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WHITE PAPER

MEASURING WATER WITH THE FLUIDSCAN® FLUID CONDITION MONITOR

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Synopsis

Direct imaging IR optics achieve the equivalent analytical capability as the FTIR spectrometer, and the unique chemometrics algorithms for accurate, repeatable and trendable TAN/TBN and water measurements. FluidScan delivers the power of a laboratory FTIR, Karl Fischer water titrator and a TAN/TBN titrator to reliability engineers who monitor the oil condition whenever and wherever they need it.

Abstract

Water in oil can manifest itself in many forms – from dissolved to emulsified, to free water with oil. How water will be present in a given oil depends on the nature of the oil formulation as well as sample preparation conditions. The FluidScan® mid-infrared spectrometer from Spectro Inc. is designed to monitor the presence of water in all the above scenarios. The device uses the fundamental chemistry that describes the presence of water in oil, providing a highly sensitive and quantitative measure of dissolved water in oil. By monitoring the presence of scattering in the oil from emulsification or the presence of free water, FluidScan alerts the user when these situations exist at critical levels. In comparing results from FluidScan to Karl Fischer laboratory titration methods, operators should take care to ensure the water status is homogenous. Quantitative comparisons can be made when the water is predominantly dissolved in the oil. In the following example , we discuss details of how to measure water with FluidScan.

The task of detecting water contamination in oil using a mid-infrared infrared spectrometer such as FluidScan is a natural fit. When water interacts with oil, signature chemical bonds are created between the water and the oil molecules, which have strong mid-infrared resonances. This means the bonded wateroil molecules preferentially absorb mid-infrared energy at specific vibrational frequencies. The natural frequencies of the bonds' vibrations cause this absorbtion. Think of the vibration of a heavy parcel attached to a spring (or multiple springs) inside a shipping container. Such vibrations will occur most prominently at the natural resonant frequency of the spring and parcel combination. The same principle applies with chemical bonds; the incident infrared light supplies the energy instead of a jolt to the shipping container as it is being loaded. For FluidScan, we are interested in a particularly sensitive oxygen-hydrogen bond resonance (O-H stretch) that occurs between the "dissolved" water and oil. Depending on the oil itself, this resonance occurs between 3200 and 3800 cm^{-1}, or 2.63 and 3.125 microns in wavelength. In most mineral-based oils this resonance will be in the vicinity of 3400 cm^{-1}. Figure 1 shows an example in typical, multi-weight motor oil.

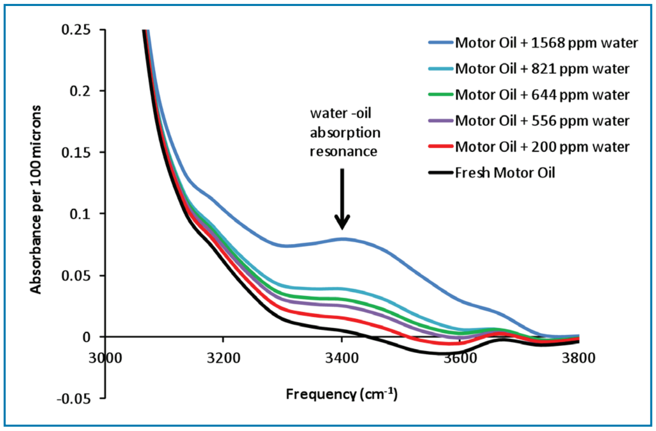

Figure 1: An example of dissolved water absorption in motor oil: FluidScan spectra depicting a series of motor oil samples with increasing amounts of water. The main absorption resonance is centered at 3400 cm^{-1}.

As in Figure 1, as more dissolved water is present in the oil, the absorption resonance continues to increase. Since this process is repeatable and driven by the fundamental chemistry of the chemical bond, precise correlations can be made between the absorption resonance and the amount of water present in the oil. This is illustrated in Figure 2, which shows excellent correlation between FluidScan-determined values for the water compared to Karl Fischer standard laboratory titration values.

FluidScan analyzes a sample and produces a ppm reading in the following manner:

• FluidScan measures the spectrum of the oil and embedded analysis algorithms quantify that the height of the water peak is based on that spectrum.

• That height is then turned into a ppm using an algorithm stored inside the device. No matter what type of oil (or biodiesel for that matter), this signature peak is present when water bonds with the oil. This enables a straightforward and reliable way for FluidScan to probe water content in oil.

• By using an algorithm to determine the true height of this peak (similar to how your eye can), other situations in oil (such as the presence of soot) with activity in this region can be eliminated from the true water determination.

• In cases where infrared peaks occur in this same mid-infrared region, such as when a significant amount of antifreeze contamination is present in the oil, FluidScan identifies and flags other peaks associated with those chemical contaminants apart from the water contamination.

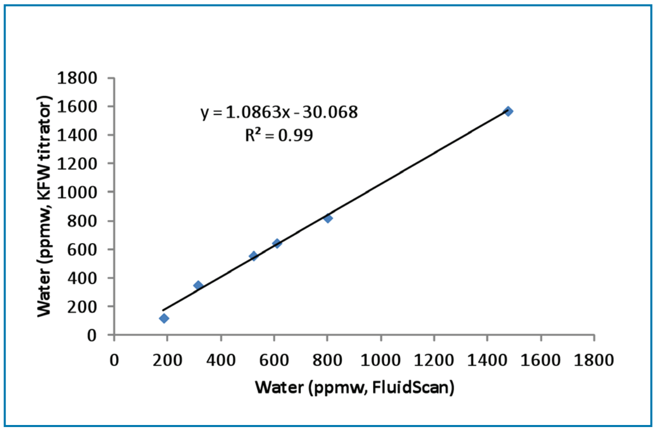

Figure 2: Comparison of FluidScan water readings from the analysis of the spectra in Figure 1 to ASTM D6304 Karl Fischer water titration.

