

Comparing Oil in Water Measurement Methods

a report by

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Oil and grease in produced water (water that is discharged along with oil and gas) is not a chemical substance. Instead, it is defined by the method specified to measure it, and these vary from one area to another. For example, the US Environmental Protection Agency (EPA) Method 1664 states: "oil and grease...are 'method-defined analytes.'" In the North Sea, an infrared (IR) spectrometer is used to define it. However, in the latter example it is not called oil and grease, but total oil or total hydrocarbons. In the North Sea, several instrumental methods are available for measuring oil in produced water; however, none 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, either as milligrams per litre (mg/l) or microlitres per litre (μ l/l). Each analytical method measures a 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 and use of treating chemicals.

Various authorities have defined oil for regulatory purposes. According to the US EPA, 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™ 113, but for environmental reasons this solvent is no longer manufactured in the US, and was replaced by the EPA with normal hexane (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 used are discussed below to illustrate the difficulties. The Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) defined oil by specifying the measurement procedure. The original procedure used an IR 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 organisation. The subject of oil in water measurement seems such a straightforward 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 when 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 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 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 other chemicals, which may exist 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, sulphur 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. Therefore, it can be seen that all the organic constituents of produced water can be measured as oil. However, if they are not measured by the defining method, they are not 'legally' oil.

Measurement Technologies

Currently, five properties are used to measure oil in produced water, four of which can be applied in the field and one in the laboratory. These are direct weight measurement (US EPA Method 1664, etc.), colour, IR absorption, ultraviolet (UV) fluorescence and particle-counting methods. Each oil measurement method can be applied in several ways. Each application has advantages and limitations, which 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, and is important because it legally defines oil in the US 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, then extract it with n-hexane. The hexane is 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 made up of those compounds that are extractable from water in n-hexane at pH 2 and remain after the hexane is evaporated. Materials not soluble in hexane are not measured and, therefore, are 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 that of n-hexane are not measured and are not oil. This method is cumbersome and requires a high level of manual skill, and it cannot be used in most field environments. As it is the required method for compliance monitoring of produced water in the US, it is important that other methods used for monitoring in the field be correlated to it. Frequently, the field instruments used do not measure the same thing, so correlations are important in the US.

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Colorimetric Methods

The colorimetric method was widely used before oil in water was measured for compliance with regulations, and is usually 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 colour, 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 coloured, the instrument is calibrated with a standard of known concentration; 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 IR energy. The instruments using IR absorption to measure oil in water target the carbon hydrogen (C-H) bond, which is common to all organic compounds. This bond absorbs IR energy at the wavelength of 3.41 microns. Since water absorbs IR energy at the wavelengths used to measure oil, measurements must be made on a sample 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 would need to be used. When these instruments were first developed, the most-often used solvent was frequently Freon™. Currently, 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 mixture. Since both types of IR instruments actually measure absorption of IR energy, the absorption measured must be assigned to a concentration. This is achieved by the calibration of the instrument (see 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 acceptable only if the ratio of the components actually detected to the total component weight remains constant or within acceptable limits.

Ultraviolet Fluorescence Methods

Aromatic compounds absorb UV radiation and 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 of both types of UV instruments. There are other components of produced water that fluoresce. Iron is a good example that is not present in the solvent extractions that recover oil from produced water, so the instruments using extractions have 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. Usually, interference is not a problem and, if it exists, it can be corrected by adjusting the instrument calibration. As with the other instruments used for measuring a specific property of oil and relating that to concentration, the calibration is effective only as long as the ratio of the fluorescence measured to the weight of oil in the sample remains constant.

Particle-counting Methods

There are three ways of measuring or estimating oil or solid particle concentration by counting particle numbers and sizes: measuring turbidity; Coulter counter, i.e. measuring batch samples in a lab or clean area; and visual recording of particles and their sizes and characteristics online. 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 the number of particles and the size of the 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 pass through the orifice they block part of its area, and the current flowing through the orifice is reduced in proportion to the size of the particle. This technology is limited because it is delicate and must be performed 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 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 carried out 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 and 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 detect only 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

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 colour, IR absorption or UV 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. The known oil concentrations are then 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, 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 the standard composition should be the same as the oil being measured and, 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 choose it to calibrate with. There are two problems with this practice. First, the oil in produced water contains crude oil, but it also contains other oils such as dissolved oil. Dissolved oil comes from the formation of 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 that of crude oil. Second, 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 the processing system.

A few 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.

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Table 1: Oil Concentration Measurement

	High Soluble Concentration	Low Soluble Concentration
Very light crude oil	?	PC > 1664
Heavy crude oil	1664 > PC	1664 ≈ PC

PC = particle count.

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 made up of mostly hydrocarbons (compounds containing only carbon and hydrogen). Most dissolved oil also contains oxygen atoms. Oxygen is relatively heavy compared with 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 recognise this factor and have data on it, but effluent oil concentrations can be underestimated by as much as 20%.

A problem that the authors have encountered illustrates a potential calibration problem with UV instruments. It is common practice to measure the soluble content of 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, it 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: good calibrating oil. If oil is defined by the instrument measurement, it does not 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 an aliquot of the oil is then placed on a plate on the instrument; the solvent is evaporated before a measurement is made. This simulates the US EPA Method 1664 analysis. If one's goal is to measure results equivalent to the results of a Method 1664 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 good for only one place in the treatment system. Treatment changes the composition of the oil in most produced waters. Most people would probably be most interested in the effluent oil from a system and would choose a calibrant that best fits 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

Since oil is defined by a particular analytical method in the US 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

ensure 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. By definition, the residue from EPA Method 1664 analysis is 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 the 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 analysed by both EPA Method 1664 and the instrument of choice. The results are then plotted against each other and 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 source 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 common. An industry standard should be developed for making correlations. Even if the standard is not perfect, at least everyone will be getting uniform results.

Comparing Field Measurements of Oil and Grease

It is important to know how the results obtained using the various methods relate 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 how it relates that measurement to oil concentration. The following discussion covers the methods previously listed: direct weight measurement (US EPA Method 1664, etc.), colour, IR absorption, UV 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 provide 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 vaporising 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 (see *Table 1*).

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 be higher when measured by EPA Method 1664 over the result when using a particle-counting method. These factors are displayed in *Table 1*. 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 that 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 extraction 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 having an effect on 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 anticipated changes will spread worldwide and the problem of meaningful measurement will become more critical. While it is understood 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. While 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, it should be emphasised that the call should be for smart monitoring across the whole system. Monitoring across the system can anticipate problems, and also optimise equipment efficiency and chemical dosing rates. After troubleshooting many systems over the years, the major problem has always been the control of solids in the system. Hence, the monitoring of oil and solids across the system at all equipment inlets and outlets that can be logged and analysed in a computer read-out will be the answer with respect to the control of lower discharge quantities of oil in produced water. ■

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