

# **PRODUCED WATER SEMINAR**

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## **Comparing Oil in Water Measurement Methods**

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## Comparing Oil in Water Measurement Methods

### Introduction

Oil and grease in produced water is not a chemical substance. It is defined by the method specified to measure it. These methods vary from one area to another. For example, in the United States EPA Method 1664 defines it. In the North Sea an infra red spectrometer was used to define it. But there it was not called oil and grease but total oil or total hydrocarbons. There several instrumental methods for measuring oil in produced water. None of them measures all the organic compounds in the water. Comparing what the commercially available methods actually measure will illustrate the problem in interpreting oil in water analysis.

Oil concentrations in water are usually reported as a mass or volume unit in a given volume of water. This is milligrams per liter (mg/L) or micro liters per liter ( $\mu\text{L/L}$ ). Each analytical method measures some property of oil that can be related to this mass or volume value. The problem is that the composition of oil in produced water varies for a number of reasons such as:

- Changes of source due to opening and closing wells,
- Level of separation treatment,
- Use of treating chemicals.

Various authorities have defined oil for regulatory purposes. According to the United States Environmental Protection Agency oil is a mixture of those components of produced water that are "extractable in hexane at pH 2 or lower and remain after vaporization of the hexane". Originally the solvent specified was Freon<sup>TM</sup> 113 but for environmental reasons this solvent is no longer manufactured in the United States and was replaced by the EPA with n-Hexane. This method measures the mass per unit volume of oil directly and is not affected by the variables listed above. All other methods must relate their measurements to oil mass or volume. How each instrument or method used correlates oil concentration to its measurement results makes interpreting and comparing oil measurement results difficult. Several oil measurement technologies and instruments that use them are discussed and compared below to illustrate the difficulties.

OSPAR defined oil by specifying the measurement procedure. The original procedure used an infrared absorption of a water extract. The authors are not familiar with the details but they are available from OSPAR or the treaty members of the organization.

The subject of oil in water measurement seems such a simple process that there should be no problem in understanding it. All the steps in the measurement procedures are simple. However, in practice there is a significant problem interpreting the results and comparing results from the use of various methods and instruments employing them. In this paper we will look in detail at all the factors in measurement down to very simple concepts and details in an attempt to make the process absolutely clear.

## **What Are the Organic Constituents of Produced Water?**

Organic compounds in produced water exist as dispersed droplets or dissolved in the water. The droplets are mostly crude oil that was dispersed in the water as a result of production operations and will contain the full range of constituents in the produced oil. In addition there may be dispersed droplets of production treating or workover chemicals and they may be in the crude oil droplets as well. The dissolved organic compounds will include oxygenated hydrocarbons such as carboxylic acids and low molecular weight aromatic hydrocarbons and aromatic acids. In sour production sulfur compounds such as mercaptans or thio alcohols may be present. Production treating chemicals are also present as soluble compounds. Sometimes the aromatic carboxylic acids make up the major portion of the soluble oil in produced water. Hence it can be seen that all the organic constituents of produced water can be measured as oil. But if they are not measured by the defining method they are not legally oil.

## **Measurement Technologies**

Currently there are five properties that are currently used to measure oil in produced water, four that can be applied in the field and one in the laboratory. These are:

- Direct weight measurement (US EPA Method 1664, et al),
- Color,
- Infrared absorption,
- Ultra violet fluorescence, and
- Particle counting methods.

Each oil measurement method can be applied in several ways. Each application has advantages and limitations that must be taken into account when using it.

### ***Direct Weight Measurement***

The gravimetric methods measure oil directly, but the oil they measure does not include all the organic compounds in the water being tested. The US EPA Method 1664 is a good example of a direct measurement method. This method is important because it legally defines oil in the United States and is specified for measuring oil concentrations for compliance with waste discharge laws.

The procedure for applying US EPA Method 1664 is to acidify a water sample to pH 2 or less and then extract it with n-hexane. The hexane is then evaporated and the residue is weighed. The weight of this residue is divided by the volume of the water sample to arrive at the concentration in weight per unit volume units (mg/L).

Using this method, only a subset of the organic constituents is measured. This subset is those compounds that are:

- Extractible from water in n-hexane at pH 2, and
- Remain after the hexane is evaporated.

