

Produced Water Sampling Procedures

By
Dan Caudle
Colin Tyrie

Introduction

As with any analysis, the measurement of a produced water parameter is only as good as the sample taken to analyze it. Sampling is a widely misunderstood process. This is especially true for produced water. Produced water is unique substance whose properties vary with the conditions under which it exists. One important property of produced water is that it contains several phases. Besides the water itself it contains:

- Dispersed oil droplets,
- Dispersed solid particles (of several types),
- Dissolved gases, and
- Bacteria.

In the production system produced water is also subject to the system pressure and temperature and its isolation from external environment. When a water sample is withdrawn a number of changes take place that can affect the oil content of the water. These include:

- The loss of dissolved gases (but no oxygen),
- pH changes occur due to the loss of dissolved gases,
- Solids that may precipitate
- Dispersed oil droplets which can separate
- Dispersed solids that may settle.

Simply put, when you take a sample it will change and the properties of the water will vary accordingly. One must take these changes into account and keep the water protected and act to preserve it from the changes. All this raises the question of what one must do to acquire a representative sample in order to analyze to determine the composition and properties of the water.

This discussion is presented to illuminate some of the problems and discuss the procedures for addressing them. The most troublesome sampling in production operations is sampling for oil and grease analysis. There are two reasons for analyzing for oil and grease in water:

- Regulatory compliance, and
- Process control.

These are similar procedures but vary in several important ways so both will be discussed and compared. Samples taken for proving compliance with permit limits are analyzed by EPA Method 1664 (ref.1). Samples taken for process control are usually analyzed in the field using an instrument that measures some property of the water which can be correlated to the official method.

What is “Oil and Grease”

Chemically speaking there is no unique substance called “oil and grease”. The term “oil and grease” is a legally defined parameter that was originally designed to control oily waste in sewage. The term was adapted in the US by the EPA to control some of the

organic waste in produced water. The US EPA defines¹ “oil and grease” as “those materials that can be extracted from water at pH 2 or less into normal hexane and remains after the hexane is boiled off”. This definition does not include all the organic materials in produced water. For example, it does not include:

- Compounds with a boiling point below that of normal hexane,
- Organic compounds which are not soluble in hexane.

The definition does include materials besides the hydrocarbon compounds that are usually regarded as the constituents of oil and grease. These include organic acids and salts (RCO_2^-), other oxygen containing organic compounds, and potentially organic sulfur and nitrogen containing compounds.

Many components of “oil and Grease” are **dispersed** in water not **dissolved** in it. This means that after sampling free oil will separate from the water and either float on top of the water or adhere to the inner walls of the sample container. Therefore oil must be extracted from both the water and the sample container in order to measure it.

EPA Compliance Sample Requirements

A representative sample must meet several requirements that include:

- Required sample container and collection procedure,
- Sample preservation methods,
- Holding times between sampling and analyses,
- Analytical procedure to be used,
- Variability and reproducibility limits to be met by the analytical procedure prescribed.

All these factors must be satisfied in order for a sample to comply with regulatory limits or analytical standards.

The definitive document for oil and grease analysis for compliance with EPA regulations is EPA Method 1664. A copy of this document is given in Appendix 1. Section 6 of the method specifies sample bottles as “Glass, approximately 1 –L, with PTFE-lined screw cap”. In practice quart fruit jars are usually used. The specific EPA requirements for sampling are listed in Table 1. This table is a copy of the Sampling Collection, Preservation and Storage given in the Section 8.0 of Method 1664.

Note that in Table 1 a lot of specific detail is given. As a practical matter the sampling procedure for produced water discharges can be summarized as follows:

- Take the sample in a one liter glass bottle. Do not pre-rinse the bottle. Once taken, the sample cannot be subdivided and the entire sample including the bottle must be analyzed.
- All samples must be grab samples. Automatic sampling equipment cannot be used.
- Samples must be acidified to less than pH 2 with acid.

¹ Offshore Guidelines for Western Gulf of Mexico

- Measurement of pH should not be performed on oil and grease samples. The amount of acid required should be determined on duplicate samples taken for that purpose.

Although Method 1664 specifies that samples should be refrigerated at 0-4 °C early on operators demonstrated in work carried out by an API work group shows that refrigeration was unnecessary if acidification was used.

The actual procedure for carrying out the analysis and calculating the results are also specified in Method 1664. Usually these details do not concern field personnel and are not discussed in this paper. The maximum holding time between sampling and analysis is specified in Method 1664 as 28 days. In practice operators usually want to know the results of the analyses well before 28 days.

Field Sampling and Analysis (Process Control Samples)

In order to ensure that the day to day compliance of the produced water stream is within the specified limits, a method of sampling has to be used to ensure that method correlates with the 1664 method. This is what is termed the “Field sampling and analysis”

Field analyses differ from laboratory analyses in several important ways. These include:

- What is measured,
- The type and size of the sample used,
- When the analysis is carried out
- Who performs the analysis,

The most important difference is that the field methods commonly used **do not measure oil and grease**. Since oil and grease is a mixture of materials some of which are dispersed in and water and others are dissolved in water. Therefore the water can include a very diverse variety of compounds. It is obvious therefore that there is no simple, accurate way to measure oil and grease in the field. So properties of the fluid are measured that they can be correlated with oil and grease. Then instruments measuring these properties are used. The instruments are calibrated using correlations to give results of oil and grease concentrations. The most common measurement targets are:

- The number of carbon hydrogen bonds in the sample (Infra Red instruments), or
- The Ultra violet fluorescence of the sample (UV instruments).

