Onsite FTIR quantitative analysis of water in mineral-based oils using a novel water stabilization technique

Application note

Energy and fuels

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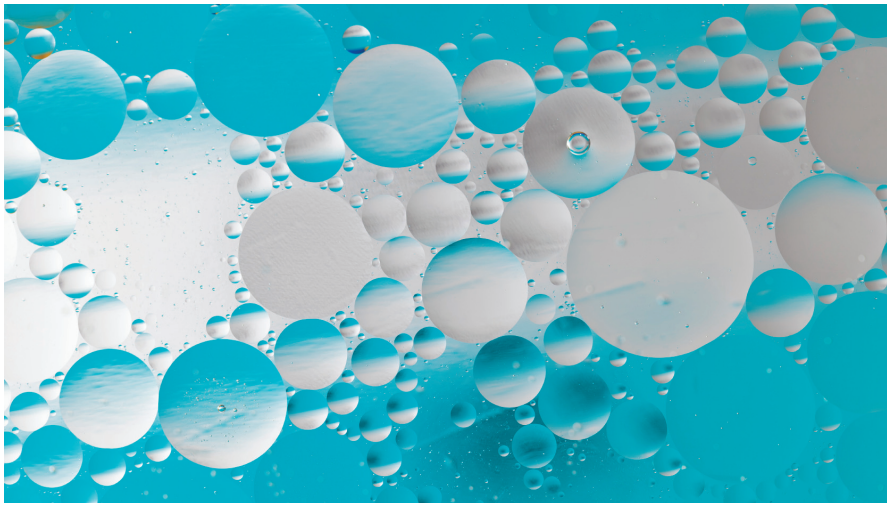

Introduction

Water is an important contaminant to monitor in all lubricating oil. Infrared spectroscopy (FTIR) provides an easy means to measure water; however, to this point infrared methods have not been able to provide the accuracy and range desired by the lubrication industry. Agilent Technologies has developed a method for the measurement of water in mineral oils that overcomes key technical difficulties. When used with the Agilent 5500t spectrometer, this method measures the concentration of water in mineral-based oils with an accuracy and range equivalent to the industry standard Karl Fischer method. This article will discuss the use of this method with turbine oils; the method has also been applied to mineral oil based hydraulic fluids, as well as gear oils.

Water in turbine oil — An important parameter to measure

The amount of water in turbine oil is critical to the performance and longevity of the equipment. Excessive amounts of entrained water in the turbine oil can cause premature failure of the turbine unit, typically due to changes in the physical properties induced by the presence of water. Physical properties of oil affected by the presence of water include viscosity (measure of the oil's resistance to flow), specific gravity (density of the oil relative to that of water), and the surface tension (a measure of the stickiness between surface molecules of a liquid). All of these properties are important for the ability of the oil to coat, lubricate, and protect the critical mechanical clearances. In addition, water in turbine oil can accelerate additive depletion and contribute to chemical degradation mechanisms such as oxidation, nitration, and varnish formation.

Onsite analysis is highly desirable

The ability to measure water onsite provides a substantial benefit in obtaining an accurate measurement of water level in lubricating fluids. Offsite analysis for trace water in oil may be compromised due to variability of water concentration introduced by storage, transportation, or shipment of a sample. Furthermore, turbine oils contain de-emulsifying additives that cause microscopic water droplets to separate from the oil and concentrate in layers at the bottom and sides of containers. This de-emulsifying action takes time to occur, and can cause large variations in analytical measurements. Also, oil samples can lose water due to evaporation and loss to the sample container walls. In a short study conducted at Agilent, samples of turbine oil with added water were measured over several days using the standard Karl Fischer method. Turbine oil was found to lose approximately 100 ppm of water over a 24 hour period. The loss of water was accelerated by mixing; the bubbles generated sped the loss of water by evaporation. To obtain an accurate picture of the amount of water in turbine oil, measurement should be made soon after the sample is pulled from the machine. This demonstrates the need for onsite analysis.

