard addition techniques was a crucial requirement. While most new and used oils contain additives and/or contaminants, which provide some degree of polarity, thereby facilitating moisture incorporation, it is difficult to disperse water in additive-free base oils, and it is effectively impossible in polyalphaolefins (PAO), the base oils commonly employed in synthetic lubricant formulations. Although PAO calibration standards of limited stability had been developed for our previous study[10] using hexylamine as a moisture carrier, a carrier with basic characteristics was considered problematic since the DMP/water reaction is dependent on acid catalysis. After substantial experimentation, 1,4-dioxane
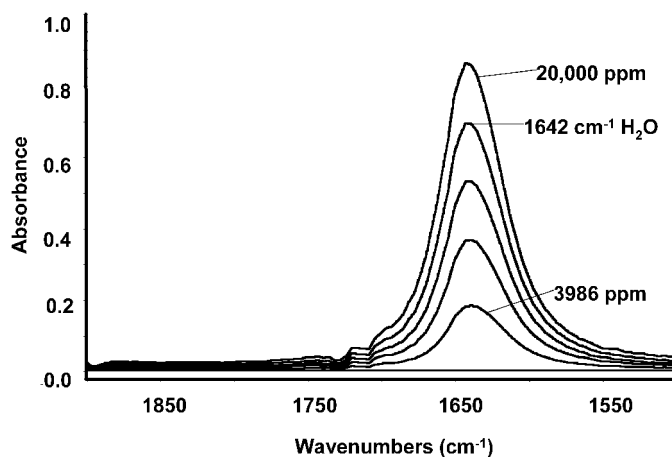
was found to be an excellent carrier, capable of holding up to 2% (20000 ppm) moisture. The use of this carrier allowed dispersions of up to 2000 ppm water in PAO to be prepared, with even higher levels of moisture being dispersed into formulated new and used oils.

Figure 3 shows the water δ(HOH) absorption band at 1642 cm^{-1} in the FT-IR spectra of a series of the primary standards prepared by addition of water to dioxane at levels of 0–20000 ppm. The plot (not shown) of moisture content vs. absorbance at 1642 cm^{-1}, measured relative to a baseline at 1850 cm^{-1} (Abs$_{(1642/1850)}$), was slightly curvilinear over this range of moisture contents, the respective quadratic and linear regression equations being:

$$\text{ppm } H_2O = -1.88 + 22.4 Abs_{(1642/1850)} + 1849 Abs^2_{(1642/1850)}$$

$$r = 1.000 \qquad SD = 4 \text{ ppm} \qquad (1)$$

$$\text{ppm } H_2O = -174.7 + 24028 Abs_{(1642/1850)}$$

$$r = 0.999 \qquad SD = 159 \text{ ppm} \qquad (2)$$

Clearly, the quadratic equation yields a better fit, having a CV of 0.04% vs. 1.6% for the linear regression estimate. However, the linear regression estimate is adequate for general purposes. The spectra of these primary standards remained practically invariant for over two months without the use of septum closures if care was taken to minimize exposure to air by keeping the containers tightly closed. Even if moisture were to ingress over time, the moisture contents of these standards can readily be redetermined by recording their spectra again and processing the spectral data through Eq. 1 or 2.

A set of six calibration standards having moisture contents ranging from 0 to 2000 ppm were prepared by gravimetric addition of the primary standards to PAO in a 1:9 ratio. These calibration standards were run through the FT-IR moisture analytical protocol (Fig. 1), but without the quench step. Figure 4 presents the differential spectra obtained for the six calibration standards, illustrating the loss of moisture (decrease in δ(HOH) band at 1642 cm^{-1}) due to its reaction with DMP and the production of acetone (increase in ν(C=O) band at 1717 cm^{-1}). To compensate for any moisture present in the PAO or reagents, the differential spectrum of the 0 ppm
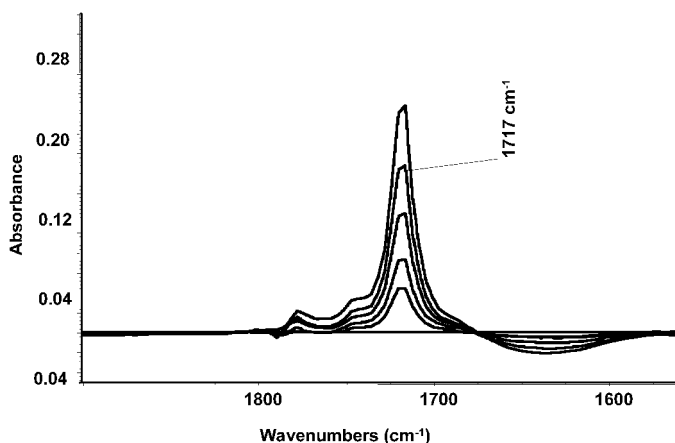
FIG. 4. Differential spectra of water/dioxane/PAO calibration standards obtained by the procedure shown in Fig. 1, illustrating the production of acetone (1717 cm^{-1}) and the concurrent loss of water (1640 cm^{-1}) due to the reaction of water with DMP. The differential spectrum of the 0 ppm standard has been subtracted from each spectrum.