Materials not soluble in hexane are not measured and are, therefore, not oil. The compounds extracted from water include both dispersed oil droplets and dissolved organic compounds if they are soluble in hexane. However, all materials soluble in hexane that have boiling points below n-hexane are not measured and are not oil.

This method is cumbersome and requires a high level of manual skill to use. It cannot be used in most field environments. Because it is the required method for compliance monitoring of produced water in the United States, It is important that other methods used for monitoring in the field be correlated to it. Since the field instruments used frequently do not measure the same thing correlations are very important in the United States.

### *Colorimetric Methods*

The colorimetric method was widely used before oil in water was measured for compliance with regulations. It is usually only used on very dark oils. The absorption of energy in the visible light range is used as the detection process. Since most light oils have very little color, it cannot be applied to measuring such oils in water. However, in areas where very dark, usually asphaltic oils are produced, it is still used to measure the oil in water.

As colorimetric methods detect only those oil components that are highly colored, the instrument is calibrated with a standard of known concentration and this calibration is used to convert the absorption reading to an oil concentration. One consequence of having to calibrate is that the calibration is only good as long as the ratio of the components measured to the total oil remains constant or at least within acceptable limits.

### *Infrared Methods*

Several types of chemical bonds absorb infrared (IR) energy. The instruments using IR absorption to measure oil in water target the carbon hydrogen (C-H) bond, common to all organic compounds. This bond absorbs IR energy at the wavelength 3.41 microns. Since water absorbs infrared energy at the wavelengths used to measure oil, measurements must be made on an extract of the water using a solvent that does not absorb IR radiation. Many organic compounds contain bonds other than C-H bonds. Many of the compounds comprising soluble oil are carboxylic acids. Each acid group contains two oxygen atoms and the molecules weigh much more per C-H bond in them than hydrocarbons (compounds containing only carbon and hydrogen atoms). If the ratio of oxygen containing molecules to total weight does not remain constant errors will result in the oil analysis.

Once a sample is extracted, the oil measurement can be achieved either on the extract or on the oil residue left after evaporation. This extract contains all the organic material in

the water that will extract into the solvent including both oil droplets and some water soluble organic compounds if the pH is low enough.

IR methods measuring the absorption of the extract solution must use a solvent clear to IR radiation. Since the IR instruments measure the absorption by C-H bonds, this means a solvent that does not contain C-H bonds. When these instruments were first developed the solvent used was frequently Freon<sup>TM</sup>. Presently a variety of non hydrocarbon solvents are commercially available.

In both types of IR instruments the oil reported is not the oil measured. Each instrument is calibrated with a standard sample of known concentration and the instrument is adjusted to read that concentration. Since both types of IR instruments actually measure absorption of IR energy the absorption measured must be assigned to a concentration. This is done by the calibration of the instrument (See discussion of calibration below). Therefore, measurements made on duplicate samples by each type of instrument would yield the same concentration. However, the absorption value for the instrument measuring oil in extracts would have a higher absorption value than the one measuring oil in a residue. The calibration is only good if the ratio of the components actually detected to the total component weight remains constant or within acceptable limits.

#### *Ultra Violet Fluorescence Methods*

Aromatic compounds absorb ultra violet (UV) radiation and emit it (fluoresce) at another wavelength. Almost all produced waters contain aromatic compounds. The amount of fluoresced light is proportional to the concentration of aromatic compounds in the water. Therefore the amount of fluorescence measured is proportional to the oil in the water sample. Assuming the composition of the oil in the water sample remains constant a relationship can be developed between fluorescence and oil concentration.

Since UV radiation is not absorbed by water, oil determinations can be made directly on a water sample or an extraction of the water using a suitable solvent. Both types of measurement are common. Most instruments measuring oil directly in water are used as continuous monitors to control treatment processes. Both types of UV instrument are used to ensure compliance with discharge limits.