Measuring water in turbine oil

Karl Fischer (KF) coulometric titration is typically used to determine the amount of water in turbine oils. KF has some practical drawbacks for onsite analysis including complicated sample preparation, the use of hazardous and expensive chemical reagents, and the length of time required to perform the analysis. With these issues in mind, KF analysis is considered the 'gold standard' method for analyzing water in oil because it provides accurate and precise answers. Under ideal conditions, KF has an accuracy of 3 to 5% for prediction of water in turbine oil.

FTIR spectroscopic analysis eliminates many of the concerns associated with measuring water via KF titration. The spectroscopic method, can be performed in far less time than KF measurement, does not require hazardous reagents, and when a rugged and easy-to-use FTIR system such as the Agilent 500/5500 Series instrument is used, FTIR is ideal for onsite analysis. KF titrations require about 10 to 15 minutes to perform, with the instrument properly conditioned and equilibrated overnight. For KF analysis, the oil must be carefully weighed before and after injecting into the titration vessel, using a high precision balance. Weighing errors can adversely affect the accuracy of the KF analysis. Following each KF analysis, the KF coulometric titration instrument takes another 5 to 10 minutes to re-equilibrate. In contrast, the FTIR analysis takes about 2 minutes to perform and the instrument is immediately ready for the next sample analysis after a simple cleaning with a tissue.

Though the FTIR analysis is faster and easier than the KF method, FTIR has the reputation of being less accurate for the prediction of water. We have carefully studied the errors associated with conventional FTIR methods and found a means to eliminate those errors. We have developed a method for measurement of water in mineral oils that produces accuracy comparable to the KF method. When the potential errors due to weighing in the KF method are taken into account, the likelihood of error is even less with this new FTIR method.

Water in turbine oil — FTIR methods

Conventional methods

Methods to directly measure water in mineral oils have been available for over 30 years. The ASTM E2412 method measures the concentration of water directly from the water band near 3350 cm^{-1}; the area of this band is linearly correlated to the concentration of water. Figure 1 shows several spectra of water in turbine oil with the location of the water absorbance highlighted. In this method, the oil is measured in transmission using a 100 micrometer pathlength cell.

Issues with conventional methods

The ASTM 2412 method was originally designed for use with motor oil. Motor oil contains additives that solvate the water into the oil. Motor oils routinely contain 1000 to 2000 ppm of water. The methods developed to measure water in these oils by FTIR were targeted at large concentration and had correspondingly large errors associated with them. Turbine oils, on the other hand, solvate significantly less water, typically 50 to 100 ppm. Greater amounts of water will form small droplets and eventually settle to the bottom of the turbine oil. A method based on ASTM 2412 was developed to measure water in turbine oil. The method showed variability of up to 40% on replicate samples of the same oil. Oils which have been formulated to quickly separate water, such as Mobile DTE and Chevron GST, showed even worse reproducibility due to the separation of the water. A second method measuring the neat oil was developed. In the second method a partial least squares (PLS) algorithm was used to account for baseline differences in the oil. This method predicted better; however, the results were insufficient for machinery maintenance. Figure 2 shows the results from a calibration of water in Mobile DTE and Chevron GST turbine oils using the second method. The plot shows the actual concentration measured by Karl Fischer versus the predicted concentration measured by the PLS FTIR method. The error in this method is ±250 ppm; clearly insufficient for machinery maintenance.

The primary reason the conventional method for measuring water in oil by FTIR produces a high error in turbine oils is water separation; water separates

