

SOURCES OF ERROR IN OIL IN WATER MEASUREMENTS AND THEIR IMPACT ON COMPARING OIL IN WATER MONITORS

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1 INTRODUCTION

The technology for measuring oil in produced water is changing in response to regulatory changes and the need for reducing environmental impacts. Evaluating new measurement technology and methods for measuring oil is complicated by the nature of oil as a parameter. Since, in effect, oil is defined by the method specified to measure it; comparing methods can be a complicated process. In searching for improved measurement technology two issues are frequently misunderstood. One is that the definition of oil is not considered. Oil in produced water is a mixture of various chemical components and the composition of these mixture change from one source to another and also from time to time in the same source stream. Most or all methods for measuring oil do not quantify all the components of oil but only some of them. Measuring some property of the mixture and relating it a calibration solution of known concentration does this. Different methods measure different properties and therefore may give different answers if not correlated to the defining method.

The other issue frequently confusing method testing is a tendency to focus on the quantification step. The entire analytical process is composed of three steps:

1. Collecting the produced water sample.
2. Extracting the oil from the sample, and
3. Quantifying the oil extracted.

Each of these steps has its a set of errors associated with it. Potential errors in the steps are not all of the same magnitude. The quantification step is likely to be much less variable than the other two steps. If so then differences in results when comparing the analysis of replicate sets of samples, one resulting from the defining method for oil and the other resulting from a potential new measurement technology may result from sampling and extraction errors not differences in the methods. In doing such comparisons it becomes important to account for errors introduced by the analytical steps that were not changed.

If regulatory bodies are to allow alternative methods they need data on which to determine comparability of the alternative methods. Operators who want to get an alternative method approved need data to know that they are in compliance with regulations. This paper examines these two issues raised above and their impact on the selection of an analytical method for measuring oil in produced water.

2 THE OBJECTIVE OF AN OIL ANALYSIS

Oil discharge limits were developed to control the amount of oil entering the sea from produced water discharges. Such control is achieved using measurements of oil in the produced water leaving the water processing equipment. Based on these measurements changes are made in the process overtime to keep the oil discharged within regulatory limits. However, all measurements are subject to errors. A value determined with a given method always has associated with it an uncertainty caused by the potential errors to which the method is subject. This uncertainty is quantified by measuring multiple replicate samples and calculating the standard deviation of the values. This can be expressed as a fixed concentration. For example, methods used offshore are probably no better than +/- 5 ppm. In most cases oil concentrations lower than 5 ppm cannot be reliably distinguished from zero. Using the rules of simple statistics a range can be calculated that would contain the true value of the oil concentration some arbitrary percentage of the time. For example an average measured value might be found to be 22 ppm and if repeated measurements were made the true value is estimated to be between 17 ppm and 27 ppm 87% Of the time. The operator's objective is to determine whether or not his produced water discharge is staying in

compliance. This means that he has to know not only the value of the measured oil concentration but also its variability.

Variability can cause the operator two types of problems:

1. If the oil concentration is close to the limit, is it in compliance or not?
2. If a new method is being tested, does it give the same results as the old method or not?
That is, are the values statistically the same or not?

Since the variability is determined by the sources of error in the analytical process, one must understand what can cause errors and minimize the errors especially when comparing analytical methods.

3 THE MEASUREMENT PROCESS

Although the analysis for oil in water is seemingly a simple procedure, it is actually complex process, involving three important steps:

- The sampling process,
- The extraction process, and
- The quantification Process.

Each of these steps is subject to errors that cannot be eliminated entirely but can be controlled and quantified. Training is necessary for analysts doing these measurements in the field. Engineers designing water treatment systems should also be aware of design requirements for sampling points. Understanding potential errors in oil analysis is necessary to avoid them. Interviews with operators in Gulf Of Mexico and other offshore operations indicate that the process is not well understood.

3.1 The Sampling Step

The objective of sampling is to get a representative the portion of the produced water stream. In comparing oil measurement methods the samples being compared should, of course, have the same composition. Some factors that can affect the representative nature of a sample are:

- Variability of the produced water stream,
- Flow conditions in the pipe or vessel containing the sample point,
- The cleanliness of the sample point,
- The sample container, and
- The integrity of the sample.

