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## **Measuring Oil in Water: A Sanity Check**

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### **Abstract**

Reliable measurements of oil in water are becoming increasingly important to the petroleum industry. As the percent content of water in crude climbs higher, the need to increase the percent of oil recovered from the water treatment systems also climbs; efficiency in water removal corresponds directly to the bottom line for oil producers. Additionally, particularly on offshore platforms, there are stringent environmental regulations which need to be met.

The majority of well-proven techniques for measuring oil in water are “laboratory based”, typically using either gravimetric methods or IR (Infrared) Spectroscopy. However, lab-based measurements are too time-consuming for the realities of production environment. In particular, a water treatment system really needs to be monitored in several places in order to determine the efficacy of each treatment stage (and also for troubleshooting the process). This really requires an on-line or at least “at-line” monitoring approach for best results.

Over the years, several different methods have been proposed and used in the industry in order to accomplish real-time monitoring of oil in water content. Some of the more common methods tried include UV (ultraviolet) fluorescence, light obscuration, acoustic backscattering, IR absorption and digital imaging. All of these techniques claim to be able to measure oil in water accurately.

In this paper, we will take three actual instruments and compare their results against a standard EPA testing lab results. Solutions of known oil in water concentration were mixed in the laboratory, and samples of each were run through the different instruments and also sent in parallel to a certified EPA testing lab. The results were then plotted together to get a snapshot view of how each instrument did versus the results from the independent lab. The results show that all techniques exhibit variance, and that no two instruments produce the same result. The point of this exercise is not to “prove” that any one technique is more accurate. Rather, the point to be made is that manufacturers’ specifications for accuracy should be at least “calibrated” to known and accepted measurement techniques.

### **Why Measure Oil in Water?**

Reliable measurement of oil in water, particularly in produced water, is becoming increasingly more important. Initially, measurement of oil in produced water was being driven primarily by environmental regulations, particularly those imposed on offshore operations. However, as the world’s supply of oil becomes smaller, the price continues to rise and extraction is taking place on supplies having higher water content. In light of this, the need to more carefully monitor oil extraction from water has increased dramatically. Not only do the oil producers want to extract the most possible oil from the supply, but the environmental regulations are becoming more stringently enforced with time.

The first topic that needs to be addressed is that there is no real precise definition of what “oil in water” exactly is, making it very difficult to define a measurement. This looseness of definition is due to the fact that oil (and grease) in produced water is not a specific chemical compound that can be easily measured (Caudle (2007)). Oil in produced water can consist of droplets of crude oil, asphaltines, production treatment chemicals, and other organic compounds. Furthermore, some of this oil may be suspended, while some of it may be dissolved in the water. The relative percentages of dissolved versus suspended oil can vary enormously in different sources as well as in different parts of the extraction process. Unfortunately, no single method

seems to be available that can accurately (and consistently) measure both suspended and dissolved oil in produced water. So we can see that “measuring oil in water” is not a precise science; it seems, rather, that it is best defined by the method used to measure it. This is further complicated by the fact that the method defined varies depending upon the area of the world one is located in.

### **Common Methods Used: Advantages & Disadvantages:**

In the United States, from a regulatory standpoint, the EPA defines oil in water based upon EPA Method 1664. This method uses a chemical extraction and gravimetric method consisting of extracting the oil in hexane at pH 2 or lower, and weighing the residue after evaporating the hexane. One note to make is that this method only measures the organic constituents that are soluble in hexane, so, once again, it does not measure all “oil in water”. However, this method does have the advantage of being a “direct” one, meaning that it actually measures the oil directly (as defined by the method). Other methods, such as Infrared (IR) absorption and Ultraviolet (UV) Fluorescence, do not directly measure the oil content and have to be “calibrated” against a direct method. The major drawback to this method is that it is limited to being done in a laboratory environment by skilled personnel.

As mentioned before, two very common techniques in use today include Infrared (IR) absorption and Ultraviolet (UV) fluorescence. These are “indirect” methods, in that they measure something that can be “correlated” to the amount of oil in water, but do not directly measure the oil in water. In the case of IR absorption, the method is based upon the fact that the carbon-hydrogen bond common to all organic compounds will absorb IR energy at a specific wavelength. Unfortunately, water also absorbs IR energy at these wavelengths, which means that the measurements must be performed on a sample which is in a solvent that does not absorb IR. In the past, this solvent was Freon™, but the use of this solvent has long since been banned for environmental reasons. Substitute solvents have been introduced as replacement for Freon. Because IR absorption is an indirect method, the instruments have to be calibrated using samples of known concentration. Furthermore, the calibration samples have to be similar in content to the actual produced water sample in order to claim any sort of correlation between the instrument readings and actual values. (Caudle (2007)) Finally, once again, due to the use of solvents and the complexity of the measurement, this technique is limited to being done in a laboratory environment by skilled personnel.

