APPLICATION NOTE

MEASURING WATER CONTAMINATION IN INDUSTRIAL OILS: A PRACTICAL ALTERNATIVE TO KARL FISCHER TITRATION

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Synopsis

Water calibration using the FluidScan analyzer provides accurate determination of total water contamination in an oil sample of 1000 and above for all turbine oils and from 1 ppm and above for a growing number of turbine oils. The analysis provides an alternate option to to the traditional Karl Fisher (KF) coulometric titration (ASTM D6304).

Introduction

Turbine oils typically are formulated to have high thermal stability, oxidation resistance, and excellent water separation. Lubricants available specifically for gas turbines or steam turbines are designed with specific additive formulations, but there are also many oils that can work with all different types of turbines. Gas turbines have the tendency to build up sludge and varnish whereas steam turbines may experience oxidation, foaming, and sludge. However, a concern of all turbine systems is water contamination. Regular and reliable water measurement in turbine oil is an important part of successful turbine operation. Severe water contamination can cause changes in the oil's viscosity, accelerated oxidation, additive depletion, and decreased bearing life. Turbine manufacturers typically recommend a warning alarm limit of 500 – 1000 ppm.

The most widely accepted method for detecting water in oil is by Karl Fischer (KF) coulometric titration (ASTM D6304) . This titration method is somewhat cumbersome, as it requires hazardous reagents, careful sample preparation, expensive equipment, and at least several minutes per analysis. However, Karl Fischer analysis for water can yield highly accurate and repeatable results when executed by a skilled operator and is the comparative method for other analytical techniques for water determination. Also, the water does not have to be fully dissolved in the oil.

The FluidScan portable analyzer can detect the light scattering of water droplets present in oil by a lift in the baseline of the infrared absorbance spectrum. Figure 1 shows several FluidScan spectra of used turbine oil samples with high levels of water contamination.

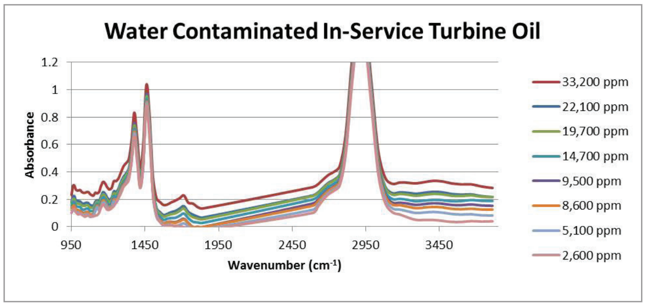

Figure 1. FluidScan spectra of used turbine oil heavily contaminated with water used to monitor a vacuum dehydration process at a power generation plant.

The degree of light scattering caused by a water-in-oil mixture indeed depends on the concentration of water present, but it also is strongly influenced by how the water is physically dispersed in the oil: the number and size of discrete water droplets present in the oil (Figure 2).

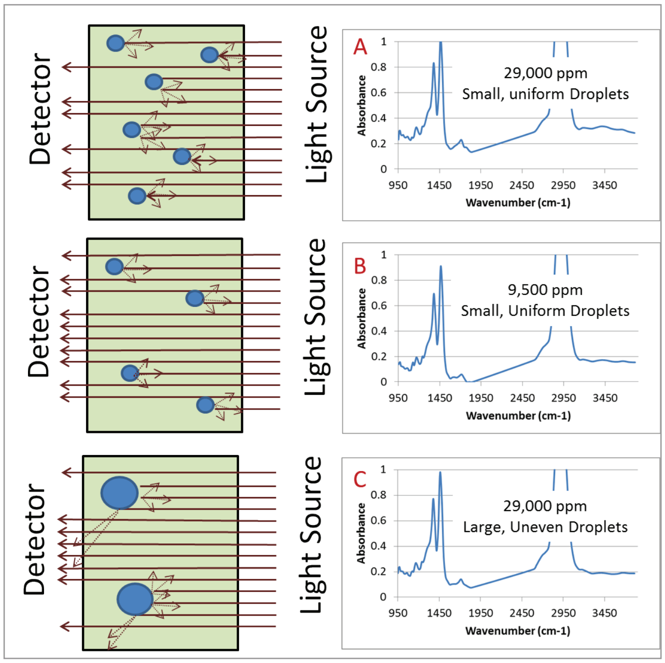

Figure 2. Graphical representation of light scattering in used turbine oil due to varied water droplets. Spectrum A is a used turbine oil with 29,000 ppm water contamination immediately analyzed after homogenization. Spectrum B is a used turbine oil with 9,500 ppm water contamination immediately analyzed after homogenization. Spectrum C is the same sample as in A (29,000 ppm) but has been allowed to sit for 45 minutes after homogenization. The change in concentration and water droplet size is apparent in the degree of baseline lift.

