

MEASURING OIL AND GREASE IN PRODUCED WATER

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INTRODUCTION

When the United States Environmental Protection Agency (USEPA) developed the National Pollutant Discharge Elimination System (NPDES) in the 1970s, oil and grease in produced water was one of the pollutants which was limited. Unlike other parameters, oil and grease is not a unique chemical entity, but is a mixture of chemical species that varies from source to source. It is defined by the method used to measure it. The implementation of limits on the discharge of oil and grease made it necessary to develop processes to remove it from produced water. In turn, the existence of these processes made necessary methods to measure their effectiveness and to control them. If one is operating a system to remove oil and grease, one must be able to measure the oil and grease in the field. It is not feasible to use the EPA's defining method in the field since it is a gravimetric method. Therefore, most operators adopted some type of field method using Freon as an extractant and a measurement using an infrared (IR) instrument. Although these methods do not measure oil and grease as measured by the EPA exactly, the results obtained using them can be correlated with oil and grease concentrations.

Because Freon has been found to be a hazard to the ozone layer, its manufacture has been discontinued in the United States. This has resulted in the EPA developing a new official method (EPA 1664) that uses hexane as an extractant. The industry also has been actively searching for replacements for field methods for the last few years. One such method using hexane extraction, evaporation of the hexane and measurement with an IR instrument is the subject of this seminar.

WHAT IS "OIL AND GREASE"? – THE DEFINING METHOD

The EPA defined oil and grease when the first guidelines for permits were issued in the 1980s. The method specified for measuring oil and grease was EPA Method 413. Soon the EPA will officially change the method for measuring oil and grease from Method 413.1 to Method 1664. Method 413.1 specifies that a one-liter water sample be acidified to a pH less than 2 and extracted with three 30 ml portions of Freon. The Freon was to be evaporated under specified conditions and the resulting residue of oil and grease was to be weighed. Method 1664 is very similar but uses hexane as the extracting solvent. Only those materials which:

- are soluble in Freon (or hexane) at pH 2 or less, and
- remain after boiling off the solvent

are "oil & grease" by definition. Produced waters commonly contain organic constituents in concentrations of 2000 to 3000 mg/l. These constituents include such materials as:

- dispersed droplets of crude oil,
- dissolved carboxylate material (organic acids, including aromatic acids, and dissolved

- phenols),
- dissolved aromatic compounds (including multi-ring compounds such as naphthalene), and
- residual treating chemicals.

Most of the organic materials in produced water **are not** oil and grease because they are either insoluble in the extracting solvent (Freon or hexane) or they are so volatile that they boil off with the solvent during analysis. Most of these materials are present in very small concentrations except for the organic acids. It is not possible to examine a chemical analysis of produced water, assuming it was possible to accurately and easily do one, and determine the oil and grease in the water. This is because the oil and grease content depends not only on the chemical composition of the water, but also on the extraction procedure.

The EPA methods are direct measurements of oil and grease because the target material is directly weighed. All other methods used to measure oil and grease are indirect methods. That is, they measure some property of the constituents of oil and grease that can be correlated to oil and grease. For example, infrared measures the concentration of carbon-hydrogen bonds in the extract. Since all constituents of oil & grease contain carbon-hydrogen bonds all of them are detected by infrared.

There is nothing theoretically or technical correct about the EPA's definition of oil and grease. It is not the only definition used in the world. For the North Sea the Oslo-Paris Commission (OSPARCOM) and in China oil and grease is defined by infrared measurements. It is important to note that compliance with the regulations is the goal and therefore, we must measure oil & grease as defined by the EPA.

HOW ARE FIELD MEASUREMENTS RELATED TO OIL & GREASE?