There are advantages and disadvantages to both types of UV instruments. There are other components of produced water that fluoresce. Iron is a good example. Iron is not present in the solvent extractions that recover oil from produced water, so the instruments using extractions has an advantage. This type of instrument is also easier to calibrate. Conversely, there is an advantage in process control to having continuous oil measurements on a process stream. Interference is not usually a problem and if it exists it might be corrected by adjusting the instrument calibration. As with the other instrument measuring a specific property of oil and relating that to concentration, the calibration is only good as long as the ratio of the florescence measured to the weight of oil in the sample remains constant

## ***Particle Counting Methods for measuring Oil and Solids***

There are three variations on measuring or estimating oil or solid particle concentration by counting particle numbers and sizes. They are:

- Measuring turbidity,
- Coulter Counter, measuring batch samples in a lab or clean area,
- Visual recording of particles and their sizes and characteristics on line.

For many years operators have monitored water quality by attempting to measure the number of discrete particles and their size in produced water. One of the earliest ways was to measure turbidity. When fine particles are dispersed in water, the water becomes cloudy due to the scattering of transmitted light by the particles suspended in the water. Prescribing an upper turbidity limit was once commonly specified to control water quality for injection. Such a limit could automatically limit the maximum particle size and the number of particles per unit volume of water. However, turbidity depends on both number of particles and the size of particles and is a very approximate measure of particle size or particle concentration. The true effect of turbidity on water quality was often determined by experience.

The Coulter Counter and its successors estimate the number and size of particles in water by passing the water through a small circular orifice of known dimensions. An electrical current is generated through this orifice. As the individual particles passed through the orifice they blocked part of its area, the current flowing through the orifice was reduced in proportion to the size of the particle. This technology is limited because it is delicate and must be done in a laboratory in order to control the parameters measured. It also does not distinguish between solid particles and oil droplets. Its usefulness as an oil in water monitor is very limited.

Modern technology has now made it possible to photograph particles in a water stream and identify their type (solid, oil, or gas). This is done with a microscopic video camera. The particles detected are counted, sized and identified using computer algorithms. This data can then be used to determine particle size distributions, oil and solids concentrations. Using this equipment the size and volume of all oil droplets in a known volume of water can be calculated and summed to determine the oil concentration in the water.

These methods can only detect what they can see. Particle counting methods cannot normally see below about two microns. This means that they cannot measure soluble oil concentrations.

## **Relating Instrument Measurements to Oil Concentrations (Instrument Calibrations)**

Direct determinations of oil weight such as EPA Methods 1664 or particle counting methods do not have to be calibrated since oil concentrations are directly determined. All other measurement methods do not directly measure oil concentrations. To get oil concentration from the measurement of color, infrared absorption or ultra violet fluorescence a relationship must be developed between the factors measured and oil concentration.

This relationship is achieved by an instrument calibration. In the calibration process, an oil is chosen as a standard. Known concentrations of this oil are prepared and measurements are taken using the instrument of the parameter they measure. For example, IR instruments would determine the IR absorbance of each standard sample. Then the known oil concentrations are plotted against the measured absorbance values and a best fit straight line through the points is determined. The relationship between the absorbance and the concentration must be linear. If it is not then it is out of the range of the instrument and lower concentrations must be used. Subsequently, when the instrument is used, the oil concentration is read from the correlation plot corresponding to the measured absorbance. Most modern instruments incorporate a computer that can be programmed to convert the measured parameter to oil concentration and directly display it on the instrument display. This same procedure is followed for colorimetric and UV fluorescence instruments except that the parameters measured are absorption of visible light and UV fluorescence.

Calibrations suffer from a number of problems. For the correlation to be valid:

1. The standard composition should be the same as the oil being measured,
2. If it is not the same composition, at least the ratio of the parameter being measured to the total oil weight in the sample should be constant.

When a calibration standard is chosen it is presuming, in effect, that the oil you are measuring has exactly the same composition as the standard oil. This is seldom the case. Many people mistakenly assume that the oil in produced water is crude oil and chose it to calibrate with. There are two problems with this practice:

1. The oil in produced water contains crude oil but it also contains other oils such as dissolved oil. Dissolved oil comes from the formation water not from the crude oil. Some treating chemicals also measure as oil. Therefore the composition of the oil in the water will be somewhat different from crude oil,
2. The composition of the oil changes with treatment. The oil in the untreated water entering the water processing system has a different composition from the treated oil exiting from the processing system.