For this reason, it is important to have representative, homogeneous sampling. A portable instrument such as the FluidScan can be used at the sampling site for immediate results where the oil and water will be homogeneous due to the turbulent motion inside the instrument. If the samples are left to settle, perhaps during transit to a designated oil analysis site or laboratory, the water will eventually separate (Figure 3). After the water has completely separated from the oil, it is difficult to get accurate measurement of the water content.

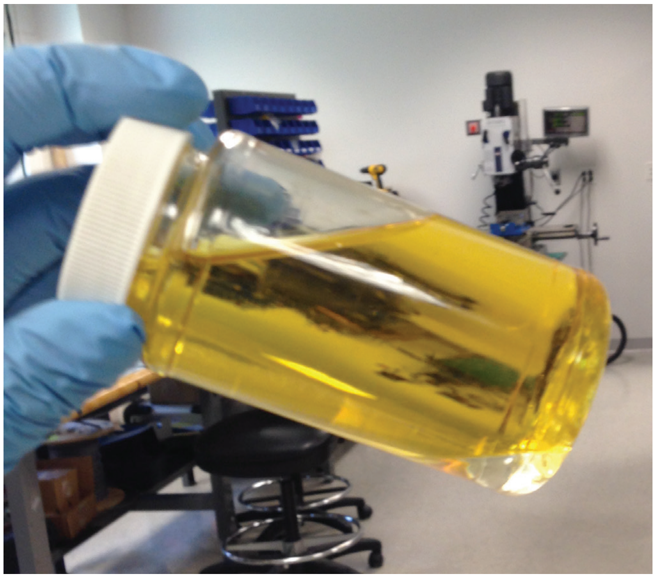

Figure 3. Sample of used Chevron GST 32, as received after shipment from a power generation plant.

Method

A new water calibration which measures light scattering due to the presence of water droplets is available on the FluidScan for the Industrial Library. The method was developed with water-contaminated samples of several popular brands of turbine and gear/bearing oils for a robust universal calibration of industrial fluids ranging from 1,000 ppm up to 65,000 ppm water. An important component of the method is the use of a homogenizer. The samples were homogenized with a CAT 120X homogenizer and allowed to sit at room temperature for 2 minutes (no more than 30 minutes) prior to measurement on the FluidScan (Figure 4).

Figure 4. Homogenizing a sample of water-contaminated oil.

Results

Sixteen samples between the range of 500 ppm and 10,000 ppm water contamination were used to test the Total Water FluidScan measurement against Karl Fischer D6304. Each sample was prepared by homogenizing them for 30 seconds on high prior to analysis. They were measured simultaneously on three FluidScans and by Karl Fischer to minimize the effects of sampling errors. The results are shown in Figure 5.

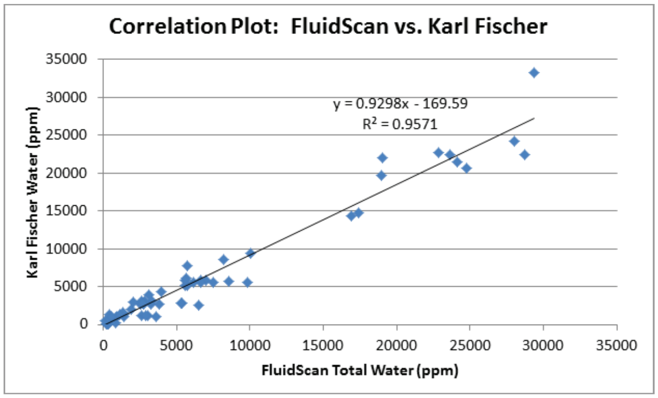

Figure 5. Comparison of the new total water measurement on the FluidScan to ASTM D6304 Karl Fischer titration method.

To demonstrate the importance of the homogenizer in the determination of industrial fluids which are designed for excellent water separability, a test set comprised on 13 in-service Chevron GST 32 oil samples from a power generation plant were analyzed with and without proper homogenization.

Group A: Samples were homogenized for 30 seconds on high (Figure 6). Before analysis, the sample bottles were gently inverted 20 times to mix.

Figure 6. Samples which after being homogenized for 30 seconds on high.

Group B: Samples were shaken vigorously by hand for 30 seconds (Figure 7) and then left to sit for several minutes to allow air bubbles to dissipate. Before analysis, the sample bottles were gently inverted 20 times to mix.