The official EPA methods for measuring oil and grease measure the oil and grease by weighing it. That is, the property measured is mass or weight. All field methods measure some other property of oil and grease. Some of the measuring principles employed by field methods and the property they measure are:

Measurement Principle	Property Measured
Infrared	Number of C-H bonds
Ultra Violet absorbance	Concentration of aromatic compounds
Ultra Violet fluorescence	Concentration of aromatic compounds
Visible Light absorbance	Color
Nephelometry	Concentration of particles or drops

If one wishes to determine the concentration of “oil & grease” as defined by the EPA method, one must establish the relationship between what the defining method measures and what the instrumental method measures. This means that for each measurement technology a condition has to be met for a relationship to exist. For the measurement technologies listed above the conditions to be met are approximately:

Measurement Principle	Condition
Infrared	The number of C-H bonds in the O&G is proportional to the weight of O&G.
Ultra Violet absorbance	Concentration of aromatic compounds is proportional to the weight of O&G.
Ultra Violet fluorescence	Concentration of aromatic compounds is proportional to the weight of O&G.
Visible Light absorbance	The color of the extract is proportional to the weight of O&G.
Nephelometry	The number of oil droplets is proportional to the weight of O&G.

None of these conditions are exactly true in all cases.

For this school, we will focus on the relationship of infrared measurements to the defining method. One advantage that infrared has is that all constituents of oil and grease have carbon-hydrogen bonds (C-H bonds) in their structure and **all of them** will be detected. This means for a particular discharge point there should be a very good correlation between infrared measurement methods and the defining method. Infrared never gives exactly the same measurement as the defining method. If we examine the constituents oil & grease listed above, we can see why this is so. Droplets of crude oil are composed mostly of hydrocarbons and they would all have about the same calibration factor between weight and IR absorbance. However, some of the hydrocarbons in the oil droplets are more volatile than Freon (or hexane) and they will not measure as oil & grease. For this reason infrared measurements made with the old Wilks-Miran instruments are almost always higher than measurements made by the defining methods. That is, it would not be surprising to find an infrared determination of 40 mg/l oil & grease corresponding to a 413.1 determination of 22 mg/l.

The organic acids and phenols that make up most of the organic content of produced water have more weight per C-H bond than hydrocarbons. This should tend to make infrared determinations that have been calibrated with crude oil lower than gravimetric determinations. However, at most, this factor could make only about a 20% difference and has not been found to be a problem. There is a long history of successful infrared measurements with EPA 413.1 measurements.

TWO KINDS OF CALIBRATION

A field instrument must be calibrated so that the instrument response gives a reproducible result and covers the concentration range of interest. This requirement is well understood. Preparing a known set of oil & grease concentrations in the extraction solvent (hexane in this case) and analyzing them with the instrument usually does this. Normally this analysis would yield percent transmittance readings or absorbance readings depending on how the instrument was set up. These results are then plotted against the known concentrations of the solutions analyzed and a best fitting straight line is determined by least squares through the points. The Wilks Infracal instrument has

several advantages in this regard, which their representatives will explain. Having such a calibration allows determination of oil and grease in arbitrary units, but these units are not legally oil & grease until they are related to the defining method. In the past this was handled by keeping two sets of numbers, the IR numbers and the official numbers. With the Wilks Infracal, if the correlation with the EPA method is known, it can be programmed into the machine and it will then read true oil and grease concentrations directly.

Why aren't the original IR readings good enough? The answer to this is that the water treating equipment must meet EPA limits that are determined by the EPA method. Therefore, the original IR readings must be converted into EPA oil and grease concentrations. You can keep a plot on the wall of your offshore measurement station or you can program the correlation into your machine.

The manufacturer usually determines the machine calibration and obtaining this calibration can be relatively straightforward. The development of a correlation between the field instrument measurements and the defining method presents a separate problem. This is discussed in the next section.

Method for Correlating a Field Method with the EPA 1664

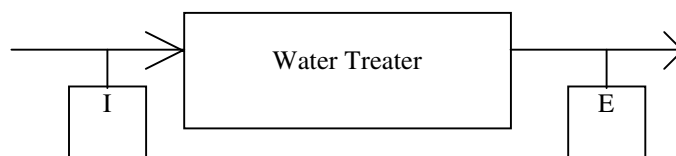
Once the field instrument is calibrated so that it will yield reproducible measurements it must be correlated to the defining method for oil and grease (EPA 1664). This correlation will allow the operator to determine what EPA 1664 would give if the value determined by the field instrument is determined. This correlation is usually in the form of a plot of 1664 oil and grease values versus oil and grease values as measured by the field instrument. This plot is determined in the following way:

- Obtain several sets (minimum of 5) of duplicate concentrations at various oil and grease values,
- Analyze one sample of each duplicate set using the field instrument and send the other sample of each duplicate set to the laboratory for analysis by EPA 1664,
- Then, plot the field values against the EPA 1664 values, and
- Determine the best fitting straight line through the data points using a least squares fit.