Some examples can illustrate the problem. An IR instrument measures the number of C-H bonds in a sample. If particular untreated oil contains 95% dispersed oil and 5% soluble oil, most of the dispersed oil will be removed by treatment, but the dissolved oil will not be removed. In this case the effluent oil could be 50% dispersed oil and 50% dissolved oil. This is important because the calibration of the IR unit, in effect, assigns a specific weight of oil to each C-H bond. Dispersed oil is mostly hydrocarbons (compounds containing only carbon and hydrogen). Most dissolved oil also contains oxygen atoms. Oxygen is relatively heavy compared to carbon and hydrogen. Although theoretically more weight should be assigned to a C-H bond for oil that contains dissolved oil. The magnitude of this problem is hard to determine because few people recognize this factor and have data on it, but effluent oil concentrations could be underestimated by as much as 20%.

A problem that the authors have encountered illustrates a potential calibration problem with UV instruments. It is a common practice to measure the soluble content of a water by first measuring the total oil content of a water sample, then treating the extract with silica gel to absorb the soluble components and measuring the oil content again. The difference in the two measurements is the concentration of soluble materials. In an attempt to measure the soluble content of the treated water it appeared that nearly all the oil in the treated water was soluble material. However, this type of instrument measures UV fluorescence and calibrates that measurement to oil content. In the treatment process dispersed oil (droplets) are removed and soluble material is not. For this particular oil, most of the fluorescing materials were in the soluble oil and were not removed. The silica gel absorption removed most of these materials from the treated sample and the instrument falsely indicated that the oil concentration was low. Then when this artificially low concentration was subtracted from the total and indicated that most of the oil in the sample was soluble oil.

One might ask what oil should be used for calibrations? The answer is that there is no good calibrating oil. If oil is defined by the instrument measurement, it doesn't matter as long as the analysis is consistent.

There is one special case where there is an optimum calibration oil. One type of IR instrument measures oil from the residue of the sample extraction. The sample is extracted and then an aliquot of the oil is placed on a plate on the instrument and the solvent is evaporated before a measurement is made. This simulates the USEPA Method 1664 analysis. If ones goal is to measure results equivalent to the results of a Method 2664 analysis, one can calibrate the instrument with residue from the Method 1664 analysis and the instrument will provide Method 1664 results directly.

It should be obvious from the above discussion that an instrument calibration is only good for one place in the treatment system. Treatment changes the composition of the oil in most produced waters. Probably most people would be most interested in the effluent oil from a system and would choose a calibrant that best fit that sample concentration.

One might, for example, use a 50:50 mix of the crude oil from the site and a mix of low molecular weight carboxylic acids.

### **Relating Instrumentally Measured Oil Concentrations To Defined Oil Concentrations (Correlations)**

Since oil is defined by a particular analytical method in the United States and this method cannot be used in the field, it caused a problem for production operations. A method was needed to control treatment processes and to assure that water discharges were in compliance. IR and UV instrumental methods were developed to fill this need. These methods do not measure oil concentration directly but can be calibrated to give an oil concentration. The residue from EPA Method 1664 analysis is by definition the material that must be measured. The common practice is to calibrate IR and UV instruments with the crude oil produced by the facility discharging produced water. The oil concentration produced by IR and UV instruments calibrated with crude oil (or some other oil of a different composition than the EPA Method 1664 results) are different from those obtained using EPA Method 1664. Correlating the instrumental results to the Method 1664 results can solve this problem. As with an instrument calibration duplicate samples covering the measurement range of interest are analyzed by both EPA Method 1664 and the instrument of choice. The results are then plotted against each other a straight line fit is made between them. The resulting linear relationship can be used to predict EPA Method 1664 results from instrumental results.

Correlations suffer from the problems that afflict calibrations. Where to get replicate samples over the concentration range needed? What effect does changing oil composition have on the correlation? The authors have found in their consulting work that problems with correlations are very common. An industry standard should be developed for making correlations. Even if the standard were not perfect at least every one would be getting uniform results.

### **Comparing Field Measurements of Oil and Grease**

It is important to know how the results obtained using the various methods related to each other. If they are different, why are they different? To answer these questions it is necessary to understand what each method measures and it relates that measurement to oil concentration. The following discussion covers the methods previously listed:

- Direct weight measurement (US EPA Method 1664, et al),
- Color,
- Infrared absorption,
- Ultra violet fluorescence, and
- Particle counting methods.

