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WHITE PAPER

Techniques for Measuring Oil in Water

Background

Oil in water analysis is a global issue that crosses many industries, analytical methods, and regulatory agencies. Due to the negative effects of oil on the environment, there are strict limits on the amounts of oil allowed in water. Failure to meet these limits can lead to heavy fines. While any industry that discharges produced water needs to test for oil in water, their specific needs can differ from industry to industry. The petroleum industry is most concerned with measuring Total Oils and Grease (TOG) in both their upstream and downstream wastewater. For industrial pretreatment of wastewater, public water treatment plants, and most other non-petroleum industries discharging produced water, it is most important to test for Fats, Oils and Grease (FOG) in their effluent. FOG differs from TOG in that it tends to contain large amounts of animal and vegetable components in the oil. FOG can be especially concerning in effluent streams because it can lead to clogged sewer lines which causes Sanitary Sewer Overflows (SSOs).

The people responsible for conducting oil in water measurements understand that the measurement can be quite challenging. Wastewater from different sources can contain many different types of hydrocarbons, each with different chemical make-ups. On top of the lack of chemical uniformity in different oils, there has been a large variety of methods developed to quantify the oil in the wastewater. While none of the following methods is perfect, each will have its own advantages and disadvantages for oil in water analysis.

NON-DISPERSIVE/FIXED FILTER IR ANALYZER

Non-dispersive/fixed filter IR analyzers are the most common method used in the field for analyzing oil in water. The use of a fixed filter enables the instrument to be simple, inexpensive and rugged. The technology requires an extraction of the oil in water sample where the solvent used depends on the type of non-dispersive/fixed filter analyzer. The extract is then dried and measured on the instrument which uses a filter centered in the region between 3.4-3.5 μm (figure 2). Although the filter is centered over the CH2 absorption peak, the bandwidth of the filter will also allow the instrument to detect the CH3 absorption peak and any aliphatic hydrocarbons attached to aromatic compounds. However, this means that high concentrations of aromatics in the sample will lead to inaccurate results. Currently there are two different types of non-dispersive/fixed filter IR analyzers that are used.

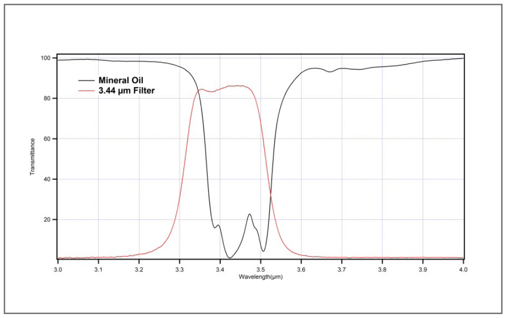


Figure 2: Infrared Spectrum of mineral oil using a 3.44 μm fixed filter

Spectro Scientific InfraCal 2 ATR-SP Analyzer

Horizontal Attenuated Total Reflection (HATR) – While HATR style instruments do not comply with any international standards, they correlate well with both EPA 1664 and ASTM D7066. Since the procedure is very similar to that of EPA 1664, HATR instruments are commonly used to pre-check the compliance of samples before they are submitted to the EPA. These instruments measure samples by evaporating a portion of the extract on the HATR crystal. This is a simple procedure for non-technical users which has the benefit of using volatile hydrocarbons such as hexane or pentane as the solvent. These volatile hydrocarbons tend to be much less expensive than CFC solvents used on transmission instruments. However, since the method requires evaporation, any volatile hydrocarbons in the oil will not be detected.

ADVANTAGES
- Ideal for field use (rugged and simple)
- Inexpensive equipment
- Simple sampling procedure
- Inexpensive solvents
- Correlates to ASTM D7066 and EPA 1664

DISADVANTAGES
- Does not detect volatile hydrocarbons
- Does not comply with any international standards

Spectro Scientific InfraCal 2 TRANS-SP Analyzer

Transmission – Transmission style instruments follow an ASTM accepted method (ASTM D7066) which requires the use of a CFC solvent for extraction. While many CFC solvents have been banned, tetrachloroethylene and S-316 are still allowed for use in oil in water analysis. While these solvents are expensive and not the most environmentally friendly option, they do provide the ability to measure volatile hydrocarbons since the extract is measured directly, as opposed to measuring the residue after the solvent (and any volatile components in the sample) has evaporated. Also, the use of a transmission cell extends the level of detection of the instrument to lower levels of oil in water compared to the HATR instruments.

ADVANTAGES
- Ideal for field use (rugged and simple)
- Inexpensive equipment
- Can measure volatile hydrocarbons
- Complies to ASTM D7066

DISADVANTAGES
- Solvents are expensive
- Solvents are not environmentally friendly
- Sampling procedure is more cumbersome

Methods for Measuring Oil in Water

GRAVIMETRIC ANALYSIS (EPA 1664)

Typical setup for EPA 1664

Gravimetric analysis measures any material extracted from an oil in water sample by a solvent and is the EPA accepted method (EPA 1664) for oil in water analysis. This means that any industry producing oil in water is required to submit samples for testing by EPA 1664 in order to avoid fines. EPA 1664 requires 1 liter of sample that is acidified to a pH of 2. The sample is then extracted 3 times with hexane and those extracts are combined and dried. The method may also use a solid phase extraction (SPE) where the sample is passed through a specific filter and then the trapped oil is dissolved into hexane. The collected extracts are distilled at 85 °C and weighed in order to determine the value. The extracts may also be filtered through silica gel in order to provide a total petroleum hydrocarbon (TPH) value as well. The sample preparation required for gravimetric analysis precludes the use of this technique in the field. This means companies are required to send in samples to a lab which is both time consuming and expensive. While this is acceptable for regulatory agencies, the companies producing oil in water need field methods to keep up operations without delay.

