

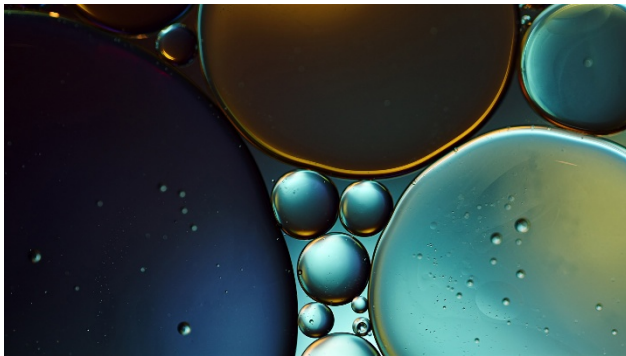
Quantification of water contamination in lubricating oils with eraspec oil and correlation to Karl Fischer titration



Besides its main functions, lubricating oil also acts as a primary diagnostic medium circulating through critical components and carrying valuable indicator data regarding equipment health. Among the parameters evaluated during routine oil analysis, the quantification of water contamination is essential for determining lubricant quality and predicting mechanical performance.

Undetected water ingress poses a severe threat to operational reliability. Even trace amounts of moisture can initiate severe degradation pathways:

- Water directly accelerates oxidative corrosion on metallic surfaces, leading to heightened component wear in moving parts.
- Excess moisture degrades oil viscosity, alters fluid dynamics, and reduces film strength, thereby severely compromising overall lubrication efficiency.
- Free and emulsified water provides a growth medium for bacteria. Biological growth leads to the premature plugging of filtration systems and unwanted odor.



Precise determination of water content in lubricating oils is an essential requirement for effective machine condition monitoring and predictive maintenance strategies.

Coulometric Karl Fischer titration according to ASTM D6304 is widely recognized as the industry reference method for quantifying water content in

liquids. For used oils, typically ASTM D6304B (oven method) is preferred as it is less prone to interference from oil additives. Titration requires reagents, and the analysis can take several hours per sample depending on the total water concentration. In contrast, FTIR-based methods, based on the IR absorption of water's OH groups, offer quick and easy analysis in minutes without the use of any consumables.

It is already known that a correlation between these two methods for a given fresh lubricant can be found. Whether these two methods correlate for in-service oils and oils with different additive packages is a question which remains largely unanswered.

To investigate such a general correlation, 14 fresh and in-service oils were measured as received as well as spiked with known water concentrations.

The samples included hydraulic fluids, gear oils, engine oils and marine oils; the water concentrations ranged from 20 ppm - 2500 ppm. The samples were sonicated for 1 hour prior to side-by-side measurements with the two methods.



A particular challenge in the determination of water is the wide concentration range, ranging from a few ppm for hydraulic fluids to many thousand ppm for in-service engine oils. To cover this range, **eraspec oil** is equipped with a 500 μm measuring cell in addition to the standard 100 μm cell used for in-service oil FTIR analysis. An additional reference cell completes the unique triple-cell design. This multi-cell design enables **eraspec oil** to automatically measure different parts of the spectrum with the optimum sensitivity based on the spectral absorbance, which offers

significant analytical advantages when measuring trace substances.

Standard FTIR in-service oil analysis as in ASTM E2412 uses the entire primary water IR absorption band (3150 cm^{-1} to 3500 cm^{-1}). In this spectral region, it is not possible to differentiate between the OH-stretching vibrations of water and those of accumulating oxidation products. Furthermore, various additives (e.g. glycol or methanol) also contain OH groups and will contribute to the IR signal.

These factors indicate that a simple spectral integration (e.g. ASTM E2412) followed by a linear calibration will not be able to accurately describe the water content in the general case of in-service oil or in oils with different compositions. To overcome these limitations, **eraspec oil** utilizes a chemometric prediction model based on Multiple Linear Regression (MLR). This model uses multiple parts of the broad OH vibration peak, together with selected spectral regions corresponding to additives containing OH groups and oxidation products.