A least squares fit can be done with a spreadsheet such as Excel, Lotus 123 or Quattro Pro. The Infracal instrument has the least squares procedure built in.

Once you are ready to develop your correlation several problems become obvious. For example, where do you get samples? They must cover a fairly broad concentration range so that you can use the correlation to measure all the oil and grease levels that you might need to measure, say from 5 mg/l to 200 mg/l. In the past the IR units used in the field were correlated with the defining method simply by running a field analysis every time an official EPA sample was taken and plotting the results. This method has several limitations. First, it takes a long time to accumulate enough values for a meaningful correlation. Second, the concentration range covered isn't usually very broad. Third, you have to report all the values obtained using the defining method **including the high ones!**

The following sample sets can give you a correlation over the range of interest for your treating equipment and you will only have to report one of them. Consider the following treating system:



If one takes duplicate samples of the following composition:

Sample Number	% of Inlet	% of Effluent
1	100	0
2	75	25
3	50	50
4	25	75
5	0	100

One sample can be analyzed using the field instrument and the other can be analyzed by EPA 1664. If one needs greater definition then this list can be expanded to include ratios such as 90/10, 80/20, etc. down to 20/80, and 10/90.

Once a correlation has been determined, a plot of it can be kept. Each time samples are taken in the field another point can be added to the correlation curve. As long as these samples remain relatively close to the correlation line, then the correlation is holding. If they begin to diverge, a new correlation should be developed. For instruments like the Wilks Infracal the correlation can be programmed into the instrument and the operator need not be concerned with it at all.

WHY DO WE NEED FIELD METHODS?

If one must meet an oil and grease limit for produced water discharges, then treating equipment is needed to remove oil from the water prior to discharge. The selection of such equipment requires a quick, simple method for testing equipment performance in the field. Operators must also monitor the performance of their water treatment processes frequently. Many production operations result in changes in water quality that may require adjustment of the water treatment system. Although many treatment systems are stable enough to operate for several days without adjustment, some operators monitor their treatment systems several times a day in order to ensure that the equipment is functioning properly.

The official EPA method is not suitable for monitoring in the field. It is very slow and labor intensive. To do it correctly requires training and practice. It requires a lot of space and doing the analysis offshore may be unsafe. Sending the samples in to a laboratory onshore is too slow. Equipment cannot be adjusted if the analyses that adjustments depend on takes several days.

FEARS, MIS-UNDERSTANDINGS AND PROBLEMS

Fear of the unknown frequently hampers the acceptance of new technology. Service laboratories are afraid of the change from Freon to hexane when the EPA replaces Method 413.1 that uses Freon with Method 1664, which uses hexane. Freon doesn't burn and hexane does. Exposure to hexane can increase some health risks. Service laboratories have had little risk of fire before hexane and now due to the large number of samples analyzed at any one time and the large volume of hexane used for each sample they are under increased risk. The concerns of the

service laboratories have caused some offshore operators to worry about these issues too. These concerns are largely unfounded, as an offshore platform is an entirely different matter. The number of analyses and the volume of hexane used are significantly smaller than in a laboratory. In addition, the risk of fire from hexane adds only a fraction of the risk that already exists from stray hydrocarbons from production operations. Analyses offshore should be done and should have always been done in a well-ventilated space secure from ignition sources.

When using Freon in the field, disposal of waste extraction solvent is a problem. This is not the case with hexane. Since hexane is a natural constituent of crude oil, waste extraction solvent can be simply recycled to the slop tank or waste oil tank.

Regarding the health risk, crude oil and gas condensate contain hexane already. The risk of exposure to hexane is no greater than it is for crude oil that is already very low.

