Will Your Oil in Water Analysis Method Match the Regulatory Method?

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The analysis of oil in water is a worldwide problem that crosses many industries, analytical methods and regulatory agencies. For those in the petroleum industry, the offshore platform oil and grease limits for produced water can be quite different from the effluent coming out of the refinery. For the expanding hydraulic fracturing industry, oil in water limits are driven by whether the frac or produced water will be treated for reuse, disposed of down an inactive well, or sent off-site for treatment.

Those individuals tasked with having to determine the amount of oil in water know it can be a challenging measurement. It is complicated by the fact that oil comes in many forms and is not a unique chemical entity. Added to the chemical non-uniformity is a number of different analytical methods that could be used, ie: solvent extraction/gravimetric, gas chromatography, solvent extraction/infrared, and solvent extraction/UV to name a few.

The measurement is, therefore, defined by the particular regulatory method used to measure it. When EPA 1664 is the regulatory method, the "oil" is anything that is extracted into hexane and remains after the hexane has been evaporated and shows up as weight. In regions where infrared analysis is the defining method, the "oil" is whatever is extracted into the solvent and has carbon-hydrogen bonds that absorb infrared light at a specific frequency. Each method is looking at different properties of oil and can potentially give different results.

The answer to the commonly asked question of how one type of oil in water measurement compares with different regulatory methods is not always simple and straightforward. Listed below are four factors that need to be considered:

1. Precision and bias for each method

There are acceptable errors for each method typically expressed in the precision and bias statement for the method. For example, EPA Method 1664 states in their "Ongoing precision & recovery" (section 17.0) that for a 100 ppm sample the acceptable range is 78 -114 ppm. If the test includes the silica gel treatment (SGT) to remove the polar organics, the acceptable range is 64 – 132 ppm. Therefore, if the result from a laboratory for a silica gel treated sample is 65 ppm and the alternate method result is 130 ppm, they are within the acceptable range.

2. Operator errors

As suggested previously, even the same method can give significantly different results. With any method where there is sample preparation, the human factor is added in. If a solvent/sample mix is only shaken for one minute rather than the required two minutes, the amount of oil extracted into the solvent will be significantly less. In some cases, it has been half the reading. The chart below shows a comparison of a five way sample split that was analysed on two InfraCal TOG/TPH Analysers (see photo) using infrared analysis and at three laboratories using the EPA 1664 hexane/gravimetric method. The results disprove the common misconception that the lab is always right.

Wilks InfraCal	Customer InfraCal	Lab 1	Lab 2	Lab
51	49	67	23	51
62	61	74	43	47
71	--	76	70	49
63	53	66	55	40
3	1	14	7	<5

3. Sampling

Sample collection and handling can cause differences for comparative testing. In order to have an objective comparison, the samples should be identical. If there is variability in the waste stream, this can be a difficult task. The old adage that oil and water do not mix holds true for wastewater as well.

Oil also likes to stick to surfaces. If sample collection containers are being reused, they should get a final solvent rinse after cleaning to remove any residual oil. For sample analysis, the solvent should either be blended in the sample container or if the sample is to be transferred to another container, the sample container should be rinsed with a portion of the solvent that will be used for the extraction. If not, any oil on the container surface will be excluded from the reading.

4. Sample Disparities

Not all oil in water samples are alike which makes it difficult when comparing analytical methods that look at different properties of the oil in order to make the measurement. Oil is a mix of chemical components that changes from one location to another--it can even change at the same location.

For example, samples often contain a mix of aromatic and aliphatic hydrocarbons. UV fluorescence only detects aromatic hydrocarbons while infrared will detect both aromatic and aliphatic hydrocarbons. The two analytical methods could give different results if the aromatic/aliphatic ratio changes.

Samples that contain volatile hydrocarbons could also show different results between EPA 1664

InfraCal Model HATR-T2	EPA 1664
31	33
15	32
17	27
23	29
15	30
20	34
10	12
12	14
12	13
2	14
25	24
19	11
13	21
10	21
17	21
17	19
15	19
13	14
13	8
13	10
14	11
13	12

and an infrared transmission method. With the 1664 gravimetric method, any volatile oils below the boiling point of hexane will be evaporated off with the solvent. With an infrared method using a transmission cell, the oil is measured directly in the solvent without evaporation and the volatile hydrocarbons will be retained. This will make a transmission infrared reading higher than an EPA 1664 result if the sample has volatile oils.

While all of the considerations listed above make it look like any correlation could be difficult, by using careful analytical procedures, understanding the composition of the waste stream and knowing the limits of each measurement system, useful information can still be generated. The table to the left shows samples from on an oil rig in the North Sea that were tested by a laboratory using EPA 1664 and the InfraCal TOG/TPH Analyser, Model HATR-T2 (see photo) which uses hexane as an extraction solvent. With this infrared method the hexane is evaporated off prior to measurement so the volatile hydrocarbons will not be retained and should give a reading closer to the hexane/gravimetric method. This example shows that infrared analysis, which has been used off-shore for over 40 years, can be a valuable tool in assessing if an oil separation system is performing to the required specifications.

So, the answer to the initial question as to whether one analysis method will match another is that most methods will typically correlate closely enough to provide operators with the information necessary to make sure their effluent does not exceed the regulatory limit. Will the numbers match exactly? Sometimes...