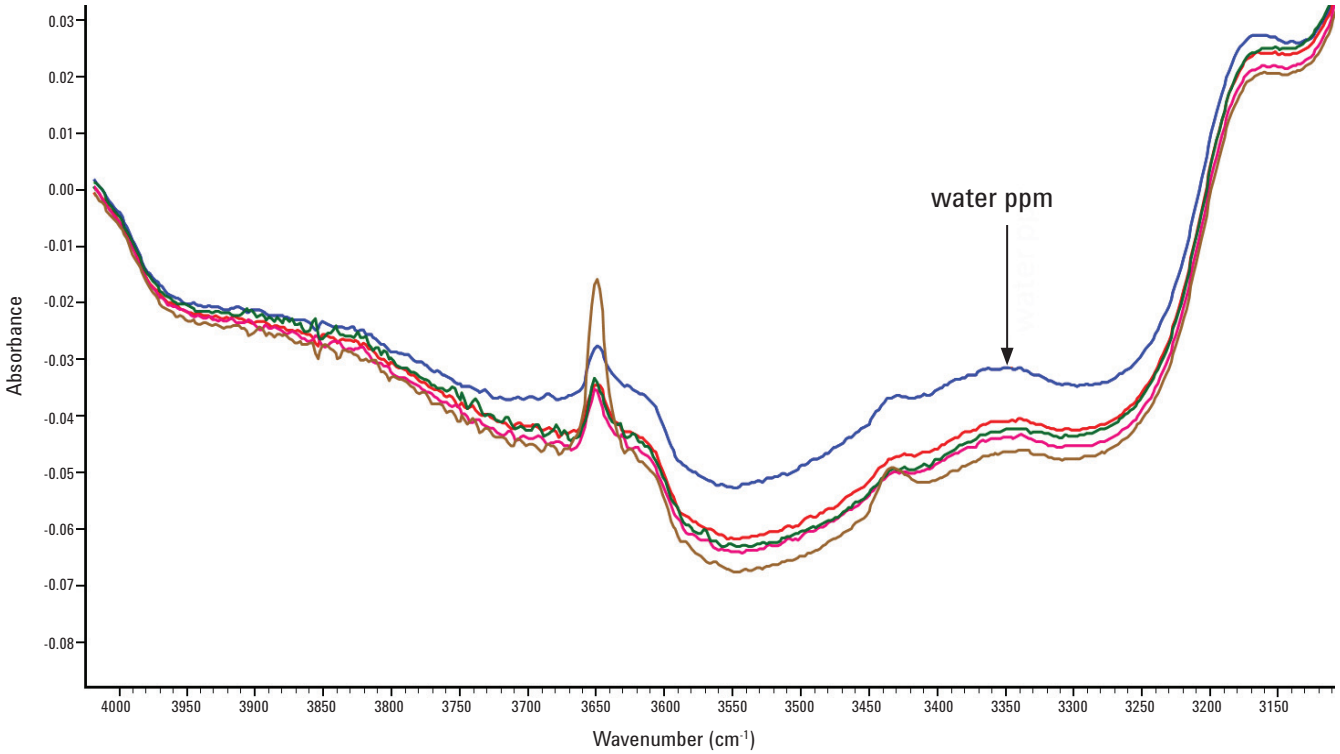

Figure 1. The overlaid IR spectra of turbine oil with the water absorbance region expanded. Water values from bottom to top are 30 ppm (red), 80 ppm (dark green), 217 ppm (light green), 533 ppm (pink), and 1460 ppm (blue).

