

# ON-SITE FT-IR QUANTITATIVE ANALYSIS OF WATER IN TURBINE OIL

BY FRANK HIGGINS  
APPLICATION SCIENTIST

## INTRODUCTION

The availability of the Portable Analyzer for Lube (PAL)<sup>TM</sup> Series FTIR spectrometers, which are compact, easy-to-use and affordable systems, provides new capabilities for real-time, on-site analysis of high value assets such as turbines. With PAL<sup>TM</sup> spectrometers, the lubrication specialist now has the ability to monitor key parameters such as oxidation, additive depletion and levels of water in lubricants. In this application brief, we will demonstrate that the PAL Series<sup>TM</sup> FTIR spectrometer has the sensitivity, accuracy and reproducibility to determine the level of water in turbine oils without the difficulties associated with the conventional Karl Fischer technique.

## 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, as soon as possible after drawing the sample, is a substantial benefit in obtaining accurate water level results. Off-site analysis for trace water in oil may be compromised due to variability of water



PAL SERIES<sup>TM</sup>

concentration introduced by storage, transportation, or shipment of a sample. Furthermore, turbine oils contain demulsifying additives that cause microscopic water droplets to separate from the oil and concentrate in layers at the bottom and sides of containers. This demulsifying action takes time to occur, and can cause large variations in analytical measurements. Also, oil samples can sometimes pick up or lose water simply depending on the type of sample container used.

## 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. However, KF analysis is considered the “gold standard” method for analyzing water in oil because it provides accurate and precise answers.

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 reagents and when a rugged and easy-to-use FTIR system such as A2 Technologies PAL Series instrument 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 on a high precision balance before and after injecting into the titration vessel. 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.

This application brief will demonstrate that FTIR spectroscopic analysis using the PAL™ FTIR is as accurate and precise as the Karl Fischer method within the analytical range necessary for measuring water in turbine oil. Using the PAL instrument, we have developed two FTIR methods for water in turbine oil and have calibrated and evaluated them against the Gold Standard Karl Fischer procedure.

## WATER IN TURBINE OIL - THE FTIR METHOD

Used turbine oil (C&C Oil Co.) was homogenized with water and aged overnight at 70°C to make a very high water standard. This standard was then diluted with various amounts of a used turbine oil mix, which contains oil in-service four months and another more degraded oil with a dark amber color. These dilutions had various amounts of water based on how much “as is” oil was added. The samples were mixed well and allowed to equilibrate for about an hour before they were analyzed by coulometric Karl Fischer titration (Metrohm 756 KF Coulometer) to determine the concentration of water. The samples were run in duplicate by KF before the infrared spectra were acquired using the PAL FTIR spectrometer. The water concentrations for the prepared standards ranged from 22-3720ppm (parts per million). The water IR absorbance measurement for each standard sample was plotted versus the corresponding KF water data to obtain a residual least squares linear regression. The IR spectra were also analyzed using a partial least squares method to develop a regression model for the quantitative predictions of water in oil.

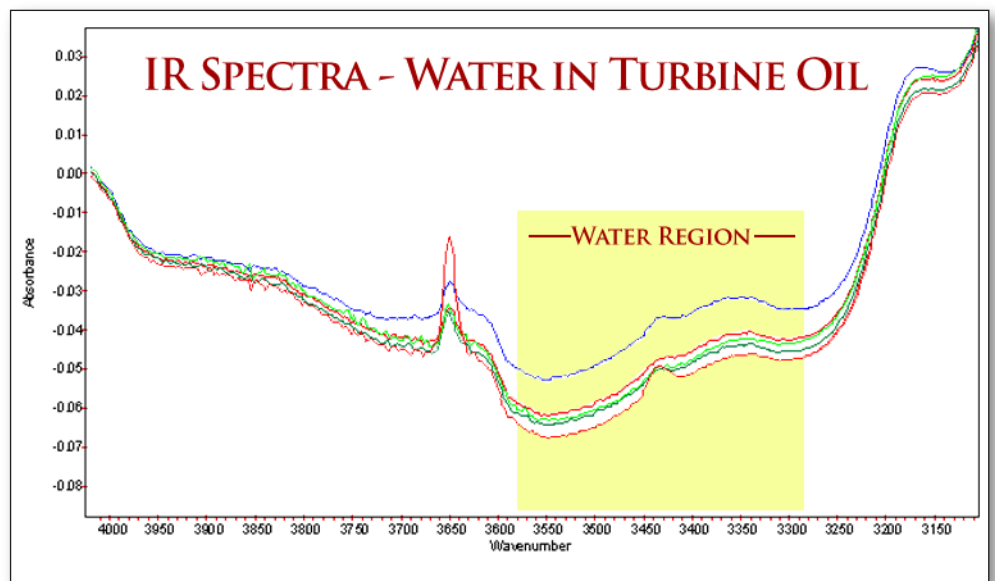
## CALIBRATION RESULTS

The IR analysis and calibration models indicate a very good correlation between the PAL Series™ FTIR measurements and the Karl Fischer water data. Two different methods were developed for the quantitative measurement

