Measuring Moisture in Lubricants with FTIR: An Alternative to Karl Fischer Titration

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Abstract

A rapid and accurate primary Fourier transform infrared (FTIR) method for the determination of moisture in mineral and ester based lubricants has been developed based on the extraction of moisture into dry acetonitrile. A Continuous Oil Analyzer and Treatment (COAT) FTIR system was programmed to allow the automated analysis of acetonitrile extracts, and the methodology was validated by analyzing 58 new and used oils, independently analyzed by the Karl Fischer (KF) method. Linear regression of FTIR versus KF results for these oils produced a linear plot with a between-method SD of ±80 ppm.

Introduction

Fourier transform infrared (FTIR) spectroscopy is a rapid instrumental technique that is widely used for lubricant condition monitoring in accordance with ASTM Standard Practice E2412 (van de Voort et al., 2006). Over the past five years, research has been undertaken by the McGill IR Group in collaboration with Thermal-Lube Inc. to facilitate FTIR condition monitoring and to broaden the scope of FTIR lubricant analysis. This research initiative has involved the design of both an automated, high-sample-throughput FTIR oil analyzer (Figure 1) and quantitative FTIR methods for the determination of acid number (AN) and base number (BN) (van de Voort et al., 2003). The development of these methods has provided alternatives to standard ASTM titrimetric procedures that offer significant advantages in terms of speed of analysis and reduced solvent and reagent use. An FTIR method that accurately detected moisture levels as low as 50 ppm was also developed (van de Voort et al., 2004), but was restricted in scope. This paper describes a new and broadly applicable FTIR method that we have developed and implemented on Thermal-Lube's Continuous Oil Analysis and Treatment (COAT) FTIR system. It also presents the results of a comparison of the analytical performance of this method by comparison with that of the coulometric Karl Fischer (KF) method (ASTM D6304), which may be considered the gold standard for the quantitative determination of water in lubricants and petroleum products, including lubricant additives, base oils, fully formulated lubricants, and automatic transmission fluids.

Principle of the Method

FTIR lubricant condition monitoring is a simple reagent-free methodology that involves the trending of a wide range of parameters, including oxidation, nitration, sulfate by-products, soot, glycol contamination, diesel fuel dilution, antiwear depletion and water contamination by measurement of various peak areas or heights in the FTIR spectra of in-service oils (or the baseline tilt of these spectra in the case of soot). However, although water contamination appears in the list of condition monitoring parameters, the adaptation of this methodology as the basis for a quantitative FTIR analytical procedure would provide limited sensitivity and accuracy owing to matrix effects and other complicating factors. To overcome these problems, we designed an alternative approach based on a simple extraction of moisture from new or used lubricants into a polar solvent followed by quantification of the extracted moisture by FTIR analysis of the solvent phase. Acetonitrile was found to be highly suitable as the extraction solvent for several reasons. First, it is sufficiently polar to be largely immiscible with both mineral- and ester-based lubricants and is capable of efficiently extracting water from them. Second,, because acetonitrile does not absorb strongly in the portions of the mid-IR spectrum where water absorbs, low levels of moisture can be detected. Figure 2 presents the OH stretching region in the spectra of a series of calibration standards prepared by addition of water to acetonitrile; these are differential spectra because the spectrum of acetonitrile has been subtracted out. Owing to the binding of water molecules exclusively to acetonitrile rather than to each other at these high dilutions, these spectra of water exhibit distinct symmetric and asymmetric OH stretching bands (3630 and 3540 cm^{-1}), rather than the single broad band normally observed. Both bands respond linearly to added water and maintain consistent ratios relative to each other over the concentration range examined (300-2100 ppm).

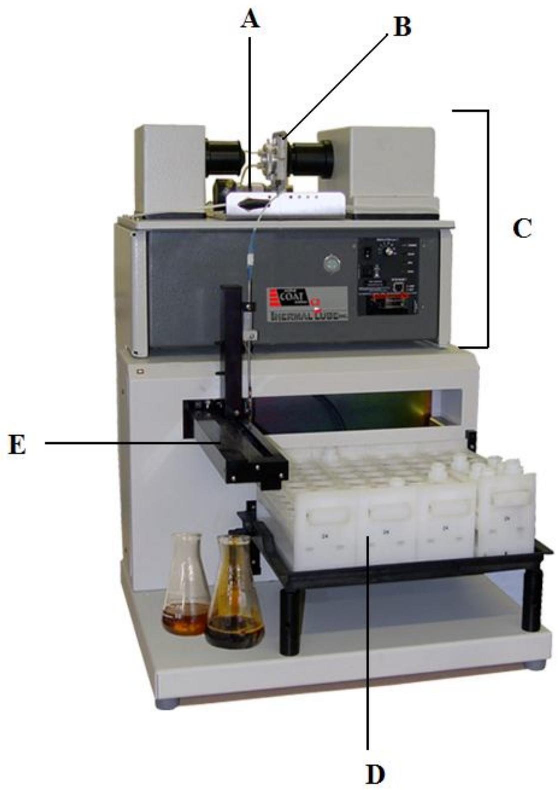

Figure 1. COAT FTIR Oil Analyzer. The system consists of a micro gear pump (A), cell holder (B), FTIR spectrometer (C), autosampler tray (D) and robotic arm (E).