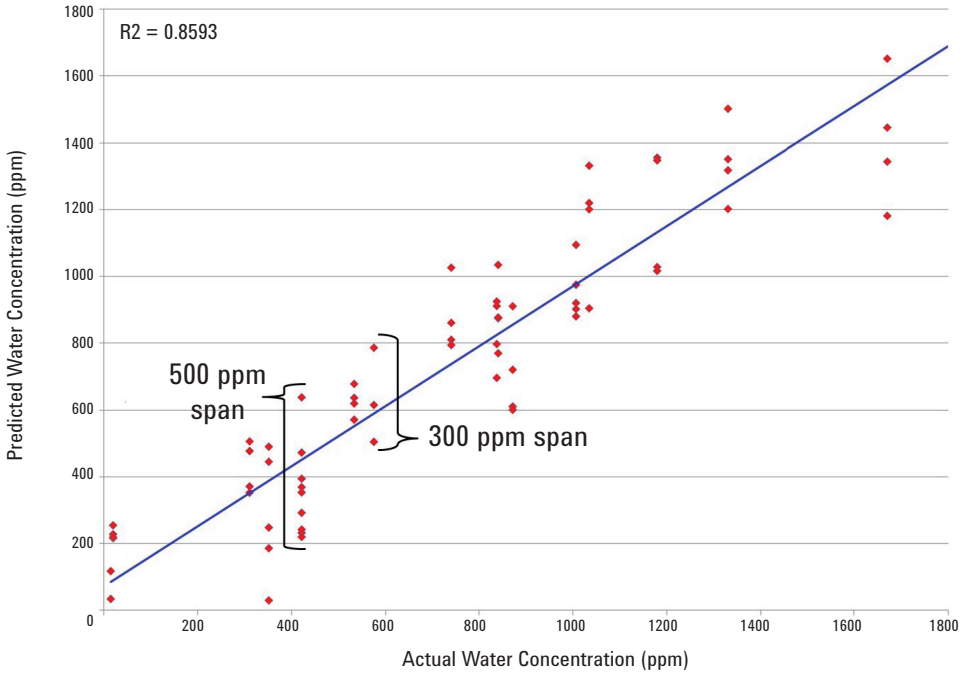

Figure 2. The predictions results for water in GST and DTE turbine oils showing the actual concentration on the X-axis and the predicted concentration on the Y-axis using a PLS calibration using conventional methodology

into small droplets in turbine oil. These small droplets scatter rather than absorb infrared light. Using FTIR, only the light that is absorbed contributes to the measurement of water. The size and number of droplets affects how much light is scattered versus absorbed; a graphical representation of scattering versus absorption is shown in Figure 3. As shown in 3a, large droplets scatter the light, whereas the small droplets shown in 3b only absorb the infrared light. The number and size of water droplets in oil depends on how well the oil was mixed, the time since mixing, and the dispersant package used in the oil. In the end, scattering increases the error and the amount of scattering varies with time and mixing. Figure 4 shows FTIR spectra of replicate measurements of water in GST oil. The oil component has been subtracted out of these spectra such that only the water remains. Two things can be observed from these spectra. Firstly, the height of the water band near 3350 cm^{-1} varies, indicating that different amounts of infrared light are being absorbed in the different samples. Secondly, the baselines also vary, indicating that the light that is not being absorbed is being scattered. The variation in the infrared absorbance cannot be accounted for by the calibration; therefore, a means of stabilizing the water in the oil is needed to reduce variability.

Agilent's water stabilization method

A method for the measurement of water in oil has been developed by Agilent. This new method uses a surfactant to distribute and stabilize the water in the oil. The surfactant creates a stable emulsion with uniform water droplet size. In addition, the surfactant helps to hold the water in the oil, leading to more consistent water measurements. These two effects lead to a reproducible absorbance measurement, which leads to a more accurate prediction of the water concentration. Addition of approximately 3% of a premixed non-ionic polyethylene oxide based surfactant blend and gentle mixing is all that is required to stabilize the water in oil. Absorbance spectra of water in Mobile DTE oil (with the oil spectrum subtracted) after addition of the surfactant measured on the 5500t FTIR are shown in Figure 5. Compared to the spectra shown in Figure 4, the OH absorbance is approximately three times higher and much more consistent. Furthermore, the baselines are flat and uniform indicating little to no scattering.

The PLS method using surfactant stabilizers to measure water in turbine oil using the 5500t FTIR was developed using two of the most popular turbine oil brands, Chevron GST 32 and Mobil DTE 797. Seventeen different concentration standards of water in turbine oil