UV Fluorescence is another common indirect measurement technique being used. UV fluorescence techniques are based upon the fact that aromatic compounds such as the oil in produced water will absorb UV radiation and fluoresce at a different emission wavelength from the excitation wavelength. The amount of fluorescing done by the sample is proportional to the amount of aromatic compounds in the water and therefore proportional to the amount of oil in the sample. This technique has a distinct advantage over IR absorption in that the measurements can be made directly from the sample since water does not absorb UV, so therefore solvents are not required. However, this method still is classified as “indirect” because it does not directly measure the oil. Other compounds in the water, such as iron, can also fluoresce under UV. So, once again, the instruments have to be calibrated using samples of known concentrations which are similar in content to the actual produced water sample being measured.

The final common method of measuring oil in produced water is through various methods of particle counting, ranging from turbidimeters at the very low end to sophisticated optical or acoustic imaging systems on the very high end. Turbidity measurements are far too coarse for modern operations, and do not produce precise or repeatable results. Coulter counters, based upon electrozone sensing, have been studied for this application. However, these systems also very limited due to having to be used in a laboratory environment and the fact that they can not distinguish between oil droplets and other particulates such as sand.

One of the most encouraging areas of development for measuring oil in produced water is through the use of imaging particle analysis. In these imaging-based systems, real time images of particles suspended in the produced water are captured, and the particles are then identified as oil, bubbles, or other particulates based upon measured image attributes. Particle imaging has several advantages: it is a “direct” method of measurement, is extremely fast, and can potentially be used in-situ at the actual process site. The major disadvantage to particle imaging systems is that they can only detect what they can optically resolve. As a result, these systems are limited to suspended oil and particulates larger than 3 microns in size, and can not measure any dissolved oil.

One of the distinct advantages of imaging-based particle analyzers over other types is that the imaging-based systems can distinguish particle shape, and therefore can potentially differentiate oil droplets from other particulates such as sand. The oil droplets should be very spherical in shape, yielding a 2D image appearing as a circle. Other particulates such as sand will be less round in shape, and will also have a more “erose” circumference. Image parameters such as aspect ratio (width/length) and “circularity” (a comparison of circular perimeter (based on ESD) to actual perimeter) can be used to separate oil droplets from other particulates in this fashion.

## Methods Used:

For the purposes of this paper, three different oil in water measuring instruments were used to collect data, with the results compared against EPA Method 1664 results performed by an independent lab. All measurements were made on uniform laboratory prepared samples of oil in water which were mixed in bulk and then divided up for measurement by the various techniques. This is a very critical point to be re-emphasized: each instrument and the EPA method were making measurements from identical samples. These samples were prepared in a laboratory to have a known concentration of oil in water. Recognizing that each method will produce different “absolute” numbers for oil in water, the object was to determine if any of the instruments would show a linear correlation with the known concentrations.

In total, four different measurement techniques were used to measure the oil in water and then compared against the known concentration values based upon the mixing parameters. The measurement techniques used were two different particle imaging systems, an IR absorption instrument, and EPA method 1664 performed by a registered independent lab.

Two particle imaging systems were tested since this technique has recently generated a large amount of interest due to its inherent potential advantages previously described. In these systems, the produced water stream is passed by a high resolution imaging system which has enough optical magnification to capture images of oil and other particulates down to about three microns in size. Because of the high magnification needed to image particles this small, a very narrow “depth of focus” is available (on the order of 100 microns or less). This means that even when viewing the produced water sample passing through a restricted imaging area (around 2mms deep), the majority of the particles will not be in sharp focus. Particles that are not in sharp focus will not yield accurate measurements; they will tend to give larger measurements than reality due to the fact that the out of focus images “spread”.

The method most commonly used to eliminate the out of focus particle images is to measure the gray-scale “edge gradient”. Basically, this measures the sharpness of the edge of the particle by looking at the gray scale values across the edge of the particle: a particle in sharp focus shows a steep gray-scale gradient, while an out of focus particle shows a much more gradual gradient.