Over the last few years, sensitivity has developed over the issue of correlating the results of field methods with the official method. This situation probably results from a mis-understanding of the intent of the EPA. In times past some operators got into trouble because they only used their field methods to screen samples being sent in for official analysis. This practice is clearly illegal if the results of such field analyses influences whether or not a given set of samples is submitted. However, the permit makes it clear that the EPA intends for the operators to monitor their equipment and to ensure that it is functioning properly (**ALL THE TIME**). Since the standard of performance is the official measurement method the field methods must correlate with it. The fact of correlation is not the important point, it is how you use the results. The next section explains the requirements of the Western Gulf of Mexico permit and illustrates what the EPA expects.

Problems are frequently encountered with field methods and they are not always the fault of the instrument being used. Some of the mistakes frequently made that do not depend on the instrument being used are:

- Inadequate mixing due to not enough energy being used and not enough mixing time (you did not shake the sample hard enough or long enough),
- Inaccurate volume measurements for both water sample and solvent,
- Too much or too little evaporation (depending on the method being used), and
- Dirty equipment.

If too little energy is put into the extraction then oil will be left in the water. If the procedure is reproducible then results will be adequate, but if they are not then the results cannot be depended on. Instrument calibrations assume certain water sample volumes and extraction solvent volumes. If these are not used then incorrect results will be reported. If the method being used depends on removing all the extraction solvent before making a measurement then high results will be obtained when too much solvent remains and low results will be obtained when too much energy is put into removing solvent because oil and grease may be removed.

PERMIT REQUIREMENTS FOR OIL & GREASE MEASUREMENTS AND THEIR IMPACT ON FIELD MEASUREMENTS

Most people are familiar with the oil and grease limits for produced water. However, these

limits are only a small part of the requirements that must be met for the discharge of produced water. This section presents excerpts from the Western Gulf of Mexico general permit that was issued in the Federal Register December 3, 1993. This permit has since been modified several times but the material presented here is still applicable. Certain passages have been bolded and presented in italics to emphasize their importance. Each excerpt is followed by comments explaining its relevance.

Part I. Requirements for NPDES Permits

Section B. Effluent Limitations and Monitoring Requirements

4. Produced Water

(a) Limitations

Oil and Grease. Produced water discharges must meet both a daily maximum of 42 mg/l and a monthly average of 29 mg/l for oil and grease. The sample type shall be a 24-hour composite consisting of the arithmetic average of the results of 4 grab samples taken over a 24-hour period. If only one sample is taken for any one month, it must meet both the daily and monthly limits. Samples shall be collected prior to the addition of any seawater to the produced water waste stream. The analytical method is that specified at 40 CFR Part 136.

COMMENT: *This is the part of the permit that most people know about. It contains the oil and grease limit and the sampling procedure for collecting the required number of grab samples.*

Section D. Other Conditions

1. Samples of waste

If requested, the permittee shall provide EPA with a sample of any waste in a manner specified by the Agency.

COMMENT: *This gives the EPA the right to take a sample any time they want to. Under a memorandum of understanding with the MMS, the MMS can take samples if they wish and send them to the EPA for analysis.*

Part II. Standard Conditions for NPDES Permits

Section A. General Conditions

2. Duty to Comply

The permittee must comply with all conditions of this permit. Any permit noncompliance constitutes a violation of the Act and is grounds for enforcement action or for requiring a permittee to apply and obtain an individual NPDES permit.

COMMENT: *This condition makes it clear that all the other conditions discussed here apply. The operator must comply with all the requirements, not just get oil and grease concentrations that meet the limit. Failure to do so can result in the need to apply for an individual NPDES permit, which is an extremely costly and lengthy process.*

7. Duty to Provide Information

The permittee shall furnish to the Director, within a reasonable time, any information which the Director may request to determine whether cause exists for modifying, revoking and reissuing, or terminating this permit. The permittee shall also furnish to the Director, upon request, copies of records required to be kept by this permit.

COMMENT: *Records must be kept on site and be available to show inspectors.*

8. Criminal and Civil Liability

Exceptions as provided in permit conditions on “Bypassing” and “Upsets,” nothing in this permit shall be construed to relieve the permittee from civil or criminal penalties for noncompliance.