The oil content of a produced water stream can vary for many reasons. Source wells can be turned on and off. Partial separation in flow lines can occur with flow changes. Flow surges can occur as a result of separation in lines. Because of these factors replicate samples need to be taken very close together in time. If several replicate samples are taken, replicates should alternate for each analytical method over the sampling period so that an estimate can be made of concentration changes over time. A very variable produced water stream will introduce a lot of error in a comparison. Therefore when developing a correlation a time should be chosen when flow variance is at a minimum.

In addition to variability in the produced water, flow conditions can also affect sample validity. Flow must be high enough to maintain mixing in the flow stream. Too low a flow could result in separation of oil in the flow line and make it impossible to get a representative sample. This is one reason for not taking samples from vessels.

Sample point condition is important. Sample points usually provide a dead spot on the inside of a line where solids, oil and bacteria can collect that are not representative of the total produced water stream. To avoid this type of contamination the sample point should be

blown down thoroughly before collecting a sample. The blow down rate should be much higher than the sampling rate and should continue until a volume is removed that is greater than the sample volume.

Another important sample point condition is length of the sample line from the process sample point to the sample container. The longer a sample line and the further from the line being sampled the more chance of introducing errors. These errors can be either positive or negative. If the sample line is too long and is not properly blown down, organic matter left in the sample line from previous sampling events can be added to the sample and the measured value will be too high. If a new line is used before it comes to equilibrium with the system it can adsorb oil and the resulting sampled value will be too low.

Sample containers and their use can cause errors due to several factors:

- Use of dirty containers,
- Contamination due to cap liners,
- Improper volume collected (or poor measurement of volume), and
- Insufficient acid to lower the pH.

It is common in the Gulf of Mexico to reuse sample containers. Unlike in the North Sea, the analyst is usually not a chemist or chemical technician. Consequently the author has observed many sites where sample containers were not cleaned well before collecting the next sample. Besides cleanliness another potential source of contamination is the cap liner of the sample container. A common sample container used offshore is a six ounce prescription bottle. The usual cap supplied with these bottles has a cardboard liner covered with a thin sheet of plastic. For one time use these caps are adequate. But for repeated use the acid in the sample bottles eventually swells the cardboard and the cap comes loose. The glue holding the cardboard to the cap is soluble in organic solvents. This glue measures as oil in infra red analyzers and can result in large errors.

The sample volume is very important. The analytical method is calibrated assuming a standard volume of sample and extractant. Actual volumes must be corrected to standard volumes for accurate results. This requires volume measurements. The equipment used limits field measurement of liquid volumes and the smallest volume difference that can be quantified may be a significant fraction of the total liquid volume being measured.

Sample volumes can affect extraction efficiencies for some oil constituents. Extraction of dispersed droplets of oil in water is very efficient and quantitative. However, water soluble organic materials present another problem. These materials are normally insoluble in organic solvents at normal pH values but become soluble at pH values of 4 or less. Although these materials are much more soluble in organic solvents at low pH values than they are in water, they retain appreciable solubility in water. Therefore, these materials are not quantitatively extracted but distribute between the extractant and water phases according to the distribution coefficient. Variations in sample volume can affect such extractions because now the extraction efficiency depends on relative concentrations that are affected by relative volumes.

Sample integrity is especially important for oil in water samples. Since the oil in the water sample contains separate phase liquid (the oil droplets) shortly after the sample is taken the droplets begin to separate and some of them adsorb to the surface of the sample container. This means that the sample can never be subdivided. Once taken all of the sample including the container has to be analyzed. If a sample bottle is over filled it has to be discarded and a new sample taken. Other factors affecting the integrity of the sample are bacterial content, temperature and sunlight. Bacteria can eat oil and lower the oil content of a sample. They are controlled by the addition of acid to a pH less than 2 or by cooling the samples to 4 ° C or both. Heat can cause vaporization losses and samples stored for more than a few minutes should be kept at ambient temperatures or cooler. The ultra violet rays of sunlight can degrade some hydrocarbons particularly aromatics and samples should be stored in the dark or at least out of sunlight. Procedures are needed to ensure that samples are protected from degradation and misuse.