A. Large droplets scatter infrared light

A. Small droplets absorb infrared light

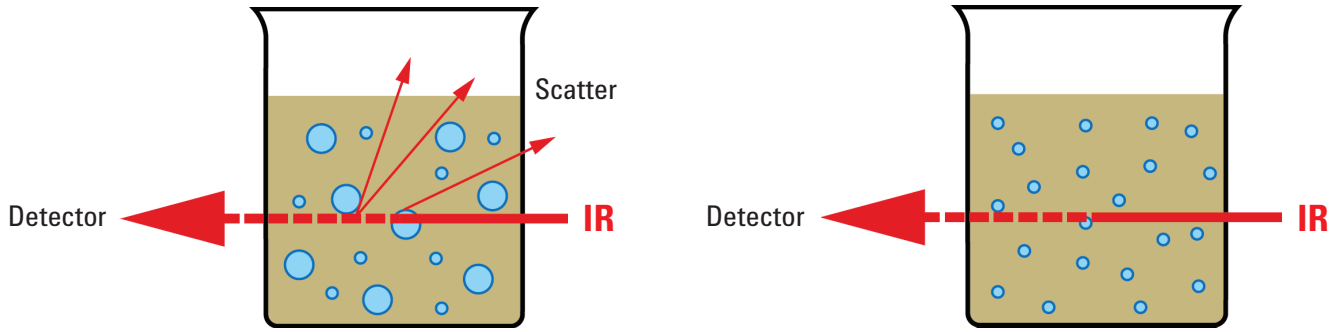

Figure 3. This is a graphical representation of A) an infrared analysis of oil with a range of water droplet sizes where the large droplets are scattering the light, and B) an infrared analysis of oil with uniform, small particles that absorb the infrared light

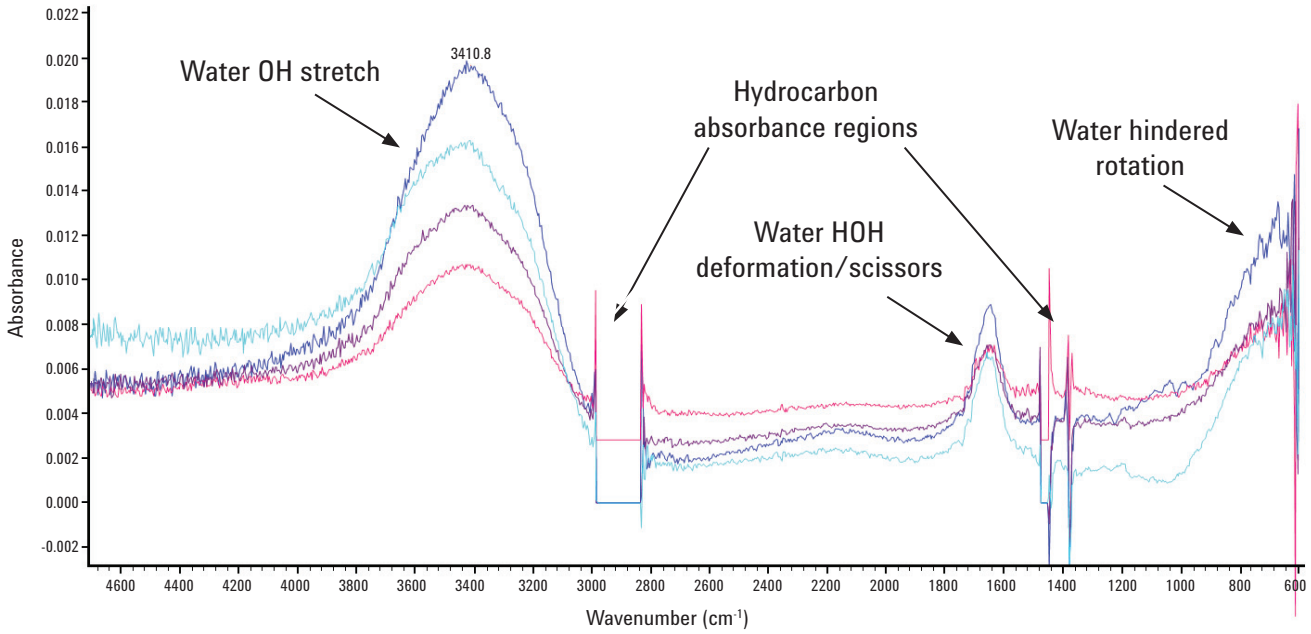

Figure 4. Overlay of four replicate measurements of 1200 ppm water in Chevron GST oil with base oil subtracted. These measurements are analogous to those used in the ASTM E2412 method. The water absorbances are non-repeatable and the baseline offset indicates scattering.

were measured on four 5500t FTIR spectrometers. The standards were prepared gravimetrically (by weight) in a range from 5 to 5300 ppm, using new oil (aged at 135 °C for 4 hours) and used in-service oils supplied by various power generation facilities. The surfactant was added by pipette and gently mixed in a circular motion in order to prevent air bubbles from entering the sample. Vigorous shaking is not necessary for the surfactant to react with water. The standards were measured by coulometric Karl Fischer (KF) titration shortly after the IR spectra were measured. The spectral data from each instrument and the KF results were used to develop a PLS method with a standard error of cross-validation (SECV) of 85 and an R^2 value of 0.9985 (Figure 6).