A discussion of these methods is beyond the scope of this paper but it is important to note that the development of the correlations and calibrations needed to convert these readings to oil and grease concentrations is a significant source of confusion and add to the complexity of getting good results with field samples.

Process control samples are usually 100 ml in volume and taken in a six ounce prescription bottle or other small glass bottle with a non absorbing cap. Common problems with field samples are caused by use (and reuse) of these sample containers. Ideally the bottles should have Teflon cap liners. See discussion below of common problems with field analyses.

Field samples are frequently done soon after the sample is taken. If the produced water being sampled has an elevated temperature care must be taken to avoid extraction solvent

loss that will result in measured oil and grease concentrations that are abnormally high. When sampling produced waters above ambient temperature it is advisable to cool the sample to room temperature before extracting the sample. See discussion below of common problems with field analyses.

In contrast to EPA Method 1664 analyses operators or technicians frequently analyze field samples. With the right kind of training and incentives they can be better than a chemist but the authors have known field analysts that apparently had no training at all.

Field Sampling and Analyses Summary

- Provide adequate training to analyst,
- Use clean sample container with the proper cap liner,
- Take the correct volume of sample and do not subdivide,
- Add acid,
- Cap tightly
- Cool if necessary, and
- Perform extraction and analysis.

Common Errors In Field Analyses

Over the years, a number of common problems with field analyses have been observed. Some memorable ones are:

Cap Glue: The caps in prescription bottles are commonly cardboard with a plastic cover. These are held in place with glue. This glue is carbon based and soluble in both hexane and Freon. This glue measures as oil and grease using IR instruments. The first use is sometimes within the limits of the analysis but the solvent vapors eventually dissolve the glue and ruin your oil and grease analysis. This problem is exacerbated when the same sample bottle is used over and over again.

Reusing Prescription bottles: Operators have been observed using the same sample bottle to take process control samples. Even when they remember to rinse it out the rinse is not sufficient to clean it.

Hot Water and Solvent Loss: When the produced water stream is at an elevated temperature, beginning the analysis before it cools sufficiently will result in solvent loss. The assumption was made when the instrument was calibrated that a given volume (10 ml) was used to extract the sample. This is a problem with both hexane and Freon but is a more significant problem with Freon and other chlorinated solvents. If 3 or 4 ml of it are vaporized then the resulting concentration may be 30 or 40% higher than the actual concentration. If your water is at a fairly high temperature than it should be allowed to cool before being extracted but even then the extractant volume should be measured and brought back to the original volume before the oil is measured.

Extraction Energy: In order to extract the oil from the water the extractant has to be intimately mixed with the water. This takes a lot of energy. Frequently analysts will add solvent to a sample and shake it for 10 or 15 seconds. *This is not adequate.* An

extraction mixture should be *vigorously* shaken for least two minutes and an analyst should measure the extraction time not just estimate it. A minute is a lot longer than most people think.

Sample Collection: Sample ports can be a barrier to achieving a representative sample from a flowline.

Some of the potential problems are:

- Position of the port on the line,
- Volume of dead space in the sample port.
- Type of flow in the line.

A worst case scenario would be a large dead space sample port on top of a horizontal line carrying a laminar flow fluid. In this case the sample would probably be predominately oil. The optimum case would be a sample port in the side of a vertical run of pipe carrying turbulent flow upward and the sample line projects into the flow stream away from the wall of the pipe. Sample ports always have a certain amount of dead space and should be blown down before a sample is taken. At least 3 to 5 sample volumes should be passed through the sample valve before the required sample is taken.

The sample protocol therefore is as follows:

- Turn on the sample analyzer and allow the meter to warm up.
- Select clean bottles for the sample
- If bottles are the ones used by the chemical company, change the caps
- Add one or two drops of HCL into each bottle to ensure the pH will be 2 or less
- Run the sample line to waste as intimated above
- Take care that the sample level is at the 100ml mark on the bottle
- **Note, do not pour water out to achieve the required 100 mls, the calibration is normally 10% dilution and hence when measuring the solvent, it should be 10% of the volume of produced water in the bottle. It is the same for volumes less than 100 ml**
- Cool the fluid to ambient temperature – 60 to 80°.
- When cooled add the 10% by volume of the solvent to be used in the extraction.
- Replace the cap on the bottle and shake for 15 seconds and then open the cap to release any trapped gas. Screw the cap back tight and repeat this process at least three times to ensure that there is no latent gas in the bottle.
- With the cap tight shake the bottles vigorously for 2 minutes.
- The monitor (IR or UV instrument) should now be zeroed to the manufacturer instruction.
- For use with the Wilks Infracal –
 - If the solvent is heavier than water then the bottle should be turned upside down and the measure sample taken through the bottle cap. If the solvent is lighter than water then the sample is taken through the cap with the bottle standing upright.
 - The sample is taken using a syringe (Usually 5 Micro liters) and then spread on the sample plate of the instrument.

- Start the timing mechanism and wait until it expires where all the solvent should be evaporated. The unit will then give a reading that is equivalent to the oil and grease that would be measured by the 1664 process.
- If the measuring device uses a cuvette then the process is similar but the cuvette or microcuvette has to be filled prior to the cuvette being placed in its instrument and the reading noted on the machine.
- On completion the monitor and/or cuvette should be cleaned with clean solvent and the water and solvent mix from the previous test disposed of in the correct manner.

References:

1. **USEPA Office of Water, EPA-821-R-98-002, PB99-121949, Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry**