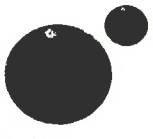
Comparing oil and grease in water testing methods

Whether trying to meet effluent limits for a National Pollutant Discharge Elimination System (NPDES) permit or comply with oil and grease limits for the Clean Water Act (CWA), it is important to understand what could make oil in water readings vary. The following factors need to be considered when comparing oil in water analysis methods:



1. Different methods measure different properties of oil

Oil comes in many forms and the measurement is defined by the regulatory method. If EPA 1664 is the regulatory method, the 'oil' is anything extracted from the water into hexane and left after the hexane has been evaporated to show 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 physical properties of oil and can potentially give different results.

2. Precision and bias statement for each oil in water 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 the 'Ongoing precision and 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 both within the acceptable range.

3. Operator differences

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. Table 1 shows a comparison of a five-way sample split analysed on two InfraCal TOG/TPH Analyzers and at three laboratories. The results disprove the common misconception that the lab is always right.

Wilks InfraCal	Customer InfraCal	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

Table 1: A five-way sample split

4. Taking oil and grease grab samples

In order to have an objective comparison, 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 be rinsed with solvent 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 original 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.

5. 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. Table 2 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 Analyzer, Model HATR-T2, 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.

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 even though the numbers may not always match exactly.

InfraCal Model HATR-T2	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

Table 2: Lab-tested oil rig samples

For more information:
http://wilksir.com/pdf/WP_Comparing_oil_in_water_methods.pdf