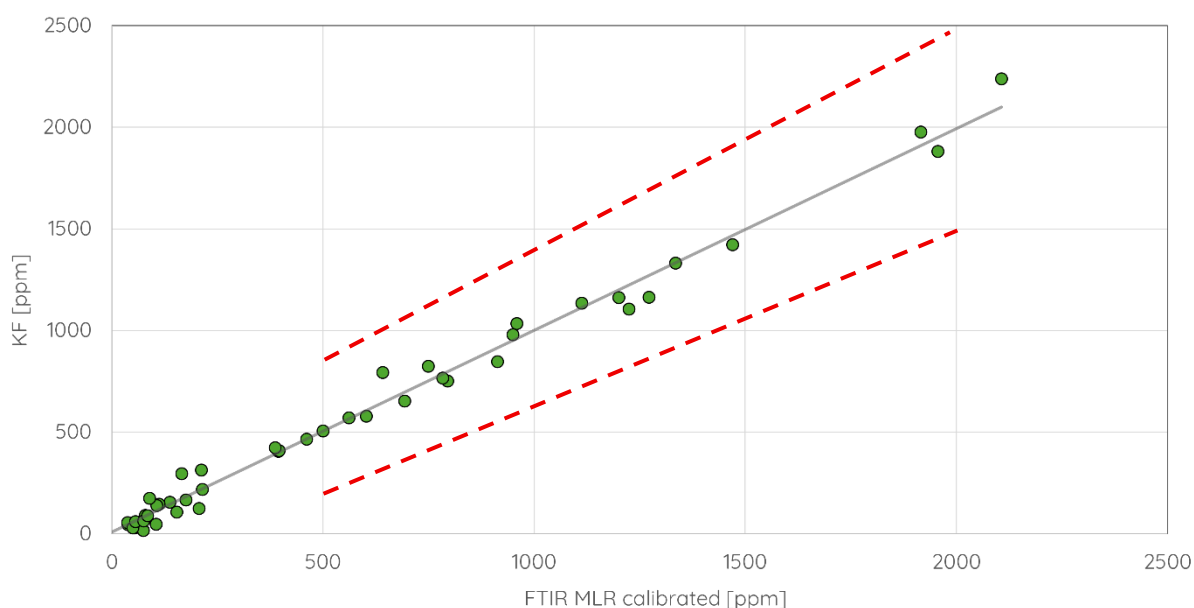


Figure 3a: Comparison of water content according to ASTM D6304 Procedure B and **eraspec oil** MLR Model for fresh and in-service oils in the full range. The red dotted line indicates the reproducibility (R) of the reference Karl Fischer method.

The correlation between the MLR model and the Karl Fischer method results are shown in figure 3a. The model displays an excellent linearity and has a root mean square (RMS) error of 57 ppm measured over the entire measurement range. Focusing on the range from 0 ppm - 500 ppm as shown in figure 3b, covering hydraulic and gear oils, the RMS error was found to be 29 ppm. These values fall comfortably within the reproducibility limits specified by ASTM D6304 Procedure B ($R = 154$ ppm at 100 ppm).

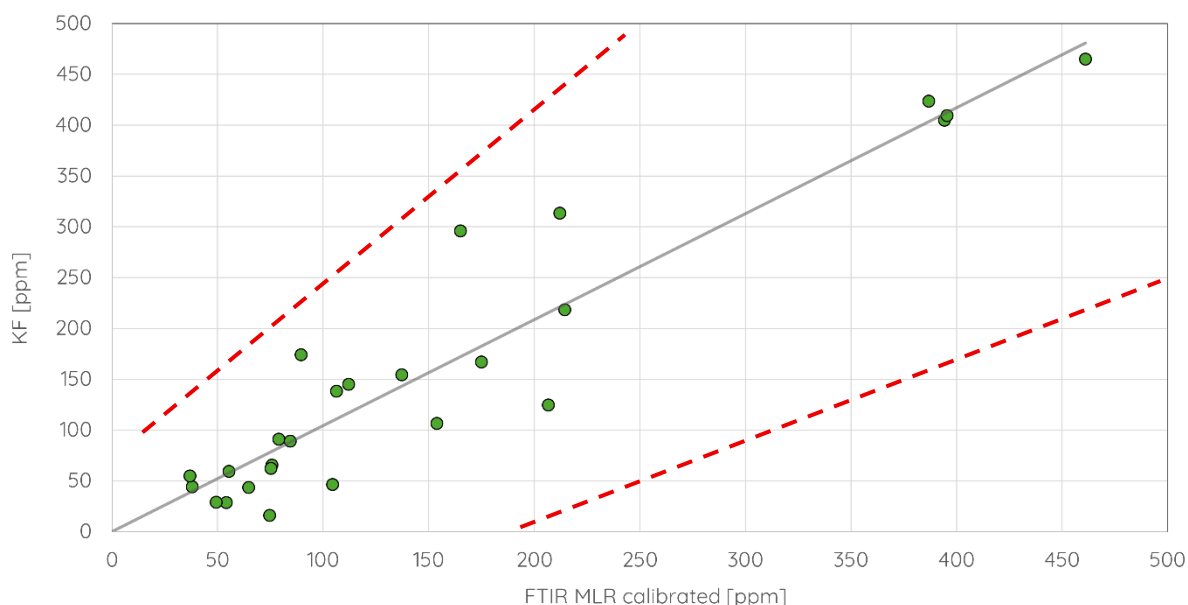


Figure 3b: Comparison of water content according to ASTM D6304 Procedure B and eraspec oil MLR Model for fresh and in-service oils with water content below 500 ppm. The red dotted line indicates the reproducibility (R) of the reference Karl Fischer method.

Conclusion

Karl Fischer titration according to ASTM D6304 B is considered the reference for determination of water in in-service lubricating oils. Although considered accurate, the long measurement time (15 minutes to hours depending on water content) and use of reagents make alternative methods without long analysis times increasingly attractive.

In this work we have demonstrated the excellent correlation between eraspec oil's chemometric model and ASTM D6304 B over a wide range of lubricants and water concentrations for both fresh and in-service oils. Due to its triple cell design, eraspec oil can determine water with an accuracy comparable to the reproducibility of ASTM D6304 B over the entire range from 20 ppm - 2500 ppm.

The model library for water prediction is pre-installed on the eraspec oil FTIR lube oil analyzer but can be easily extended by the operator.