FIG. 5. Moisture predictions obtained for a 2000 ppm PAO standard as a function of time when reacted with DMP in a sealed IR cell.

standard was subtracted from the differential spectra of the other standards. Linear regression forced through the origin (Z-regression) of moisture content vs. absorbance at 1717 cm^{-1}, measured relative to a baseline at 2150 cm^{-1} (Abs$_{(1717/2150)}$), produced the following initial calibration equation:

$$ppm\ H_2O = 8788Abs_{(1717/2150)}$$

$$r = 0.993 \qquad SD = 41\ ppm \qquad (3)$$

It was noted that recalibration over time with the same calibration standards resulted in a steady drop in the regression slope and an increase in the corresponding SD. To investigate this phenomenon, a fresh PAO standard (2000 ppm H$_2$O) was prepared and its spectrum was monitored in a sealed cell after DMP addition. The predicted moisture content of this sample slowly increased over time, reaching an improbable 11 000 ppm after ~200 h (Fig. 5). As moisture could not have entered the cell, the apparent asymptotic increase in moisture content was attributed to the slow decomposition of DMP to acetone. Hence, it was concluded that two distinct reactions occur, a rapid DMP/water reaction that is complete within 2 min, followed by DMP decomposition to acetone, which was shown to be catalyzed by residual acid, as addition of base halted the reaction. The initial rate of the DMP decomposition is negligible (~1.5 ppm/min) relative to the SD of the calibration (~40 ppm) but complicates the standardization and implementation of the methodology. This problem was overcome by incorporating a quench step after reagent addition to neutralize any residual TFA by adding TEA in a 3:1 ratio relative to the initial TFA concentration; this base was selected because it does not exhibit any significant absorption in the region used for measurement of acetone. Incorporation of this procedure not only prevented subsequent DMP decomposition but also had the additional benefit of eliminating any residual TFA as a possible source of spectral interference in measuring the ν(C=O) signal of acetone. Although the trifluoroacetate anion produced by the quenching step absorbs at ~1685 cm^{-1} and hence would be an additional

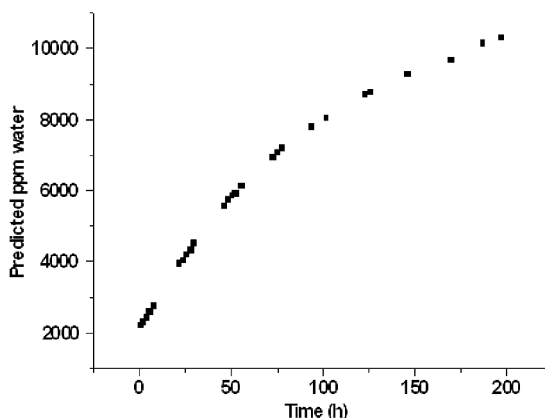source of spectral interference, centrifugation effectively removed the salt formed by the quenching reaction.

