

SOURCES OF ERROR IN PRODUCED WATER ANALYSIS**By****Dan Caudle
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The analysis for oil and grease in produced water is essential for process control and assurance that produced water discharges are in compliance. Since the official analyses for oil and grease is EPA Method 1664 and field methods are used offshore, the field methods must be correlated with EPA 1664 in order to determine the true oil and grease value. In the past few years we have found numerous operators who have trouble maintaining a reliable correlation between their field method measurements and the official analyses. Many operators have conducted studies on oil and grease analyses and attempted to set standards for their field personnel to use in monitoring treatment processes. However, there are continuing problems in understanding the analytical methods and instruments used in the field and their relationship to the official definition of oil and grease. The goal of this paper is to examine the process and identify the variables that must be controlled in order to accurately determine oil and grease in the field.

The Objective of an Oil and Grease Analysis

Oil and grease discharge limits were developed to represent the level of oil and grease that the best available treatment technology could achieve 99% of the time. This value is the maximum that can be legally discharged. One problem with complying with a concentration limit is in determining the concentration. All measurement methods are subject to errors. None is perfect. For example, if one measures a length with a ruler and the smallest unit marked on the ruler is a tenth of an inch, how close can you measure the length? Is the value 6.2 inches or 6.22 inches or 6.217 inches? At some decimal place one can no longer discern a difference. Because oil and grease measurement methods include measurements of several liquid volumes, absorbance readings, etc., 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 is usually expressed as the standard deviation of the measurement. This can be expressed as a fixed concentration. For example, all methods used offshore are probably no better than +/- 5 ppm. Certainly concentrations lower than 5 ppm cannot be reliably distinguished from zero. Therefore, if a measured value is found to be 22 ppm, for example, this means that the true value is between 17 and 27 ppm with a high degree of confidence. This assumes that the analyst was competent and was paying attention. The standard deviation can also be expressed as a percentage of the value. For example, the standard deviation for the EPA 1664 Method is published in the method and is somewhere near +/- 15% of the measured value.

The operators 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 and grease concentration but also its variability. Since the variability is determined by the sources of error in the analytical process, what can cause error really has to be understood and steps to be taken to minimize the errors in the process. The process is even more complicated since limits are set using a laboratory method that the field measurements must be correlated against. This means that not only the measurement itself can cause errors but also that the data used to develop the correlation can cause errors. When official samples are taken the operator also needs to know the oil content as measured by the field method. Being able to compare these two results is helpful in maintaining a good correlation and will aid in determining what went wrong if the official sample subsequently is found to be out of compliance. Therefore, an operator needs to understand not only the potential errors in the field measurement but also the errors in the correlation.

The Measurement Process

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

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

Each of these steps is subject to errors that cannot be eliminated, but can be controlled if they are understood. This is why it is very important to train personnel carrying out these analyses in the field and to make sure they understand what can go wrong in each step. Interviews with operators show that the process is not well understood and there is a lot of misinformation about how to do each of the steps.

The Sampling Process

The objectives of sampling are to get a sample that actually represents the produced water stream. In developing a correlation between the field method and EPA 1664 it is also important that the samples being correlated actually have the same composition. Some factors that can affect the representative nature of a sample are:

- Variability of the produced water stream,
- The cleanliness of the sample point,
- The sample container, and
- The integrity of the sample.

Upstream processes can cause flow surges that can affect treatment processes. If an individual system is subject to flow surges, it may be difficult to determine what a representative sample is. If one is collecting samples for developing a correlation it is important to know how variable the stream is. A very variable produced water flow will introduce a lot of errors in a correlation. Therefore when developing a correlation a time should be chosen when flow variance is at a minimum. Likewise, the confidence level in the correlation will be lower if flow is highly variable.

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. Therefore it is very important to blow down a sample point thoroughly before collecting a sample. The longer a sample line is 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 that measures as oil 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 value will be too low. Therefore, one should use as short a sampling line as possible. It should be in a vertical run of pipe if possible and it should be carefully blown down before sampling starts.

Several problems can result from the sampling container used:

- Contamination due to lack of cleanliness,
- Contamination due to defective cap liners,
- Improper volume collected (or poor measurement of volume), and
- Insufficient acid to lower the pH.

It is common to find operators reusing sample containers day after day. This raises doubts about the cleanliness of the sample container. Failure to wash it sufficiently can add errors to subsequent samples. The most common sample container used offshore is a 6 ounce prescription bottle. The common 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 hexane. This glue measures as oil in infra red analyzers and can result in large errors.