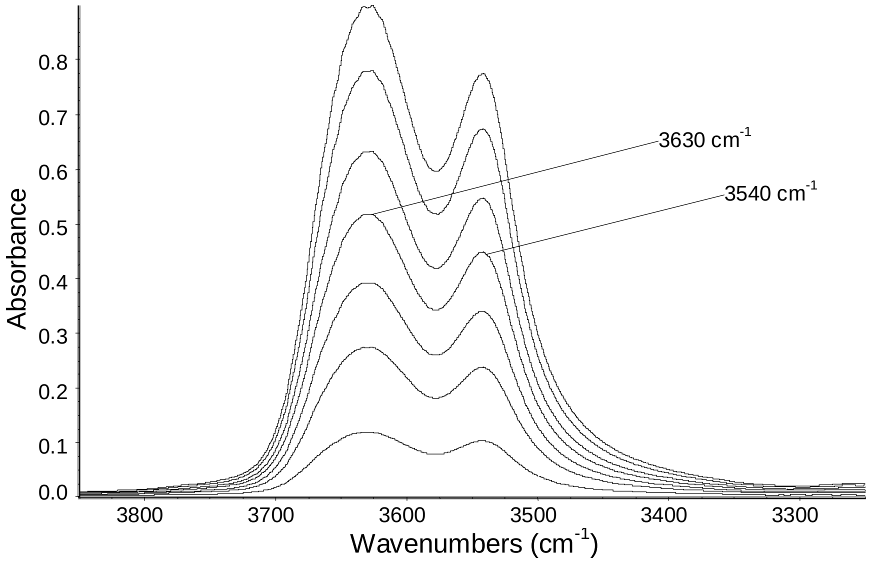

Figure 2. Differential spectra of water in acetonitrile over a concentration range of 300-2100 ppm, illustrating the two main water absorption bands, the symmetric and asymmetric OH stretching bands at 3630 and 3540 cm^{-1}, respectively

Potential Sources of Interference

In addition to extracting water from oils, acetonitrile is also capable of extracting some other polar constituents, such as alcohols, phenolic compounds, hydroperoxides, and organic acids, but not ionic constituents. Since formulated lubricants contain a wide variety of added constituents and can accumulate various undefined contaminants during the lubricant's in-service life, a number of species may be co-extracted with water into acetonitrile. Such potential sources of spectral interferences were examined by recording the spectra of acetonitrile extracts from a wide variety of new and used lubricants. Figure 3, which presents the 3650-3200 cm^{-1} region of the differential spectra obtained after subtraction of the spectrum of dry acetonitrile from the spectra of these extracts, indicates that a variety of constituents other than moisture were extracted into acetonitrile. Although measurements at either of the peak maxima of the water absorption bands would accordingly be subject to substantial interference from various co-extracted components, interference on the high-frequency side of the 3630-cm^{-1} band was judged to be minimal. This is illustrated in Figure 4, in which the spectrum of the acetonitrile extract of a mineral-based oil spiked with 286 ppm of water is superimposed on the spectra obtained after extraction of the same oil spiked with 0.2 and 0.5% (w/w) 2,6-di-*tert*-butyl-4-methylphenol, corresponding to the levels at which phenolic antioxidants are commonly present in lubricant formulations. Based on a detailed examination of a large variety of oils, 3676 cm^{-1} was ultimately chosen as the optimal frequency for measuring water in acetonitrile extracts of lubricating oils.

