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WHITE PAPER

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

Anyone involved in field analysis of oil in water will continually get the question "Does your equipment match the regulatory method?"

While the amount of oil in water is highly regulated – it can also be a challenging measurement. It is complicated by the fact that oil comes in many forms and the measurement is defined by the particular regulatory method. 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.

Therefore, 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 (Figure 1) shows a comparison of a five way sample split analyzed on two InfraCal Analyzers and at three laboratories. The results disprove the common misconception that the lab is always right.

INFRACAL A	INFRACAL B	LAB 1	LAB 2	LAB 3
51	49	67	23	51
62	61	74	43	47
71	--	76	70	49
63	53	66	55	40
3	1	14	7	<5

Figure 1

INFRACAL MODEL ATR	NTL-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

Figure 2

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 glass. 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. It 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 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 (Figure 2) shows samples from on an oil rig in the North Sea that were tested by a laboratory using EPA 1664 and the InfraCal Analyzer, Model ATR, which uses hexane as an extraction solvent. 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? Usually…

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