These methods can be subdivided into either direct measurement or instrumental methods. Direct measurement methods including particle counting methods directly

measure a defined quantity. Whether or not they give similar numbers depends on the defined quantity. For example US EPA Method 1664 measures those constituents soluble in hexane at pH 2 or less and that remain after vaporizing the extraction solvent. This definition includes both dispersed hydrocarbon droplets and dissolved organic compounds. Particle counting methods measure visually observed particles by counting them, sorting them into classes, and calculating the volume of each class by summing the volume of each individual particle's volume and dividing by the sample volume. If oil components are soluble it cannot detect them and they will not be counted. Oil concentrations measured by either method can be higher or lower than the other. For example, consider the following table:

	High Solubles Conc.	Low Solubles Conc.
Very Light crude oil	?	PC > 1664
Heavy Crude oil	1664 > PC	1664 $\approx$ PC

Two attributes of the oil in the produced water determine whether or not the direct methods will detect the components of the oil. These are the volatility of the oil and its physical state i.e. dispersed or dissolved. Droplets of a volatile crude oil could be detected and measured by particle counting methods but may boil away during the EPA Method 1664 analysis. This factor would tend to yield larger oil concentrations for particle counting methods. Produced waters containing significant concentrations of dissolved oil might appear to higher when measured by EPA Method 1664 over the result when using a particle counting method. These factors are displayed in the table above. For produced water containing droplets of a volatile crude oil and a high solubles content it is unclear which method would yield the higher oil concentration since the two factors would complement each other and cancel out differences in measured concentration. Although these methods measure slightly different things, they each have advantages in particular applications. For example, if one were evaluating oil droplet removal a particle counting method, which measures only oil droplets, would be an advantage. For compliance monitoring the gravimetric determination might be more appropriate.

If one compared the results of analyses on the same produced water using IR and UV instruments calibrated with the same oil, the results would be of the same order of magnitude and similar of magnitude but not necessarily identical. Several factors influence the oil concentration measurements:

- The calibration oil does not have exactly the same composition as the measured oil,
- The composition of the measured oil changes with treatment and this can increase the composition differences between calibrant oil and measured oil.
- The extractions solvents may be different and the efficiency of the extraction can also affect oil composition.

It is not possible to predict how different the measured concentrations will be or which instrumental method will give a higher value. When comparing IR and UV instrument

results with EPA Method 1664 results the instrumental results are almost always equal to or higher than the EPA Method 1664 results.

One might assume that IR instruments measuring the absorbance from extractant solution would give higher concentrations than an IR instrument measuring absorbance of an extraction residue, however, this type of difference is removed by the instrument calibration.

## **Conclusions**

In the past oil measurements have been focused on assuring compliance with discharge regulations. Now interest is shifting to using oil determinations to improve production operations. Changes in oil concentrations can indicate a wide spectrum of production and treatment problems. Changes in environmental policy are also impacting oil in water measurement needs. Oil measurement and how it is recorded will become a factor as the OSPAR regulations change in the North Sea. Reportedly, a new gas chromatography method is being considered and tested in the North Sea.

It is expected that the changes foreseen will spread worldwide and the problem of meaningful measurement will become more critical. While it is realized that no water treatment manufacturer constructs equipment to comply with the specifications that are set for oil in produced water, the problem is the efficient application of the equipment. Therefore the final measurement of the discharging sample will not be as important as the measurement of the changes in the separate steps of the water clarification or separation across the various stages of the equipment.

When it can be seen that the removal of 1mg/l of oil from the produced water discharge can generate many thousands of units of any currency that is involved it can be seen that the call should be for smart monitoring across the whole system.

Smart monitoring across the system can predict problems and also optimize equipment efficiency and chemical dosing rates. In troubleshooting many systems over the years it has always been prevalent that the major problem has been the control of solids in the system. Hence the monitoring of oil and solids across the system at all equipment inlets and outlets which can be logged and analyzed in a computer read out will be the answer with respect to the control of lower discharge quantities of oil in produced water.