By setting the system to accept only particles having a specified gray-scale gradient or higher, one insures that only in-focus particles are measured, yielding increased measurement accuracy. However, this does of course mean that not all of the particles are being counted. Actually, they were not all being counted to begin with due to the fact that the camera field of view can not image the entire flow area while maintaining high enough magnification to resolve the oil droplets. So, only a fraction of the total particles will be imaged and measured in these systems. However, we can make the assumption that the particles are evenly distributed in the produced water. With that assumption in mind, one can simply calibrate the whole system based upon known samples to take into account these two factors prior to calculating total oil and particulate concentrations.

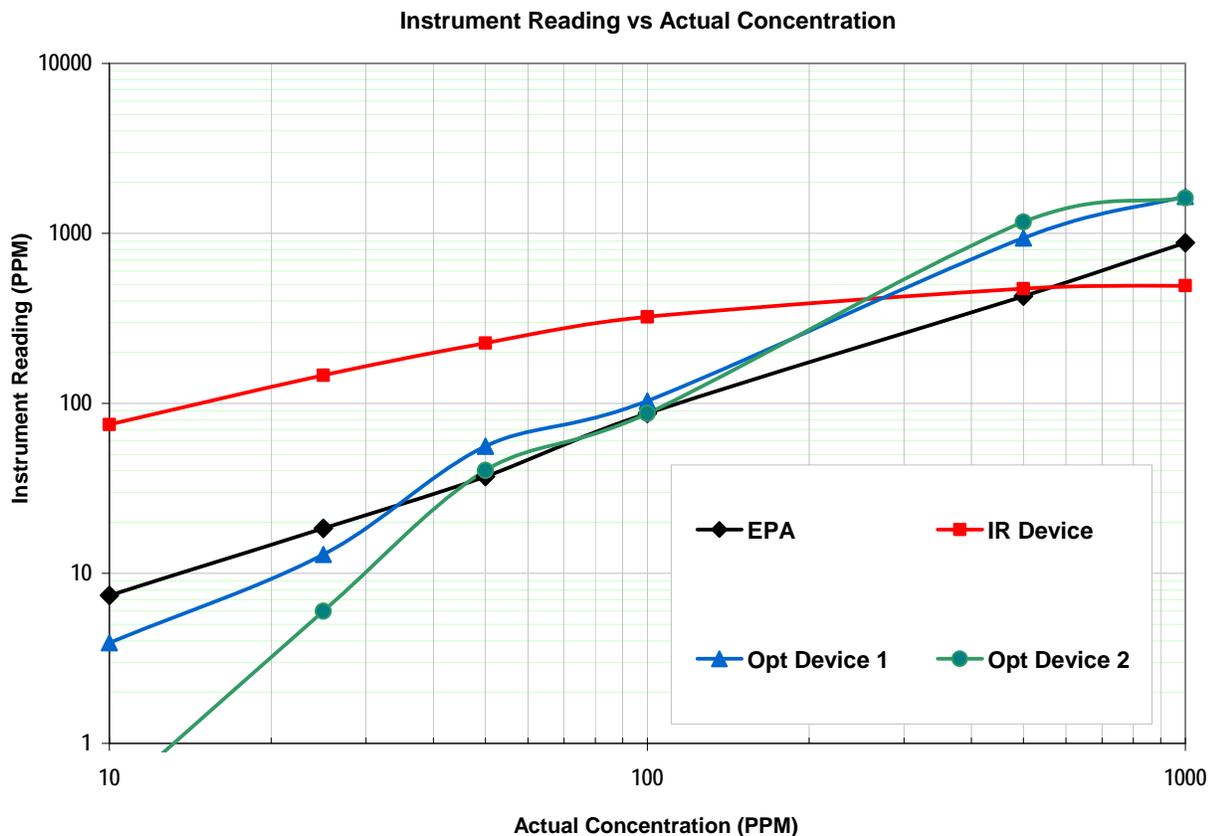
## Sample Preparation (Method):

In order to provide repeatable results, a detailed Standard Operating Procedure (SOP) was developed for mixing up batches of oil in water samples to known concentrations of 10, 25, 50, 100, 500 and 1000 PPM. A second batch of each sample was also made up with a known quantity of sand in order to see how the presence of other particulates affected the measurements. For each concentration to be measured by all methods, a single two liter batch of known oil concentration was prepared using this SOP. Once fully mixed, one liter of the mixture was placed into an EPA 1664 Method sample bottle supplied by the outside testing lab and delivered to that lab for measurement. The other methods require far less sample for measurement.