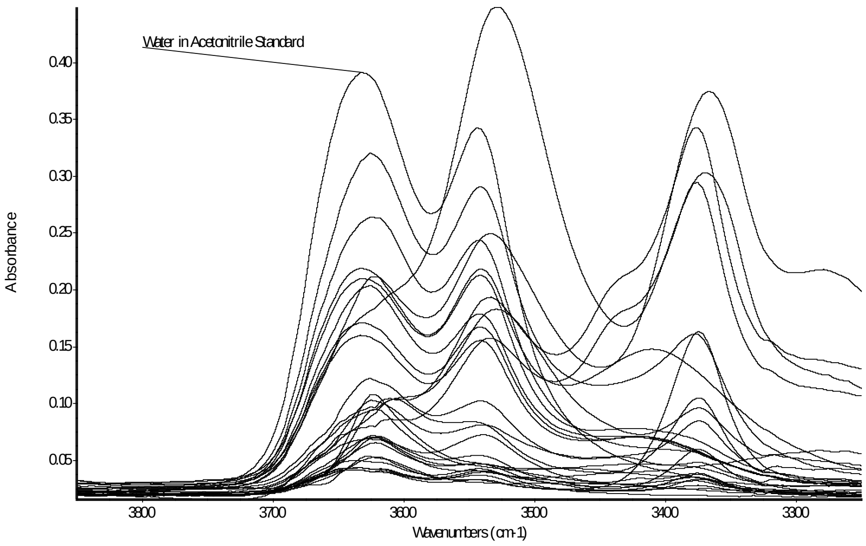

Figure 3. Differential spectra of acetonitrile extracts from a wide variety of commercial new and used lubricants in relation to a differential spectrum of moisture in acetonitrile, illustrating the spectral interferences produced by constituents extracted into acetonitrile.

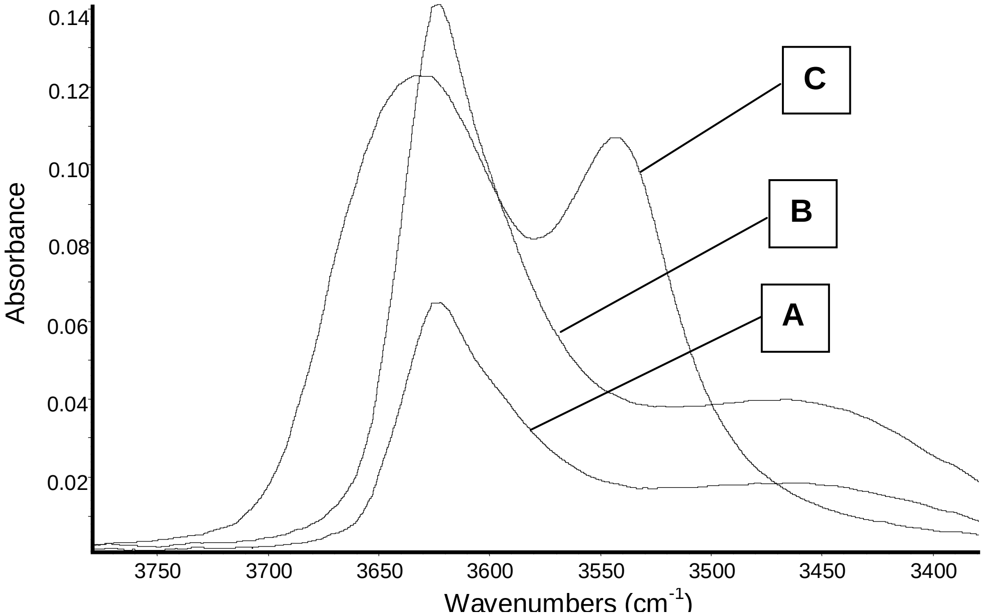

Figure 4. Differential spectrum of a mineral-based oil spiked with 0.2% (A) and 0.5% (B) 2,6-di-tert-butyl-4-methylphenol and extracted with acetonitrile and a differential spectrum of 286 ppm water (C) spiked into the same base oil and extracted into acetonitrile.

Calibration

A calibration was developed using standards prepared simply by adding water to acetonitrile at levels from 300 to 2100 ppm. Owing to the low absorptivity of acetonitrile in the spectral region of interest, a cell pathlength of ~1000 μm could be employed. After subtraction of the spectrum of the dry acetonitrile from the spectra of the standards, the following calibration equation was obtained using absorbance measurements made at 3676 cm^{-1} relative to a baseline at 3738 cm^{-1}:

$$H_2O\ (\text{ppm}) = 5427.3 * A_{3676/3738\ cm^{-1}} - 15.0 \qquad SD = 10.9 \qquad R^2 = 0.999 \qquad [1]$$

As indicated by the regression SD of ~11 ppm, the long pathlength allowed very high sensitivity to be attained. This equation was programmed into the COAT system to analyze the moisture content of the acetonitrile extracts of lubricant samples automatically, providing results directly in ppm moisture. A routine to automatically correct the results for any partial miscibility of oil samples with acetonitrile was also incorporated in the calibration.

Analytical Protocol

For sample preparation, 10 g of sample is weighed (±0.0001 g) on an analytical balance into a tared 50-mL clinical centrifuge tube, and 15 mL of acetonitrile (kept dry over 4-8 mesh 3Å molecular sieves) is dispensed into the tube using a re-pipette. The samples are mixed vigorously for 20 min using a multi-sample, reciprocal-action shaker, and then the oil and acetonitrile phases are separated by centrifugation for 10 min at ~10,000 rcf (relative centrifugal force). The upper acetonitrile layer is transferred into a 20-mL autosampler vial, which is then capped with a septum cap having a Mylar liner. The vials are loaded into the autosampler tray of the COAT system for automated FTIR analysis.