When present, however, water will not always be able to fully bond with the oil and produce an infrared absorption resonance associated with such dissolved water. In fact, this is our most common experience: "They mix like water and oil."

This means they do not mix very well at all. Fortunately, in machinery with its elevated fluid agitation, temperature and pressure conditions, water will often be able to dissolve or bond up to the saturation level of the oil. Saturation means the available sites on the oil molecules that form a water-oil chemical bond have been used up. Saturation levels can vary between 500 ppm in a hydraulic to 3000+ ppm in engine oil. Once you reach saturation, the water in the oil tends to emulsify and form small globules in the oil. In cases of extreme water contamination, free water, which can settle anywhere in the machinery, will be present. Water can also be driven to these states due to the design of the oil itself, where additives to the oil may act to prevent oil-water bonds from forming except under extreme conditions or as the oil ages.

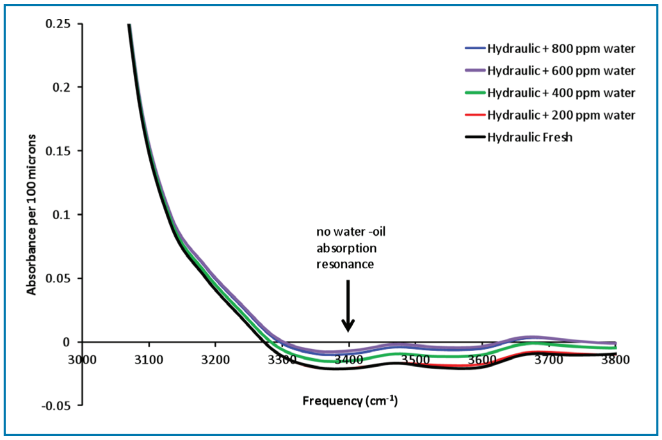

Figure 3: Infrared signature of emulsified and free water in oil: The presence of such contaminants is marked by elevated absorption across the infrared with no peak, a signature of the scattering of the infrared light by the water.

In cases where emulsified and free water are present in the oil, these contaminants tend to scatter the infrared light passed through the oil by FluidScan. Figure 3 shows the example spectrum of emulsified and free water present in a water resistant, synthetic hydraulic oil.

The signature effects of scattering, rather than the absorption of infrared light by the oil-water mixture, is a broad but small elevation of the absorbance spectrum of the oil across the infrared spectrum. The infrared light scatters off the water globules in all directions. Rather than transmitting straight through the oil, infrared light is lost from the system and is recorded as a drop in transmission through the oil and it is recorded as an increase in absorbance. This situation is unstable since the water itself is inhomogeneous within the oil. For example, the emulsified water, when pulled from the machinery, may settle to the bottom of the container as free water, if it is left to sit too long. This will completely change the amount of scattering in the oil, making the quantitative determination of emulsified or free water difficult. Indeed ASTM standard Karl Fischer methods quote a wide lab-tolab reproducibility of 700 ppmw for a 500 ppmw sample (ASTM D6304 Procedure C), even though such apparatus are more sensitive than that, partially due to this lack of stability of water in oil.

In these cases, FluidScan's embedded algorithms search for this increase in the absorbance spectrum and warn the user to the presence of the water if it is above pre-defined thresholds. An alarm of "Significant Free Water Detected" will be present on the Results screen to alert the user that this situation is occurring. It is relatively straightforward to distinguish this type of activity from true absorbance or other types of scattering (such as soot again), because they tend to affect the infrared spectrum gathered by FluidScan in a much different manner. In these situations, FluidScan will provide an indication rather than a quantitative reading of the total amount of water, and therefore quantitative comparison to laboratory Karl Fischer titrations techniques cannot be made. A quantitative value of dissolved water in ppm, however, will still be provided by the device. Such a dissolved water value alerts the user when the oil, even if not designed to take on water, is dissolving water and reaching its saturation limit due to weathering and the persistent presence of water in the oil. However, it should not be confused with a total water ppm reading.

Summary

In summary, the FluidScan mid-infrared spectrometer is an excellent mechanism to detect the various manifestations of water contamination in oil.

• Dissolved water provides an unambiguous, repeatable and large absorption resonance, which FluidScan can readily quantify and track for virtually any oil type.

• The presence of emulsified and free water is also identified by FluidScan via their characteristic infrared scattering, and alerts the user when they reach a critical level. Depending on the makeup of the oil itself, either dissolved or emulsified/free water may be more prevalent.

• Many oils (such as most motor oils) are designed to dissolve as much water as possible in order to remove it from the machinery. In these cases, dissolved water peaks are readily observed and their quantification, up to the saturation point, is highly accurate.

• Other oils, including hydraulics that are apt to encounter significant water well beyond the saturation limit of any oil type, are designed for their demulsibility characteristics (i.e., their ability to reject bonding with water) so the water may be removed from the system by other means.

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