Any false or materially misleading representation or concealment of information required to be reported by the provisions of the permit, the Act or applicable regulations, which avoids or effectively defeats the regulatory purpose of the permit may subject the permittee to criminal enforcement pursuant to 18 U.S.C. 1001.

COMMENT: *If misleading information is given to the EPA it may subject the person providing it to criminal penalties.*

Section B. Proper Operation and Maintenance

1. Proper Operation and Maintenance

The permittees shall ***at all times*** properly operate and maintain all facilities and systems of treatment and control (and related appurtenances) which are installed or used by the permittee as efficiently as possible and in a manner which will minimize upsets and discharges of excessive pollutants and will achieve compliance with the conditions of this permit. Proper operation and maintenance also includes ***adequate laboratory controls and appropriate quality assurance procedures***. This provision requires the operation of backup or auxiliary facilities or similar systems which are installed by the permittee only when operation is necessary to achieve compliance with the conditions of this permit.

The permittee shall provide an adequate operating staff which is duly qualified to carry out operation, maintenance and testing functions required to ensure compliance with the conditions of this permit.

COMMENT: *The permit specifically requires that the discharge comply with the oil and grease limits all the time. A major reason that a field method is needed is so that the operator can assure himself that he is in compliance all the time without having to report the results on the Discharge Monitoring Reports (DMRs). The person taking the required official samples for compliance testing by EPA 1664 is also required to be trained.*

Section C. Monitoring and Records

1. Representative Sampling

Samples and measurement taken for the purpose of monitoring shall be representative of the monitored activity.

COMMENT: This requirement means that you cannot use the field method to choose when to sample for EPA 1664 analyses. Furthermore you cannot avoid taking the official samples if you know that some field operation may cause them to be high. Using the field method to circumvent the regulatory requirements is illegal and could constitute a criminal violation. Specifically you must believe that your system is operating in a typical manner when you take official samples.

2. Record Contents

Records of monitoring information shall include:

- a. The date, exact place, and time of sampling or measurements;
- b. The individual(s) who performed the sampling or measurements;
- c. The date(s) and time(s) analyses were performed;
- d. The individual(s) who performed the analyses;
- e. The analytical techniques or methods used; and

- f. The results of such analyses.

COMMENT: *When official samples are taken for analysis by EPA 1664, this information is required. Much of this information is also a good idea for field analyses.*

4. Additional Monitoring by the Permittee

If the permittee monitors any pollutant more frequently than required by this permit, using test procedures approved under 40 CFR Part 136 or as specified in this permit, the results of this monitoring shall be included in the calculation and reporting of the data submitted in the Discharge Monitoring Report (DMR). Such increased monitoring frequency shall also be indicated on the DMR.

COMMENT: *One of the reasons for using field methods is that they are **NOT** official methods and do not have to be reported. If a system is malfunctioning and it is being worked on to bring it back into compliance, all the analyses made to check progress do not have to be reported if a field method is used.*

Section E. Penalties for Violations of Permit Conditions

1. Criminal

Negligent Violations. The Act provides that any person who negligently violates permit conditions implementing section 301, 302, 306, 307, 308, 318, or 405 of the Act is subject to a fine of not less than \$2,500 nor more than \$25,000 per day of violation, or by imprisonment for not more than 1 year, or both.

Knowing Violations. The Act provides that any person who knowingly violates permit conditions implementing sections 301, 302, 306, 307, 308, 318, or 405 of the Act is subject to a fine of not less than \$5,000 nor more than \$50,000 per day of violation, or by imprisonment for not more than 3 years, or both.

False Statements. The Act provides that any person who knowingly makes any false material statement, representation, certification in any application, record report, plan, or other document filed or required to be maintained under the Act or who knowingly falsifies, tampers with, or renders inaccurate, any monitoring device or method required to be maintained under the Act, shall upon conviction, be punished by a fine of not more than \$10,000, or by imprisonment for not more than 2 years or by both.

COMMENT: *These show the penalties that an operator may be subject to if they do not follow **ALL** the provisions of the permit. In addition, it should be remembered that the term “knowingly” is also applied when the courts deem that the person or company “should have known” even if there is no actual knowledge. That is, you are responsible for knowing what you are doing!*

June, 1998