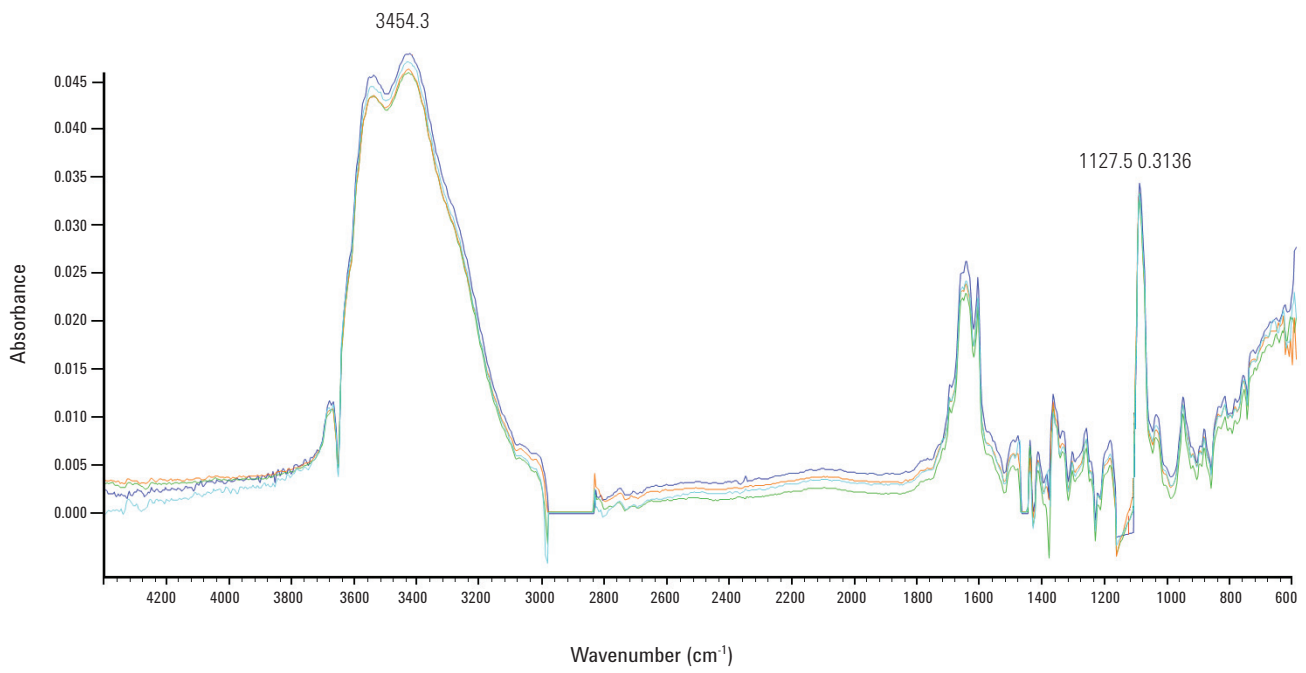

Figure 5. Overlay of four replicate measurements of 1200 ppm water in Mobile DTE oil with Agilent's surfactant mixture added (base oil subtracted). The surfactant provides a uniform water absorbance and little to no scattering due to water droplets in the oil.

The PLS method results were processed with three factors and four out cross-validation; the preprocessing included mean centering, thickness and baseline correction. The surfactant was found to contribute 25.5 ppm of water to each sample, which was therefore subtracted from the KF results prior to PLS method development. Calibration results of this method are shown in Figure 6.