Because the diluent and reagents cannot be kept absolutely dry, a procedure was developed to correct for any moisture contribution by these constituents. As shown in Fig. 6, this procedure involves analyzing a sample of the diluent in accordance with the standard protocol, maintaining the same ratio of diluent to reagent as in the case of sample analysis. The predicted moisture content for this "reagent blank" is then adjusted to take into account the volume of oil present in samples being analyzed, based on an assumed oil density of 0.83 g/mL, to obtain the "reagent blank correction". In the software developed for routine implementation of the FT-IR moisture analysis methodology, the value of the "reagent
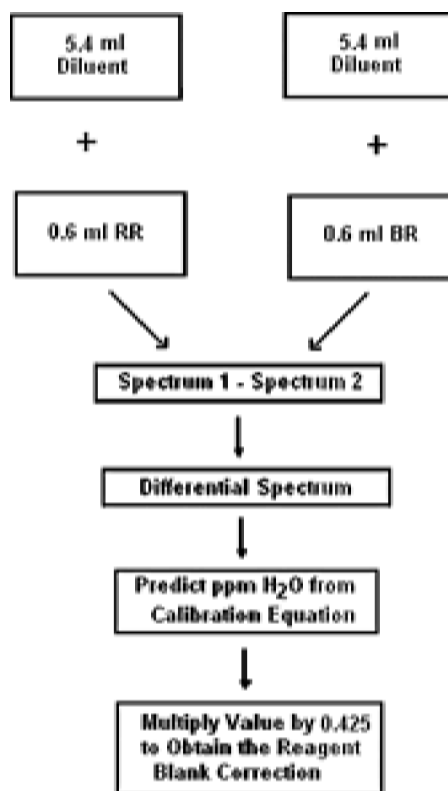

FIG. 6. Reagent blank correction procedure used to compensate for any moisture present in the reagents and diluent.

blank correction'' is determined automatically when the operator types in ''Reagent Blank'' in the sample name/title field and is also automatically subtracted from the values determined for all subsequent samples until the next ''Reagent Blank'' entry.

Incorporation of the quenching step and blank correction into the analytical protocol stabilized the calibration and confirmed the validity of the initial calibration (Eq. 3). A simpler non-reaction-based calibration procedure was also investigated. This approach involved the preparation of pseudo-standards representing varying levels of water (0–2000 ppm) by gravimetrically spiking PAO with a 1:2 solution of acetone/methanol, where these molar proportions correspond to those resulting from the complete reaction of water with DMP. After subtraction of the PAO spectrum from the spectrum of each of these pseudo-standards, the ppm moisture represented by the acetone/methanol spike was plotted against the peak height of the acetone $v(C=O)$ band, which was shifted in the spectra of these pseudo-standards to 1720 cm^{-1}. Z-regression produced the following equation:

$$\text{ppm } H_2O = 8601\,\text{Abs}_{(1720/2150)}$$

$$r = 0.999 \qquad SD = 11 \text{ ppm} \qquad (4)$$

The slope of the pseudo-standard plot is very similar to that obtained using the reaction-based calibration procedure (8601 vs. 8788), implying that acetone/methanol-spiked PAO standards could provide a simple alternative means of calibration, this protocol having the advantage of being impervious to contributions from moisture pick-up.

Standard Addition Validation. Although FT-IR analysis for moisture was shown to be workable using PAO as a model oil, the true test lies in whether the methodology yields accurate values when commercial formulated oils, both new and used, are analyzed. Of particular concern is the pervasive presence of substantial amounts of base in formulated diesel and motor oils (typically having BN values in the range of 1–14 mg KOH), as basic additives are commonly included in such formulations to counteract (neutralize) the accumulation of acidic constituents formed by oxidation or entrained in them by combustion blow-by. Thus, in these types of samples neutralization of the acid added with the diluent in the standard protocol might leave an insufficient amount of acid to catalyze the DMP/water reaction. To investigate the effect of the presence of various amounts of base, model oils were formulated by adding DDA to PAO to attain BN values ranging up to 20 mg KOH/g, and each formulation was spiked with the water/dioxane primary standards to produce oils containing 0–2000 ppm water. Each BN series was analyzed by the standard protocol (Fig. 1) and the ppm water added was regressed against Abs$_{(1717/2150)}$, the regression being forced through the origin so that the slopes could be compared. A series of commercial oils of various types, known to contain basic additives, as well as some in-service used oils, were also spiked and analyzed in the same manner. The Z-regression slopes and respective SDs for both the DDA-spiked PAO and the commercial oil samples are presented in Table I.

For the base-spiked PAO series, the slopes are fairly

TABLE I. Z-regression slopes and SD values obtained for the standard addition of water/dioxane primary standards to PAO and commercial oil samples.