Validation and Comparison to Karl Fischer Titration

Extraction Efficiency. Ten samples of different types of lubricating oils were spiked with various amounts of water (200-1000 ppm) and then mixed vigorously on a reciprocal-action shaker to ensure that the water was well dispersed in the oil. The amounts of water in these samples were then determined by the acetonitrile extraction/FTIR method. Recoveries of >90% were achieved with a 20-min mixing time, confirming the capability of acetonitrile to efficiently extract most of the water present in lubricating oils.

Repeatability and Reproducibility. Twelve oil samples were analyzed in triplicate within the same run and on three different days to evaluate repeatability and reproducibility, respectively. The data obtained are summarized in Table 1. The average SD for repeatability was ~8 ppm and the average SD for reproducibility was ~80 ppm.

Accuracy. The accuracy of the FTIR method was assessed by comparison of the FTIR-predicted moisture contents of 58 validation samples with the results of KF titration. These validation samples included a variety of new oils as well as used oils provided by the Naval Engineering Test Establishment (NETE; Montreal, PQ, Canada), Insight Services Inc. (Cleveland, OH), and the U.S. Armed Forces Technical Support Center (TSC) of the tri-service Joint Oil Analysis Program (JOAP). KF analyses of all these validation samples were performed at NETE using a Mettler Toledo DL32 (Columbus, OH) apparatus equipped with a WAP and employing Hydranal (Sigma-Aldrich Inc., St. Louis, MO) KF reagents for moisture quantification. Figure 5 presents a plot of the FTIR moisture predictions vs. the KF results and illustrates that the FTIR method tracks the moisture content of the oils in the same manner as the KF method, with an overall standard error of prediction (SEP) of ~80 ppm relative to the KF reference values. The SEP is comparable to the SD for reproducibility of the FTIR method and indicates excellent agreement between the FTIR and KF results.

Table 3. Repeatability and reproducibility data for quantification of water in 12 oil samples (mean and SD of 3 replicates).

Sample no.	Type of oil	Repeatability		Reproducibility	
		Mean (ppm)	SD (ppm)	Mean (ppm)	SD (ppm)
1	New motor oil	361.7	1.53	324.2	50.34
2	Used motor oil	755.7	10.12	666.6	108.31
3	Used motor oil	552.3	2.52	511.4	84.75
4	New bearing oil	-5.0	8.54	39.3	50.95
5	New turbine oil	31.0	10.54	67.3	52.08
6	New engine oil	473.3	4.04	504.4	102.60
7	Polyol ester oil	342.7	10.69	467.6	207.43
8	New hydraulic oil	77.3	8.08	83.4	64.72
9	New gear oil	96.7	10.12	104.2	62.34
10	New turbine oil	86.3	8.39	92.1	53.24
11	Used motor oil	547.0	11.79	554.0	74.75
12	Used motor oil	590.7	9.29	584.2	65.24

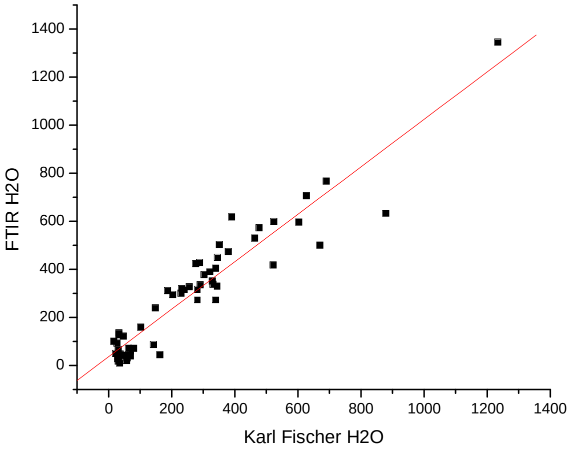

Figure 5. Regression of FTIR moisture predictions vs. the KF results for 58 used and new oil samples.

Conclusion

The results of this study indicate that the FTIR analysis of acetonitrile extracts of lubricants is a viable and accurate means of determining moisture content in a wide range of lubricants. The rate of analysis on the COAT system employed in this work is 72 acetonitrile extracts/h. Accordingly, this FTIR method provides a practical instrumental alternative to KF analyses, allowing for the rapid, automated determination of moisture with a high degree of accuracy. This methodology may be implemented together with other FTIR methods developed in our laboratory for the automated analysis of lubricants, including AN and BN as well as lubricant condition monitoring, thereby replacing several conventional, tedious physical and chemical methods by FTIR methodology. As such, FTIR analysis offers substantial benefits to commercial oil analysis laboratories in terms of both sample turnaround and cost savings.

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