The method was validated with an independent validation set of standards prepared at 500 ppm, 1000 ppm, 2000 ppm, 3000 ppm, and 5000 ppm of water, with the surfactant added prior to the IR spectral analysis on four 5500t FTIR spectrometers.

The average error of prediction for the validation set was 5%, and the prediction values from one of the instruments are compared to the KF values in Table 1. The relative standard deviation of the predictions are less than 2% (1000–5000 ppm) and <5% (500 ppm).

Table 1. The predicted water (ppm) in turbine oil (5500t system) versus the actual KF results.

5500t (ppm)	KF (ppm)	Difference (ppm)	% Error
508	504	4	0.8
1054	965	89	9.2
2043	2002	41	2.0
2946	2838	108	3.8
4710	4753	43	0.9

Note: The ~1000ppm sample in Table 1 may stand out due to a slightly higher relative error than expected. This is most likely due to a low bias in the KF measurement for this sample. Several factors—such as changing the KF solvents, humidity/drift, sampling procedure, or sample mixing—can cause this level of KF error. The 1054ppm FTIR value is more trusted since replicate measurements can be made in quick succession for confirmation and there are fewer sources of experimental error in the FTIR technique.

The Agilent water stabilization method eliminates the major cause of error in measuring water in oils by FTIR. In addition to lowering error in both the calibration and validation results, the surfactant served to increase the absorbance of water by three times.

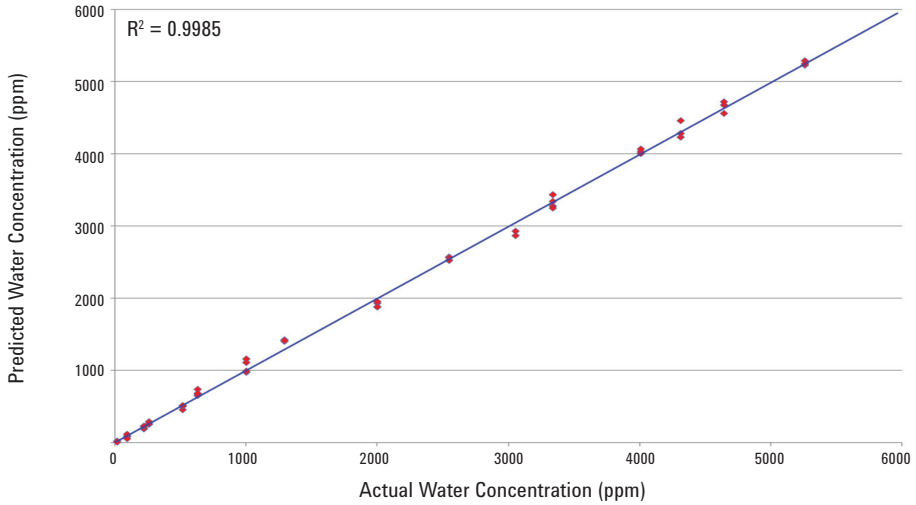

Figure 6. Calibration results of surfactant method showing good correlation of actual versus predicted concentration for water in Chevron GST and Mobile DTE turbine oils.