	Slope	SD (ppm)
DDA-spiked oils		
PAO (BN = 0)	8788 (*8601*)[a]	41 (*11*)[a]
PAO (BN = 4)	7695	63
PAO (BN = 8)	7773	77
PAO (BN = 16)	7381	55
PAO (BN = 20)	15320	530
Commercial oils		
Valvoline All-Climate	7609 (*7735*)[a]	88 (*9*)[a]
Quaker State FCI	6896	10
MotoMaster Formula 1	8512	127
Havoline Formula 3	6460	139
Castrol GTX SAE 5W30	7758 (*7984*)[a]	37 (*12*)[a]
Castrol GTX SAE 20W5	7360	19
Used oils		
Transit bus oil	8031	112
Compressor oil	7531	67
Gear oil	7933	84
Summary	Mean slope ± SD	Mean SD
All oils[b]	7656 ± 581	70

[a] Results obtained for oil spiked with 1:2 acetone/methanol.
[b] Excluding PAO (BN = 20).

consistent up to BN 16, the BN 20 series having a much higher slope, representing a dramatic decrease in response. This data implies that there is sufficient acid in the diluent to catalyze the DMP/water reaction for oils having BN values of up to 16 mg KOH/g. For the commercial new and in-service used oils, the slopes, although somewhat more variable, are all fairly comparable to those obtained for the base-spiked PAO samples, with the SD of 581 around the mean of all the slopes reported in Table I representing a CV of 7.6%. Included in parentheses in Table I is some ancillary slope and SD data for the pseudo-standards as well as two commercial oils similarly spiked with acetone/methanol mixtures to represent the products of the reaction of water with DMP. The slopes in all three cases are comparable to those for their water/dioxane-spiked counterparts, while the SDs are significantly lower, indicating that the use of pseudo-standards is a viable alternative approach to calibration. It is noteworthy that the maximum of the acetone absorption band for the pseudo-standards is shifted by several wavenumbers from its position in the spectra of the water/dioxane-spiked calibration standards (1720 vs. 1717 cm^{-1}), indicating that matrix polarity differences are a potential source of slope variability between oils, although extinction coefficient variability may also contribute. Among the slopes for the commercial oils, the largest difference from the slope for the calibration standards (i.e., PAO with BN = 0) is 6460 vs. 8601, which would translate into ~33% overprediction of moisture content in this worst-case scenario. This error could be roughly halved by using the mean slope in Table I instead of the calibration slope and could be substantially reduced by employing an oil-specific calibration.

As noted earlier, the absolute determination of moisture in lubricants is problematic except for very simple lubricant formulations (e.g., transformer oils) because the results are strongly dependent on oil formulation/composition. In this regard, the interlaboratory reproducibility

of the ASTM standard method obtained in in-service oil crosscheck programs is >50% of the sample mean.[11] As such, the FT-IR method should provide adequate accuracy for most lubricant quality control or condition monitoring applications. If higher accuracy is required, a custom calibration can be devised using the oil of interest as the calibration matrix rather than PAO. Although not considered in this paper, the use of the methanol ν(OH) absorption band at $\sim$3500 cm^{-1} as the basis for quantitation instead of the acetone ν(C=O) band has also been found workable but requires some modification of the methodology. For ester-based lubricants, this approach is the only analytical option because the intense ester ν(C=O) band, though cancelled out by differential spectroscopy, leaves little or no energy for the accurate measurement of the acetone band.

CONCLUSION

Validation of the FT-IR method developed in this work by standard addition indicates that this method can provide estimates to within $\sim$30% of the amount of moisture in a variety of oil matrices with the use of a single calibration equation simply based on water/dioxane-spiked PAO calibration standards. When higher accuracy is required, estimates to well within 7% can be obtained through the development of oil-specific calibrations. Thus, signal transduction in combination with differential FT-IR spectroscopy appears to be a viable approach for the determination of moisture in lubricants, similar in principle to the stoichiometric KF method, but using a spectrometer rather than an electrode. As a result, the analysis is simplified and more reproducible, with a concurrent reduction in reagent costs/disposal, and automation is facilitated, allowing for increased analytical throughput without sacrificing accuracy. Although this methodology has been developed in the context of lubricant analysis, the protocol devised should be adaptable to almost any non-polar matrix that has no strong absorptions in the ν(OH) and/or ν(C=O) regions. Last, but not least, the water/dioxane primary standards developed in this study may well be useful for calibrating and validating KF systems, as well as providing a means by which the FT-IR moisture analysis methodology can be assessed by others.

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