The following list gives examples of sampling practices the author has used for ensuring representative samples:

- Make sure sample point is adequate (vertical run upflow is best).
- When gathering comparison samples to test a new analytical method measure a series of samples on short time intervals using your existing method to determine how fast the oil content of the water stream is varying.
- Blow down the sample point for at least 10 sample volumes flowing at a rate higher than the sampling rate.
- Use a clean container (new is best).
- Use a cap with a Teflon liner.
- If it is not analyzed immediately store it in a cool, dark place.

These are illustrative of the conditions encountered by the author and would not necessarily be appropriate in every case.

The uncertainty introduced by sampling is possibly the largest source of error in the oil measurement process. Measurement of the volume of a nominal one liter sample using a graduated cylinder can be 25 ml or more. Variations in the actual oil content of the water stream can result in differences of 5 to 10 ppm over short periods of time. These potential errors added to sample point cleanliness and sample container contamination make the sampling step a significant source of error.

3.2 The Extraction Step

The objective of the extraction process is to make a quantitative transfer of the oil in the water sample to the extracting solvent. This process is affected by:

- The volatility of the solvent (solvent loss during the extraction process),
- The amount of energy put in to the mixing process (how much mixing energy is used),
- The lengthy of time that the sample is shaken,
- The solvent capacity of the solvent (How soluble are oil & grease components are in the solvent),
- The distribution of water soluble materials between the solvent and water, and
- Emulsification of the solvent in the water.

Solvents used in oil in water analyses vary in volatility. Both high temperature and vigorous shaking tend to promote evaporation of these solvents. All of the field analytical methods assume that the ratio of extraction solvent volume to sample volume remains constant during the analytical procedure. This problem is more critical for Freon 113. The author's experience indicates that solvent recovery after extraction can be as low as 60% to as high as 85%. For Freon 113 it is rarely higher. More importantly the recovered volume varies with sample temperature, extraction energy used and extraction time. For every extraction using Freon 113 or any similarly volatile solvent the volume of the extract should be diluted back to the original volume before the oil & grease determination is made. A few analysts in the Gulf of Mexico have claimed that volume compensation is not necessary because if one does and extraction consistently, the loss will be relatively constant. Since the field results must be correlated to the official method anyway, the correlation will take care of the solvent loss effect. However, when the field measurement is the official measurement solvent correction is necessary. Solvent volatility problems can be partially avoided and can be compensated for. For example, if the water stream being sampled is hot, the sample should be cooled to ambient temperature before being extracted. Once extracted, for procedures using volatile solvents, the extraction volume should be measured after extraction and diluted back to original volume before the actual concentration measurement is made.

In addition to their effects on solvent loss the amount of energy put into extracting a sample and the time spent shaking it with the extracting solvent has a significant effect on extraction efficiency. All the solvent must be in intimate contact with all the water for enough time for all the oil droplets to dissolve on the solvent and all the water soluble materials to equilibrate

between the solvent and water. The author's experience has been that two full minutes of vigorous shaking is required to guarantee that most of the oil is extracted. Manual shaking should be at a rate of 100-120 strokes per minute. Times and speeds for shaker tables and other devices should be determined.

It is obvious that if oil is not soluble in a solvent then that solvent is not a good candidate to use in oil analyses. However, no two solvents have identical capacities for dissolving oil. The author has observed cases where a single milliliter of crude oil would not dissolve completely in a liter of Freon 113. Oil in produced water is a mixture of components and not all of them may be soluble in a given solvent. The US EPA Method 1664 has problems with asphaltic crude oils. Asphaltenes are not usually soluble in low molecular weight aliphatic solvents such as normal hexane. Any analyst contemplating changing extraction solvents should be aware that the new solvent may cause changes in what is measured and will likely result in redefining oil. That is the new method will not necessarily give the oil concentration as the old one.