of water in oil using the PAL Series™ FTIR spectrometer. The first is a relatively simple conventional IR absorbance model following Beer’s Law that uses the region of the IR spectrum in which water strongly absorbs, known as the O-H stretch region. The second method uses multiple regions of the IR spectrum with partial least squares (PLS) chemometric modeling to reduce the effects of noise, baseline variance, and other interfering factors.

## BEER’S LAW MODEL

In the first method, a peak area absorbance measurement provides a detection limit of about 30ppm water in oil (Figure 1). The IR spectra of 15 samples with KF water values ranging from 7-270ppm were used to build a linear calibration curve that follows Beer’s Law (Figure 2). The weakest water absorbance in Figure 1 is new turbine oil with 30ppm of water (Red) and the strongest water absorbance is shown in blue with a KF water value of 1460ppm. The calibration plot is shown in Figure 2 with a correlation coefficient of  $R^2=0.977$  and a standard error of validation (SEV) of ~40ppm (20-270ppm range). The addition of higher water concentration standards to the calibration improves the correlation coefficient to  $R^2=0.996$ . Therefore, this calibration is optimized for the low levels of water (<500ppm), but is still quite accurate for predications of higher water levels above 500ppm if necessary.



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

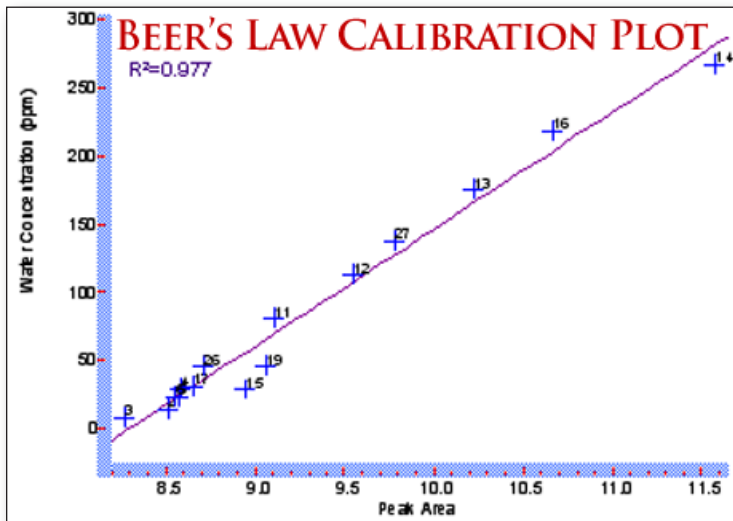


Figure 2: The calibration plot of KF water values (ppm) versus peak absorbance area for water in turbine oil using a Beer's Law peak area method.

### PLS MODEL

The PLS chemometric model uses more sophisticated mathematics to develop models that are typically more robust and accurate than the conventional Beer's Law IR absorbance method demonstrated above. Whereas both the PLS and the Beer's law quantitative methods for water in oil are sufficient for classification into 100ppm ranges (i.e. <100ppm, 100-200ppm, 200-300ppm, etc.), the PLS method provides the most accurate KF water prediction values over the whole range of 30-1500ppm.

In order to develop the PLS method for water in oil, we used 23 standards covering a range from 7-1460 ppm water. We then recorded the IR spectrum and measured the water level by the KF method. The two sets of results were correlated with partial least squares and the predicted versus actual KF values are plotted in Figure 3 and indicate a correlation coefficient of  $R^2=0.990$ .

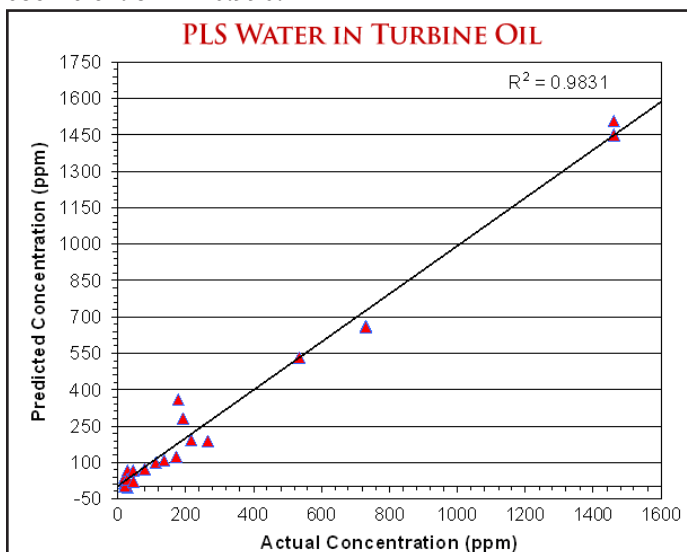


Figure 3: The PLS predicted versus actual plot of KF values using ML FT-IR spectrometer.