Figure 7. Sample which was shaken vigorously by hand for 30 seconds. To the eye, the opacity looks similar to the homogenized samples even though the water is not uniformly dispersed in the sample.

A plastic disposable pipette was filled from the middle of the bottle, and the same aliquot was used to dispense fluid into KF vials and onto the FluidScan flip-top cell. The results are shown in Figure 8.

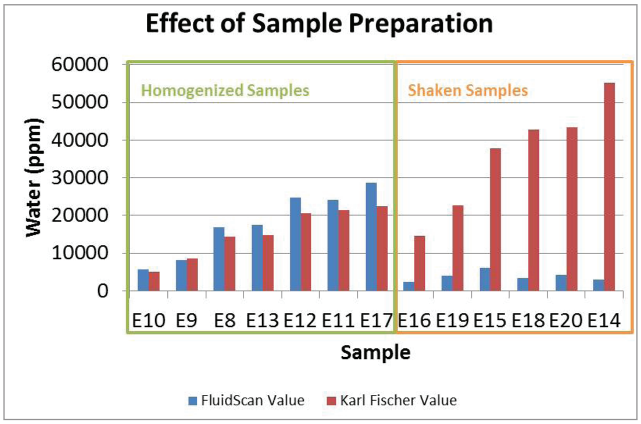

Figure 8. The samples prepared with a homogenizer showed great agreement between the calculated water concentration on the FluidScan and Karl Fischer result. The samples that were shaken by hand were not accurate.

Clearly, the sample preparation method has a large effect on the results. All samples prepared only with vigorous hand-shaking (Method B) had unacceptably large error, and in fact, never measured higher than 6,000 ppm water on the FluidScan. Even though the hand-shaken sample appeared opaque similarly to the homogenized samples, a hand-shaken mixture of oil with water is not truly homogenous. For at site analysis, a fresh oil sample measured immediately at the sampling site should be homogeneous with uniform water droplet size from the turbulence and shearing inside the machine.

The new, improved water measurement for turbine oils is now available on the FluidScan for all turbine oils from 1,000 ppm and above. If the total water calibration <1,000 ppm is not available for a fluid the total water detected is <1,000 ppm, the FluidScan will report the traditional E2412 dissolved water result and alert the user with a message "Free Water may be present <1000 ppm" (Figure 9). This is a benefit over the old water calibration for FluidScan because the old method just reported the dissolved water peak and left the user to wonder whether there was free water present in the oil.

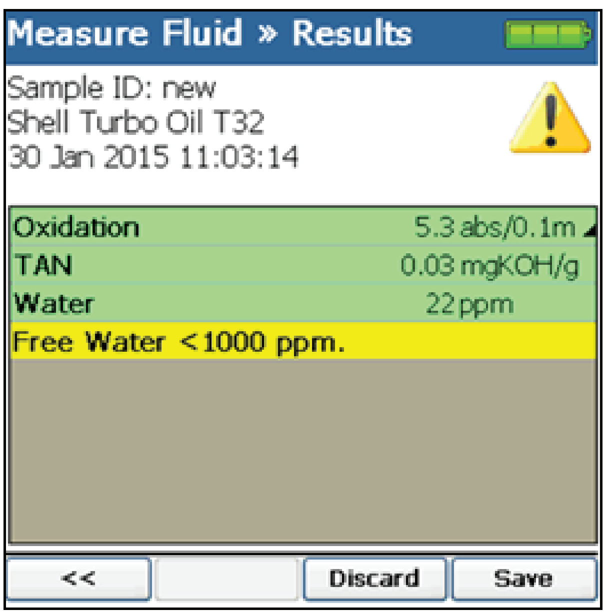

Figure 9. The warning message to the user that free water may be present in a sample up to 1000 ppm.

Conclusion

The new FluidScan method for analysis of water contamination in turbine oils is a robust, reliable method capable of providing immediate alert of severe water contamination. The largest contributor to the variation is the sampling. Hand-shaking is not sufficient for obtaining a homogeneous sample and reliable results for water measurement on the FluidScan. Immediate analysis at-site or the preparation of samples prior to analysis with a commercially available homogenizer is recommended for the best results. With best practice sampling technique, results correlating within 20% to Karl Fischer can be achieved. The new FluidScan water calibration provides accurate determination of the total water contamination in an oil sample of 1,000 and above for all turbine oils and from 1 ppm and above for a growing number of turbine oils. A benefit over the previous water calibration based on E2412 is that the FluidScan will alert the user when the total water is less than 1,000 ppm if a more accurate determination cannot be provided.

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