Freon 113 is not really a very good solvent for many crude oils or at least some of their components. If solvent capacity is a problem for a particular application the solution may be to use either a higher solvent to sample ratio or a better solvent. However, if one of these alternatives is used one must show that the results are consistent with the defining method for oil. The United States has a problem specific to their offshore application. The EPA defines oil, in the United States by EPA Method 1664. Originally EPA Method 413.1 originally defined oil. These methods are gravimetric methods which cannot be done offshore by non-experts. Any method used in the field must correlate to them. A similar situation exists in the North Sea differing only by the defining method. Any change in analytical procedure must be shown to be consistent with the defining method. If it is not consistent differences in analytical result may be perceived as errors.

For water soluble materials there may be an additional problem with the extracting step. In the case of these materials, it is not a matter of simply dissolving these substances in the solvent but equilibrating them between the solvent and the water. At equilibrium the amount of a material in each phase that has limited solubility in the two liquids depends on the distribution coefficient. For some field methods there is a choice of solvents. If a particular water treatment site has water with high levels of water soluble materials then this factor should be considered in choosing a solvent.

Occasionally water may contain surface active materials that promote the emulsification of the extraction solvent in water. Emulsions can cause two types of problems in oil grease extractions. First, it is hard to recover the solvent for use in the analysis. Even if you get enough back to analyze you cannot check the volume and adjust it to the original volume if that is required. Second, the stabilizing layers around a dispersed droplet can interfere with the transfer of materials across that interface. Emulsion problems are not always obvious. If they are not and extracting solvent is held up in the water and perceived as solvent loss then the reported result will be low. The presence of emulsions in produced water extractions should be a warning to the operator that there are other problems with the water treatment system. While that problem is unsolved water analyses may be unreliable.

Extraction errors can be very significant if they are not recognized and accounted for. Even if the two methods measure the same thing extraction errors can make it difficult to compare them. If they do not measure the same thing the results will be very misleading if the comparison is not viewed as a correlation. If two methods differ then it is appropriate to develop a correlation and test the correlation in order to compare them.

The following points should be considered when extracting water samples for oil analysis:

- Choose a solvent that is compatible with your instrument. Determine how your choice of solvent affects the defining method for oil.
- Ensure that the chosen solvent will dissolve your oil and for WSOs has a distribution coefficient favoring the solvent. Compare distribution coefficients for each solvent.

- Take steps to control the sample temperature prior to extracting (or choose a less volatile solvent if necessary).
- Correct volume of extract if necessary.
- Shake sample for at least 2 minutes at a rate of 100 or more shakes per minute (or mixing conditions that exceed these). Be consistent over all samples extracted.
- If the sample has emulsion problems check the process system. If emulsion are suspected text for them.

3.3 The Quantification Step

Quantification presents two separate challenges. One is due to the relative precision of quantification measurements as compared to the precision of sampling and extraction. The other is due to the fact that different measurement technologies measure different properties of the mixture termed "oil" in produced water. Frequently when analysts attempt to compare methods for measuring oil in produced water they focus on comparing the response of the instrument used for the quantification step. Both of the challenges mentioned above make such a comparison extremely difficult to quantify.

Most oil in water analytical methods used in the field make use of some type of electromagnetic spectra. For example, originally, in the North Sea, oil in produced water was defined by an infra red absorption method. Constituents of the oil absorb the IR radiation in amounts proportional to the amount of oil present. Another type of spectra used is the ultra violet (UV) spectra. When a water extract is subjected to ultra violet radiation some of its constituents absorb the incident radiation. When the higher energy levels created by this adsorption return to their ground state the energy released is emitted as another ultra violet radiation (UV). This process is termed fluorescence. This fluorescence can be measured and related to the concentration of absorbing constituents in the oil. Both of these technologies are highly sensitive and reproducible. The standard deviation of the absorption and fluorescence values is orders of magnitude lower than the reproducibility of an extraction or the ability of an analyst to take identical samples. However, it may be impossible to see differences when comparing replicate samples because the uncertainty due to the other two steps in the analytical process can mask differences in the quantification step.