For the three remaining instruments to be tested, the sample was placed in a beaker on a stirrer plate with stirring set on low (especially important for the samples containing sand in order to keep the sand in suspension), and sample was drawn from the beaker for each instrument from the same location in the beaker (bottom fourth). For each measurement, multiple measurements were made to insure repeatability, with the results averaged.

## Measurement Results:

As previously discussed, the samples made were at known concentrations of 10, 25, 50, 100, 500 and 1000 PPM. Recall also that there were two (versions) of each sample, one with just oil, and the second with added sand to see how the addition of other particulates (more like real world conditions) affected the measurements. Figure 1 below shows the normalized results for the sample containing oil only:



**Figure 1: Instrument Readings versus Actual Concentrations for each oil-in-water measurement technique (samples with oil only).**

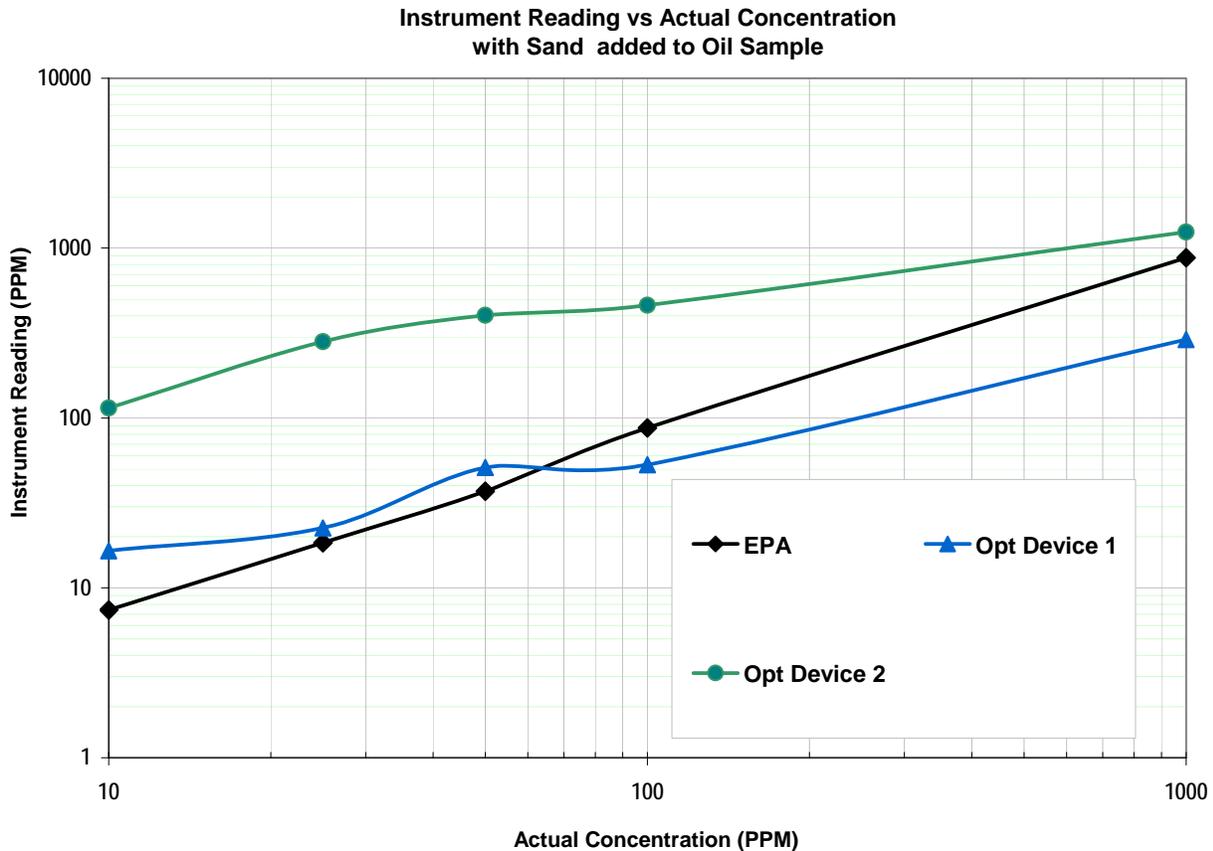
The EPA Method 1664 results show the closest tracking to actual concentrations. This should come as no surprise, since as previously stated, this method actually *defines* measurement of oil in water from a regulatory standpoint in the US. So the method has been optimized to produce these results, and can therefore be viewed as somewhat of a “self-serving prophecy”. As also noted earlier, this method can only be performed in a laboratory environment, and is therefore inappropriate for field use. However, *because* this method *defines* oil in water content, it should ultimately be used to confirm calibrated results found with other methods, at least in the US. In other words, this method should be the reference that all other techniques calibrate back to (again, in the US at least).