The sample volume is very important. Nominally most field methods use 100 ml samples. The objective in sampling is to get a sample as near to 100 ml as possible and then measure the volume and correct the concentration based on the actual volume. However, some offshore analysts assume all volumes are 100 ml and don't correct for volume. Some may correct for volume but take samples that are significantly different from 100 ml. This may affect the extraction efficiency.

Most water soluble organics are acidic and if the pH of the water sample is higher than the pK of the acids making up the soluble materials they will not extract into the solvent. Acid has the additional job of controlling bacterial growth that could eat some of the oil

in the sample and cause errors in the measurement. Normally this is not a problem with offshore analyses because the samples are usually analyzed immediately. However, if samples are taken for special studies and held for shipment onshore for analyses, it could be a problem.

Sample integrity has two aspects:

- The actual handling of the sample, and
- The records associated with it.

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.

Sample records are important because a sample is of no use unless it can be documented to represent the sample point. This means that the sample and the results of analyses performed on it have to be identified and recorded. Details are easily forgotten! If several samples are collected and taken back to a central point for analyses they should be marked all the relevant information: sample point, time, sample taker, etc.

The Extraction Process

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 hard you shake it),
- The length 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.

Both Freon 113 and hexane are relatively volatile. 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 than for hexane. In 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. Our experience has shown that from 1.5 to 5 ml of the Freon 113 is lost in an extraction. A few operators claim that volume compensation is not necessary because if one does an 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, solvent loss is not constant. It can vary with temperature, shaking speed and time that the sample is shaken.

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 near 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.

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. This is a well recognized problem and several major oil companies have reportedly studied this problem. The results of these studies do not always reach the operators who are actually doing the field analyses. Our experience has been that two full minutes of vigorous shaking of a six ounce bottle is required to guarantee that most of the oil is extracted. Shaking should be at a rate of 100-120 strokes per minute.

It is obvious to us all that if oil is not soluble in a solvent then that solvent is not a good candidate to use in oil and grease analyses. However, no two solvents have identical capacities for dissolving oil. We have found cases where a single milliliter of crude oil would not dissolve in a liter of Freon 113. Others have shared similar experiences with us. Even EPA 1664 has problems with asphaltic crude oils. Asphaltenes are not usually soluble in low molecular weight aliphatic (straight chain) solvents.

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 a higher solvent to sample ratio. Most field methods recommend a single extraction with a 1:10 solvent to sample volume ratio. For water streams containing oils that are not very soluble the ratio may have to be adjusted upward to 1:5 or more.

For water soluble materials there may be an additional problem with the extracting solvent. 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 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 before 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. 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.

The Quantification Process

In the field, "oil and grease" is quantified by measuring some property of it that can be correlated to the actual oil and grease value. Using this measured value the oil and grease concentration is predicted using a correlation relationship to the official method. Several instruments are available that measure on such property. The technologies employed include infra red absorption (IR) and ultra violet fluorescence (UVF). For IR instruments two applications are commonly used:

- Measurement of the absorption of an IR beam transmitted through a cuvette containing the sample extract, and
- Measurements of the absorption of an IR beam refracted along the surface of a crystal that has had the sample extract placed on it and the solvent evaporated.

Desktop UVF instruments usually measures the fluorescence from a sample extract in a cuvette that is excited by UV light focused at right angles to the detector. IR and UVF instruments measure different properties of the oil and grease constituents and have different limitations. The two technologies can not be directly compared but must both be correlated to the official method and comparisons made using the correlations.

Most operators search for a field instrument to meet their measurement needs begin by focusing on which of these technologies is the "best". However, most field measurement problems are much more likely to be due to sampling and extraction and not the final quantification step. A technology and an instrument using it should be chosen on the operators' needs and preferences and not on which instrument is the most accurate or precise. There is probably no such thing as the "best" instrument independent of individual needs.

The operation of any of the instruments can introduce errors in the analytical results. Greasy hands on a cuvette can leave oil that is included in the analytical results. Careless placement of extract on an IR plate for evaporation can leave some of it outside the measurement area and will not be measured corrected.

Potential long term errors due to instrument operations are likely to be due to a poor understanding of the technology leading to misuse of the instrument. One can choose the wrong instrument but that is not the instrument's fault.

Error Relationships in the Whole Process

If potential errors in all three steps in the analytical process are carefully examined, it will be seen that the first two steps: sampling and extraction are likely to produce far larger errors than the quantification step. As a practical matter, the first two steps will introduce so much error that the results of any one instrument cannot be said to differ from any other instrument measuring oil and grease in produced water. This assumes that the instruments are calibrated properly, correlated properly and the correlation is checked on a regular basis, and used carefully and correctly. The difference in instruments comes in how easy and conveniently it is to do these things for a particular application and how easily it is to train personnel to do them.