Since oil is a mixture of constituents, it is quantified by measuring some property of the mixture that can be related to a known oil concentration. It is important to note that for both IR absorption and UV fluorescence the property measured is not common to all constituents of the oil. Using IR technology, carbon hydrogen (C-H) bonds absorb the IR wavelength used and the amount of energy absorbed is proportional to the number of C-H bonds in the extract. Therefore, in effect, infra red absorption gives a value that is proportional to the concentration of hydrogen bonds present in the sample extract. However, many of the constituents of oil in produced water also contain other bonds such as carbon oxygen (C-O, C=O) bonds. Using the North Sea definition of oil, if the IR instrument is calibrated with known concentrations of oil the IR absorption measurements can be related to oil concentration. However, this assumes that the "oil" in the water is the same as the oil used to calibrate the instrument. Commonly crude oil from the system is used to calibrate IR instruments. The Offshore Operators Committee and the American Petroleum Institute In the United States have sponsored several research projects that have shown that this is not the case. A similar situation exists for UV fluorescence but for that technology what is measured is the concentration of constituents that absorb UV light and fluoresce. Aromatic compounds are usually the major contributors to fluorescence in oil from produced water. Most of the constituents of oil are not aromatic. For both IR and UV methods a calibration with a standard oil is required to relate the factor measured to oil concentration.

Measured oil concentration values using one method may be different from those using another method. This is why a defining method is needed. Theoretically, regulatory bodies will decide what should be measured and a method that measures that parameter. This happened de facto when IR absorption was originally specified for measuring oil in North Sea produced water. In the United States the EPA originally defined oil using method 413.1. This method species extracting a one liter water sample with Freon 113, evaporating the Freon 113 and weighing the residue. This residue was then defined as oil and grease. Since this

method could not be performed offshore, operators adopted field methods, which then had to be correlated to the defining method. Alternative methods could conceivably be used in the North Sea if they were acceptable to the authorities and a procedure was established to get the correlations approved.

At the NEL Oil Monitoring Workshop in 2001 mention was made of a proposal being debated by the authorities for changing the method for measuring oil in produced water. There are several alternatives if this were to happen. One is to redefine oil. Simply specify that henceforth oil is what is measured by the new method. Another is that the original definition is retained but measurements must (or can be) using the new method and a correlation must be established between the two. A third alternative would be to use two definitions, each of which applied under specified circumstances.

Correlations also introduce errors into the measurement process. In simple form a correlation is a plot of the results of analyses of replicate samples using two different methods against each other. Fitting a straight line through the data defines their relationship. Since each set of data used in the correlation was subject to the uncertainties in the analytical process used to determine it the uncertainty in the resultant correlation includes the errors of both. This is a major problem in the Gulf of Mexico where operators are frequently confounded by poor correlations between their field instruments and the defining method used for gathering data reported to the EPA.

4 Identifying and Quantifying Differences in Oil Monitor Results

Oil in water analysis results for produced water, as any measurement does, always contain an element of uncertainty. Because of this there is an oil concentration value below which the oil concentration cannot be quantified. For US EPA Method 1664 this value is about 5 mg/L for most oils. The exact oil concentration is not actually known. However, around the reported value one can set ranges, which have confidence limits for containing the true oil concentration. The wider the range the higher the confidence that the true oil concentration will be found in it. These ranges are calculated statistically from the standard deviation of the measurement and the number of values used in determining the value. This variability is due to the factors discussed above. This variability is important because it determines the confidence an operator has that his discharge is in compliance with discharge limits. Another important impact of variability in oil in water analysis is its impact on testing of oil monitors.

When comparing two monitors for measuring oil in water there are two questions that must be answered:

1. Are the two instruments yielding comparable results? And
2. If they are not yielding comparable results, are differences due to analytical error?

Consider, for example, the comparison of an IR absorption monitor calibrated with crude oil from the same platform producing the water to a UV fluorescence monitor calibrated with the same crude oil. Assume the average results of several analyses using each instrument do not agree with each other. Is it because they are not measuring the same thing or because the standard deviation of both analyses are too large to permit a definitive answer? This question can be answered with statistical calculations if enough data was gathered. However, less data would be needed if everything possible was done to minimize errors in sampling and extracting.

If the two do not yield comparable results it is still possible to use either but they must be correlated to the defining method assuming one or both are not that method. There would be much less confusion about oil in water analysis if an explicit definition of oil was agreed on and published by the regulatory authorities.