### PREDICTIONS

To validate each FT-IR method, 15 unknown mixtures were made by mixing used turbine oils with hydrated turbine oils, and running them by KF (in duplicate) and by FT-IR (in triplicate). The coulometric KF performance was verified using 100ppm and 1000ppm NIST reference standards. It was found that thorough mixing was important to obtain quality data, due to the heterogeneous nature of water in turbine oil. Environmental and experimental factors caused the KF duplicate measurements to typically vary by 30-60ppm, measured consecutively in the 100-1000ppm range. The FT-IR water predictions indicated similar variations in replicate measurements of the same sample. The averages of the replicate measurements by KF and FT-IR are compared in Table 1. Good agreement with the KF measurements is observed for both FT-IR methods, however, the PLS predictions are statistically better in the 100-1500 ppm range. The standard deviation between the averaged PLS predictions and the averaged KF data (0-700ppm range) are all below 30ppm, except for one sample (#11). The Beer's Law method predictions are better in the 0-100ppm range, and are sufficient to classify the water concentrations into ranges as follows: <100ppm, 100-200ppm, 200-500ppm, and 500+ppm.

### PREDICTIVE RESULTS TABLE

Validation Sample	Beer's Law (ppm water)	PLS (ppm water*)	KF (ppm water)
Turbine Oil 1	26.5	-	27.5
Turbine Oil 2	160	194.6	199.7
Turbine Oil 3	125.2	139	145.1
Turbine Oil 4	15.1	-	12.4
Turbine Oil 5	21	-	19.8
Turbine Oil 6	63	64.5	40.8
Turbine Oil 7	251.8	219.3	215.3
Turbine Oil 8	117.9	70.3	111.1
Turbine Oil 9	539.3	685.4	663.3
Turbine Oil 10	350	300	246
Turbine Oil 11	340.7	367.3	285.7
Turbine Oil 12	251.8	244.4	206.5
Turbine Oil 13	2979.3	3780.5	3674
Turbine Oil 14	1100.3	1375	1027.5
Turbine Oil 15	1219.2	1541.9	1362.4

Table 1: The validation set of averaged FT-IR ppm water predictions are compared to the averaged coulometric KF ppm water values in turbine oil unknowns.

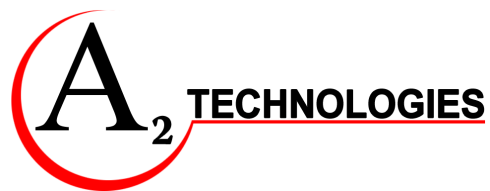
\*PLS model is not valid below 30ppm water.

## CONCLUSIONS

We have shown that the A2 Technologies' PAL™ FTIR Spectrometer is capable of measuring water in oil at the levels that are critical to the reliable operation of the turbine equipment. The capability of measuring water in turbine oil by FTIR spectroscopy eliminates the issues associated with Karl Fischer measurements including the need for expensive and hazardous consumables, the time required for the KF measurement as well as the dependency on the skill of the operator and the operating condition of the KF equipment.

As importantly, the ability to measure water levels at-site via FTIR means that the results will be more accurate, more reproducible and obtained far more rapidly than samples that are sent for off-site analysis to a traditional oil analysis lab. We have observed that low ppm levels of water are observed to change on an hourly basis if left open to air - a sample that initially was 200ppm can have less than 100ppm if left in an open sample container overnight. This is also true if the sample container is not filled to the top, and water can evaporate into the head space (air) of the jar. One can only imagine the level of error that is introduced when half filled jars are sent to off site labs.

The PAL Series™ FTIR spectrometer can detect water at the necessary warning levels. The system can alert when water reaches 100ppm and then issue a critical warning if the water reaches 200ppm. In addition to the analysis of water, A2 Technologies' Mobility spectrometers can measure the depletion of additives and determine the levels of oxidation and nitration by-products in turbine oils.



[WWW.A2TECHNOLOGIES.COM](http://WWW.A2TECHNOLOGIES.COM)

14 COMMERCE DRIVE. - DANBURY, CT 06810

NORTH AMERICA: 203.312.1100 - INTERNATIONAL +44 (0) 7765970210