On-Site, Low Level Quantitative FTIR Analysis of Water in Oil Using a Novel Water Stabilization Technique

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Water is an important contaminant to monitor in all lubricating oil. Infrared spectroscopy (FT-IR) 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. A new method for the FTIR measurement of water in mineral oils has been developed which overcomes key technical difficulties. When used with an on-site FTIR 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 patent pending method has a range of water in oil from 50 to 5,000ppm and an average error of less than 5%. 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.

There are several key parameters for which infrared spectroscopy provides highly accurate information about a lubricating fluid, all simultaneously in less than a minute. This article will examine the new technique in measuring the level of water present in a lubricant, however, FITR is also ideal for the on-site measurement of the amount of oxidation and nitration by-products, the amount of anti-wear, anti-oxidation and extreme pressure additives that remain in the lubricant.

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.

On-site analysis is highly desirable

The ability to measure water on-site provides a substantial benefit in obtaining an accurate measurement of water level in lubricating fluids. Off-site 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, samples of turbine oil with added water were measured over several days using the standard Karl Fischer technique. 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 on-site analysis.

Measuring water in turbine oil Karl Fischer (KF) coulometric titration is typically used to determine the amount of water in turbine oils. Karl Fischer has some practical draw backs for on-site analysis including complicated sample preparation, the use of hazardous and expensive chemical reagents, and 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, Karl Fischer has an accuracy of 3 – 5 % for prediction of water in turbine oil.

FTIR spectroscopic analysis eliminates many of the concerns associated with measuring water via Karl Fischer 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 is used, FTIR is ideal for on-site analysis. Karl Fischer titrations require about 10-15 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 analysis the KF instrument takes another 5-10 minutes to re-equilibrate. The FTIR analysis takes about 2 minutes to perform and 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 a reputation of being less accurate for the prediction of water. A new FTIR method for measurement of water in mineral oils which produces accuracy on par with the KF method.

Water In Turbine Oil – FT-IR Methods

Water Stabilization Method

A new method (patent pending) has been developed for the measurement of water in turbine oil by A2 Technologies. 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 and 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 necessary to stabilize the water in oil. Absorbance spectra of water in Mobile DTE oil (with the oil spectrum subtracted) after addition of the surfactant, as measured on the portable FTIR system, shown in *Figure 2*. Compared to the spectra shown in *Figure 1*, the OH absorbance is approximately three times higher and much more consistent.

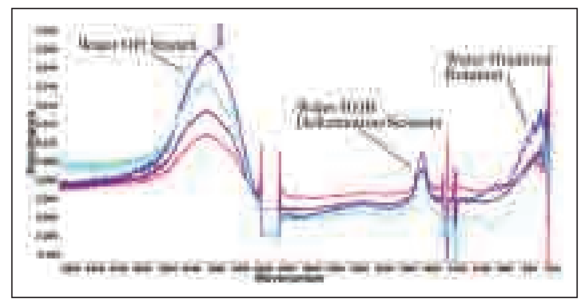

Figure 1: Overlay of 4 replicate measurements of 1200ppm water in Chevron GST oil with base oil subtracted. These measurements are analogous to those used in the ASTM E2412 method. The water absorbances are non-repeatable and the baseline offset indicates scattering

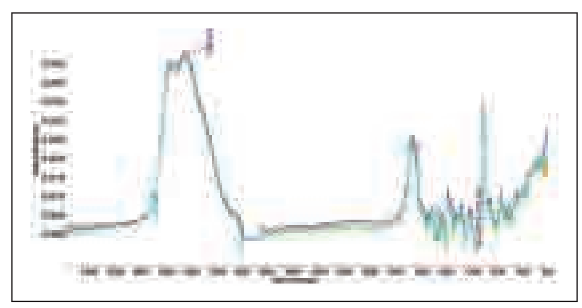

Figure 2: Overlay of 4 replicate measurements of 1200ppm water in Mobile DTE oil with A2 surfactant mixture added (base oil subtracted). The surfactant provides a uniform water absorbance and little to no scattering due to water droplets in the oil.

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 portable FT-IR spectrometers 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 were measured on 4 FT-IR spectrometers. The standards were prepared gravimetrically (by weight) in a range from 5-5300ppm, using new oil (aged at 135°C 4hrs) 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 emulsify the 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 R2=0.998 (*Figure 2*). The PLS method results were processed with 3 factors and 4 out cross-validation, the preprocessing included mean centering, thickness and baseline correction. The surfactant was found to contribute 25.5ppm of water to each sample, which was therefore subtracted from the KF results prior to PLS method development. The method was validated with an independent validation set of standards prepared at 500ppm, 1000 ppm, 2000ppm, 3000ppm, and 5000ppm of water, with the surfactant added prior to the IR spectral analysis on four PAL FT-IR 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 below. The relative standard deviation of the predictions are less than 2% (1000-5000ppm) and <5% (500ppm).

PAL (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

Table 1: The predicted water (ppm) in turbine oil (PAL system) vs. the actual KF results.

The 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. Clearly, the surfactants reduce the droplet size of the water and form micelles which absorb, rather than scatter the infrared light. 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 which is not stabilized by surfactant loses approximately 100 ppm of water over a 24 hour period due to evaporation. This is independent of the measurement technique. Samples which have been treated by the surfactant mixture lose less than 10 ppm of water over the same period, helping to reduce the need for immediate sample measurement.

The Water Stabilization method provides an easy way to measure the concentration of water in turbine oil accurately. The surfactants are non-volatile, non-corrosive, non-flammable and safe for use in non-lab settings. This method provides accuracy comparable to a Karl Fischer analysis in a shorter amount of time without toxic reagents.

Conclusion:

Infrared spectroscopy provides an easy to use way of 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 A2 Technologies Water Stabilization Method (patent pending) 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.

Figure 3: A Portable Analyzer for Lubrication (PAL) FTIR Spectrometer.