The IR Absorption instrument measures consistently higher than actual concentration up to 500 ppm, and then less than actual concentration. Below 50 ppm, however, it tracks very closely to the actual concentration and could easily be normalized to match the actual graph. It appears that above 50 ppm the instrument seems to saturate and maintain roughly the same value. Given that most of the regulations for produced water allow discharge below 40 ppm, this instrument can obviously be used for this purpose. Remember, however, that this instrument requires a laboratory environment and solvents to be used, making it inappropriate for field usage.

Optical instrument 2 tracks relatively well to the actual concentrations, but only above 50 ppm. Below 50 ppm, the instrument reads low versus actual, dramatically so as concentration becomes lower. This instrument would require very careful calibration and monitoring in order to be trusted for measuring produced water discharge with an aim of proving environmental compliance.

Optical instrument 1 appears to track the closest to actual concentrations over the entire range measured from 10 to 1000 ppm. It appears to measure slightly low at concentrations below 35 ppm, and slightly high at concentrations above that. However, it stays close enough to linear correspondence with the EPA 1664 results that it appears to be an accurate instrument for measuring oil in water from 10 to 1000 ppm.

Figure 2 below shows the same results for the oil samples with sand included:



**Figure 2: Instrument Readings versus Actual Concentrations for each oil-in-water measurement technique (samples with sand added).**

This graph shows that the addition of sand to the samples seems to add more variability to the reported measurements. Note that there is no measurement recorded for the IR device due to the fact that this technique would have filtered out the sand before testing anyway. With the optical instruments, accuracy comes down to the ability of the image analysis software to properly differentiate between oil droplets and other particulates (in this case sand). As previously discussed, this is done by looking at the relative “circularity” of the particles. The oil droplets will image as near perfect circles (2D projection of a sphere), while the other particulates will have a more “erose” surface. Two factors enter into this calculation: image resolution and types of measurements/algorithms used. If there is not enough image resolution to properly determine circularity, then it will not be possible to segregate oil droplets from other particulates. This is why optical imaging techniques really can not be used for droplets sized below 3 microns in diameter.

The second factor in determining the accuracy of differentiating between oil droplets and other particulates is the type of measurement and algorithms used to make the determination. The most simplistic is to measure the width and length of the particle and divide them to determine aspect ratio (width/length). A particle with an aspect ratio near one will typically be either circular or square, although odd shapes can lead to the same result in some cases. A better measurement is some form of mathematical “circularity”, usually based upon theoretical versus actual perimeter. In the graph above, it appears that optical instrument #1 appears to do a better job of differentiating sand versus oil, as its measured results stay closer to the actual concentration. Since both instruments have the same optical resolution, we must conclude that the difference seen here is due to a more accurate algorithmic determination of circularity.

**Conclusions:**

This effort was by no means an exhaustive characterization of how well any of these instruments perform on measuring oil in water. However, the intent is to point out that different measurement techniques each have positives and negatives which the user should be aware of. A strong understanding of how the measurement technique works is necessary in order for the user to understand exactly what is being measured. Furthermore, it is extremely important for any measurement technique to be validated and calibrated against known test samples in order to most accurately characterize the method's performance. Finally, as can easily be seen when comparing the results of the "oil-only" samples against the "oil plus sand" samples, it is critical that all calibration activities be conducted using known samples which are as close as possible to the "actual content" of the produced water samples which will be analyzed in the end.

**References:**

Caudle, D.C. and Tyrie, C.C. 2007. Comparing Oil in Water Measurement Methods. *Exploration & Production: The Oil & Gas Review* 2007 – Issue 11 – November 2007 : 31-35