ADVANTAGES

- EPA accepted method (EPA 1664)
- Can use SPE in order to use less solvent
- Can determine TPH value separately

DISADVANTAGES

- Analysis can only be done in a lab
- Procedure is long and cumbersome
- Requires large amount of solvent
- Expensive and time consuming for companies to send in samples

GAS CHROMATOGRAPHY – FLAME IONIZATION DETECTION (GC-FID)

www.brown.edu/Research/Evchem/facilities/shared

Agilent GC-FID

GC-FID is an ISO (ISO 9377-2) approved method for the determination of oil in water. Unlike other methods, GC-FID analysis can provide details on different types of hydrocarbons in a sample as well as the total amount of oil in water. The GC-FID method first requires the sample to be acidified and extracted by a solvent (hexane or pentane). The extract is then dried/purified and injected into the GC instrument where a carrier gas moves the extract through the column. Once the GC column separates the different types of hydrocarbons, each type is burned and detected by the Flame Ionization Detector (FID). The sum of all the responses from each of the hydrocarbon types is calculated in order to determine the total oil in water. While GC-FID is a precise method for oil in water analysis, it is mainly suitable for lab use due to the expense of the equipment and the need for technical users.

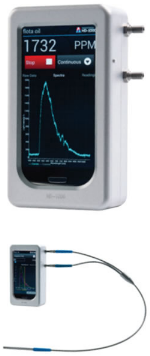
ADVANTAGES

- Provides details on different hydrocarbons present
- Follows ISO 9377-2
- Precise

DISADVANTAGES

- Mainly suitable for lab use
- Equipment is expensive
- Equipment requires trained personnel

UV FLUORESCENCE



Advanced Sensors UV Fluorescence Analyzer

UV Fluorescence is a common field technique for oil in water analysis which typically uses either a UV lamp or a Laser Induced Fluorescence (LIF) as a light source. Because it does not require a solvent extraction, the technology is ideal for online analysis of a wastewater stream. UV fluorescence works by illuminating an oil in water sample with UV light. The aromatic hydrocarbons in the sample emit fluorescent light that the instrument can detect. The amount of oil in water in the sample is based on the intensity of the light emitted. Instruments that contain a UV lamp typically use a by-pass stream for analysis, however LIF instruments can use probes that are fitted in-line with the produced water stream so that a by-pass stream is not required. While UV fluorescence is a great technology for detecting aromatic hydrocarbons, it will not detect any aliphatic compounds. Since typical oil in water samples are mainly aliphatic, any change in the ratio of aliphatic to aromatic hydrocarbons can drastically affect the results.

ADVANTAGES

- Requires no solvent
- Can be setup as an online system
- Inexpensive
- Ideal for field use

DISADVANTAGES

- Only detects aromatic hydrocarbons
- Does not follow any international method

QUANTUM CASCADE LASER INFRARED (QCL-IR)

Eralytics QCL-IR Analyzer

QCL-IR is a new infrared method being used to measure the content of oil in water. This method differs from other technologies in that it is measuring the CH3 absorption peak located in the region 1350-1400 cm^{-1} (Figure 1). This means that a cyclic hydrocarbon such as cyclohexane can be used as an extraction solvent. The advantage of a cyclic hydrocarbon as a solvent is that it is more environmentally friendly and much cheaper than chlorofluorocarbon (CFC) solvents. The method works by first extracting and drying the oil in water sample with cyclohexane or cyclopentane. The extract is then measured on the instrument and the intensity of the absorbance in the region of 1350-1400 cm-1 is correlated to a concentration value. The extract may also be filtered in order to measure TPH separately. While the measurement in this region of the spectrum allows for more ideal solvents, it limits the instrument to detecting only CH3 compounds. This means that any aromatic or cyclic hydrocarbons in the oil will not be detected. However, most oil hydrocarbons contain CH3 and this method has shown to correlate very well with other international standards such as EPA 1664, ASTM D7678 and ISO 9377-2.

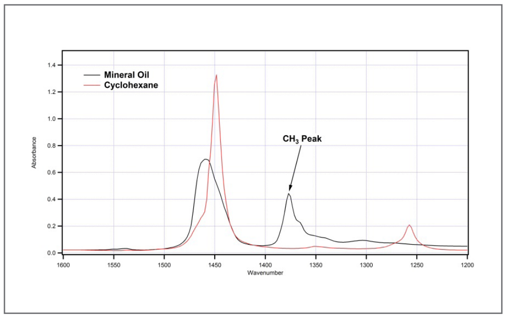


Figure 1: Measurement of oil in water by QCL-IR

ADVANTAGES

- Does not require CFC solvent
- Can be used in the lab or field
- Correlates to internationally approved methods
- Can measure TPH separately

DISADVANTAGES

- Only detects CH3 compounds
- Does not follow any international standards
- More expensive than other types of IR equipment

Summary

There are several methods available for both laboratory and field analysis of oil in water. The choice of methods depends on budget, location of testing, time, and other factors. The most important thing is to consistently test for the amount of oil in water in your wastewater stream in order to avoid any regulatory fines and prevent potential damage to environment.

Resources

- ASTM International D7066-07: Standard Test Method for dimer/trimer of chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination
- EPA Method 1664, revision A (1999): N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar material) by Extraction and Gravimetry
- ISO – ISO 9377-2:2000 (2000) Water quality – determination of hydrocarbon oil index – Part 2: Method using solvent extraction and gas chromatography

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