Note: For a more in depth review of this topic, please see the write up by Dan Caudle of Sound Environmental Solutions, Inc. for the Oil in Water Monitoring Workshop 2002 titled "Sources of Error in Oil in Water Measurements and their Impact on Comparing Oil in Water Monitors". http://www.wilksir.com/pdf/SourceforErrors.pdf

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Eclipse Model Advances Guided Wave Radar Technology

Magnetrol International (Netherlands), have launched the ECLIPSE Model 706 guided wave radar (GWR) transmitter, a level control solution that advances guided wave radar technology with improved performance for a wide range of level and interface control applications.

The ECLIPSE Model 706 is designed to provide outstanding accuracy, reliability and safety for virtually all process industries. Latest-generation features include:

Enhanced Signal Performance – The ECLIPSE Model 706 innovative GWR circuitry achieves both a higher transmit pulse amplitude and improved receiver sensitivity, resulting in a signal-to-noise ratio (SNR) that is nearly 300% higher than competitive GWR devices. This assures precise, dependable control for every level application, including extremely low dielectric media, extended measuring ranges, and punishing conditions where foaming, boiling or flashing can occur.

Overfill Capable Probes – Magnetrol offers the only guided wave radar transmitter on the market with a complete line of overfill capable probes. Unlike other GWR transmitters that use algorithms to inter level readings in top-of-the-probe dead zones, the ECLIPSE Model 706 measures true level to within specification all the way up to the process flange. Coaxial and single rod overfill capable probes can be installed in various configurations on the vessel, even when the risk of flooding exists.

Advanced Diagnostics – The ECLIPSE Model 706 takes the user interface experience to new levels of convenience and functionality. The LCD diagnostics convey critical real-time waveform and trend data with outstanding ease of use. Additionally, the ECLIPSE Model 706 can be preconfigured online prior to shipment, to ensure plug-and-play transmitter commissioning and automatic capture of echo curve during upsets.

The ECLIPSE Model 706 transmitter provides safe, efficient and cost-effective liquid level and interface control, and is virtually unaffected by fluctuating process conditions including density, dielectric, viscosity and specific gravity.

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Transformer Oil Quality Monitoring - Online, Continuous, Plug-and-Play

Oil quality in high voltage transformers is critical to both safety and efficiency. OilQSens® from **cmc Instruments GmbH** (Germany) is a unique, new oil condition monitor, online and continuous. It detects changes in oil quality much earlier than traditional technologies such as dissolved gas analysis (DGA).

For established power supply companies, asset protection is key to their profitability. Predictive maintenance clearly has benefits over rigid inspection and maintenance intervals. OilQSens® is earlier and more sensitive than other technologies.

Compared to Dissolved Gas Analysis (DGA) the measurement is continuous not sampling, requires no consumables, is virtually maintenance free, requires no technical skill to operate and yet is as much as half the price of leading DGA brands.

OilQSens® is set to become the new standard for continuous monitoring of transformer oil quality. It accurately shows the aging of oil and also directly correlates to water in oil. The readings are fully temperature compensated for accurate comparison of data over long periods of time.

OilQSens® is easy to install or retro-fit. The decentralised, web based monitoring system makes results available anywhere in the world.

cmc Instruments GmbH manufacture trace moisture analysers, gas generators, filter systems for process gases and the new OilQSens® and WearSens®- patented, online system for oil condition monitoring in different applications.

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Monitoring High Temperature Industrial Installations

An application report from **FLIR Systems** (France) details how the German Bayernoil refinery complex has used a FLIR infrared furnace camera to monitor its hydro reformers enabling them to keep the installations up and running efficiently.

Stable high temperatures and efficient combustion in refinery furnaces, heaters and boilers are mandatory for a continuous output of high-quality oil derivates. The high temperature hydro reformer installations at Bayernoil run 24/7 and at 100% capacity to satisfy the high demand for their petroleum products. Hence the major importance of condition monitoring and preventive maintenance of furnaces and heat supply.

Using a FLIR GF309 furnace camera - the application report details how engineers regularly inspect the different types of furnaces at the three Bayernoil sites. Calibrated for measurements of up to 1,500 °C, the FLIR GF309 furnace camera provides temperature reading across entire high-temperature surface areas, enabling a faster inspection in critical or potentially hazardous environments. The FLIR GF309 furnace camera's protective shield is designed not only to reflect the heat away from the camera and its user, but also entirely cover the area of a furnace inspection window.

The information gathered by the furnace camera has helped Bayernoil to determine when furnace temperature sensors need to be exchanged; indicate if the temperature of piping stays within acceptable safe limits; provide information if productivity can be raised and to assess the condition of the furnace burners to determine whether they have to be adjusted or cleaned.

Using the FLIR Reporter software suite on the GF309 furnace camera - Bayernoil engineers are able to gather and analyse their findings and to share them with the process safety, production and maintenance specialists at the plants, enabling them to assess and optimise production.

Overall Bayernoil have found that the FLIR GF309 furnace camera has given them key information on the thermal load of their furnace and piping installations enabling production optimisation and an improvement in operational safety. They expect the infra-red camera to be amortised within two years.

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