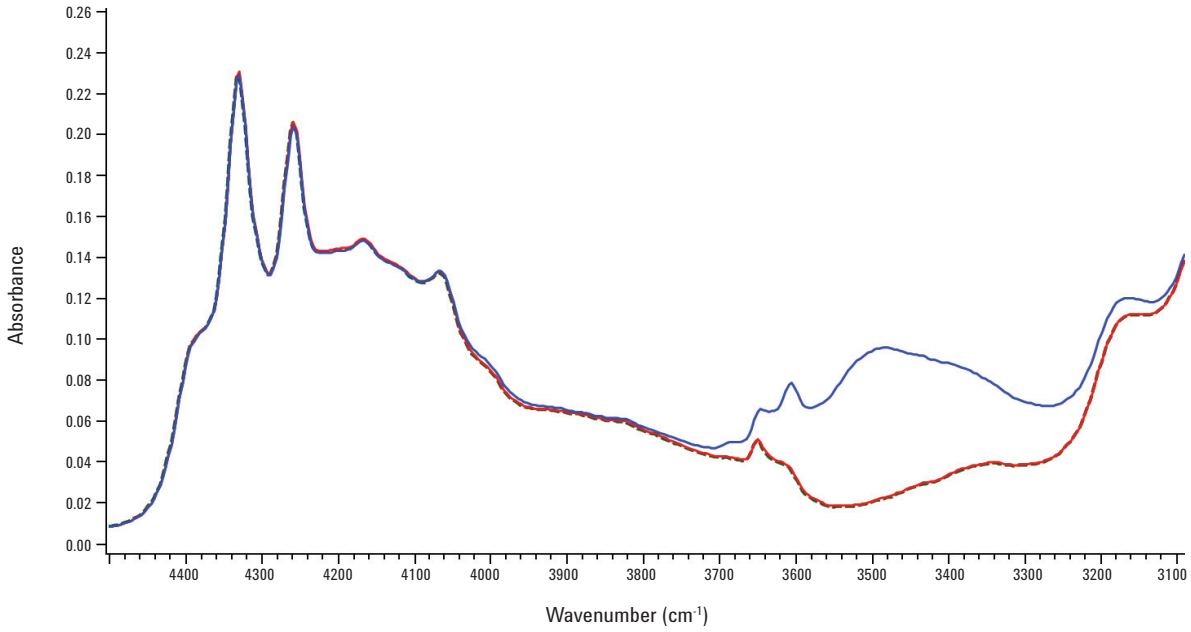

Figure 7. The water OH stretch region of the overlaid FT-IR spectra of turbine oils. The blue and red spectra both contain 1120 ppm (0.112%) water. The Agilent Water Stabilizer is added to the oil in the blue spectrum but is not added to the other oil (red). The dashed green spectrum is the turbine oil blank with no water or stabilizer added, and indicates no additional water absorbance is measured unless the water stabilizer is added. There is a small OH stretch absorbance contribution (blue spectrum) in the 3500cm-1 region from the surfactant water stabilizer.

This increase in water absorbance is shown in Figure 7, where the IR spectra of two turbine oil samples with the same amount of water (1120 ppm) are overlaid. The blue spectrum is from the 1120 ppm water sample with the surfactant water stabilizer adde. The red spectrum is the non-stabilized oil spectrum with 1120 ppm water. The dashed green spectrum is the same turbine oil without water or stabilizer. The non-stabilized 1120 ppm spectrum (red) is nearly indistinguishable from the blank turbine oil. Clearly, the surfactants reduce the droplet size of the water and form micelles which absorb, rather than scatter the infrared light. Some portion of the water may also be fully dissolved in the surfactant.

This water IR absorbance increase using the surfactant is strongest in mineral oil lubricants such as turbine oils, hydraulic oils, transformer oils, diesel oils, crude oils, and compressor oils, but also greatly improves the water measurement in oils designed to hold water such as crankcase or gear oils. In addition to improving the accuracy and repeatability, the surfactant also improves the stability of the water in the oil from day to day. A sample of turbine oil that is not stabilized by surfactants loses approximately 100 ppm of water over a 24 hour period due to evaporation. This is true independent of the measurement technique. Samples that have been treated by the Agilent surfactant mixture lose less than 10 ppm of water over the same period.

The Agilent water stabilization method provides an easy way to accurately measure the concentration of water in turbine oil. Premixed surfactant stabilizer, calibrated dispensers, sample vials and methods for use with the 5500t FTIR instruments are available in kit form. The surfactants are non-volatile, non-corrosive, non-flammable and safe for use in non-lab settings. This method provides accuracy comparable to a KF analysis in a shorter amount of time without toxic reagents.

Conclusion

Infrared spectroscopy provides an easy to use method for measuring water, oxidation and additive depletion in lubricating fluids. Until now, however, the water measurement was subject to errors due to the non-uniform dispersion of water in certain oils. The Agilent water stabilization method solves these problems and provides accuracy comparable to the industry standard Karl Fischer analysis. The method uses non-hazardous surfactants to create a uniform dispersion of the water in the oil. This method is easy to use and portable for true on-site measurement of water in oil.

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