

New ASTM Test Method Offers Quick and Easy Oil and Grease Measurement for Water and Soil Samples

Sandra Rintoul

140 Water Street
South Norwalk, CT 06854
Tel: 203-855-9136
Direct Tel: 831-338-7459
Fax: 203-838-9868
Email: srintoul@wilkir.com

author

Onsite Field Measurement of Oil and Grease

A quick and easy field analysis method for determining oil and grease concentration levels is important for both offshore oil platforms and soil remediation sites. Prior to the Montreal Protocol, infrared (IR) analysis using Freon as an extraction solvent was a widely used field and laboratory method. In 1999, the U.S. EPA promulgated Method 1664A to replace existing Freon methods. Method 1664A uses gravimetric analysis and hexane for the extraction process rather than Freon. Gravimetric analysis is a laboratory method and cannot be transported to the field for onsite measurements. In addition, hexane is not a suitable solvent for infrared analysis using transmission sampling techniques as it contains hydrocarbons. Therefore, the hexane must be removed through evaporation. If not, the hydrocarbons in the hexane will contribute to the oil and grease concentration measurement. Because of the measurement capabilities, simplicity and portability of infrared analysis, the ASTM felt it was important to find an alternate solvent to Freon and develop a suitable infrared oil and grease method.

New ASTM Method D7066-04

With the manufacture of Freon 113 banned by the Montreal Protocol in 1995, the old ASTM method (D 3921) that used infrared analysis and Freon 113 had to be replaced. Numerous oil and grease applications including U.S. EPA Methods 413.2 and 418.1 and ASTM Method D 3921 used Freon as the extraction solvent. The new ASTM Method D 7066 - 04, **Standard Test Method for dimer/trimer of chlorotrifluoroethylene (S-316) Recoverable Oil and Grease and Nonpolar Material by Infrared Determination**, uses a similar extraction procedure with a more ozone friendly solvent called S-316.

A variety of infrared instruments can be used with ASTM Method D 7066-04, from full spectrum Fourier Transform Infrared (FTIR) spectrometers to portable, relatively inexpensive fixed filter infrared analyzers such as the Wilks InfraCal TOG/TPH Analyzer in Figure 1. FTIR spectrometers can be found in most testing laboratories and are used for many applications in addition to oil and grease analysis. Portable, fixed filter infrared analyzers are application specific which makes them easier to use in the field or in-plant by personnel with relatively little training.



Figure 1

ASTM Infrared Test

Method Ideal for On-Site Use

For screening or pretest applications, a government approved method is not always necessary. What is more important is get-



Figure 2

ting an accurate result in a short amount of time. The U.S. EPA Method 1664A cannot be performed on offshore oil rigs, yet the produced water must be constantly monitored to ensure the waste stream is in compliance with discharge regulations. Sending a sample to an onshore laboratory is expensive and can take several days to several weeks. With the composition of the waste stream constantly changing, oil and grease results need to be known as soon as possible. For remote soil remediation sites, expensive excavating equipment can be put on hold while waiting for a laboratory result. Having a result within 15 minutes keeps the operation moving. Infrared determination of oil and grease concentration levels is quick and accurate and the ability to do the analysis onsite greatly expands its usefulness. With simple fixed filter infrared analyzers, non-laboratory personnel can easily perform the analysis. Figure 2 (photo of onsite analysis)

Extraction Procedure

Similar to Current Methods

The ASTM Method D 7066-04 has a similar extraction procedure as D 3921 and U.S. EPA Methods 413.2 and 418.1. Greatly simplified, the sample is acidified, solvent (S 316) is added and after two minutes of shaking, a separatory funnel is

used to remove the solvent from the bottom of the sample. For TOG (Total Oil and Grease) the extract is then placed in a quartz cuvette to be measured by the infrared spectrometer or analyzer. For TPH (Total Petroleum Hydrocarbons) the extract is passed through silica gel to remove the polar organics and then placed in the quartz cuvette. A beam of infrared light goes through the cuvette filled with extract and with either a filter set for C-H absorbance in a fixed filter infrared analyzer (Figure 3) or the FTIR spectrometer set to scan 2930 cm⁻¹, and the hydrocarbon content is measured.

The extracted hydrocarbons absorb infrared energy at a common IR wavelength and the amount of energy absorbed is proportional to the concentration of the oil and grease in the solvent. The infrared absorbance value can be correlated directly to ppm, mg/liter or mg/kg. Like Freon, S-316 can be reclaimed.

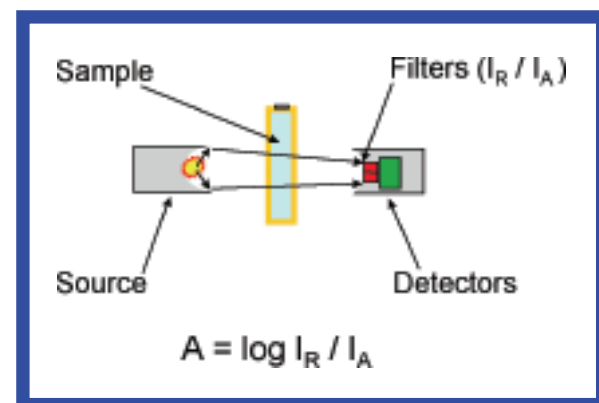


Figure 3: The Measurement of IR Absorption of an Oil Sample with Fixed Filter Analyzer and a Cuvette

Comparing Different Oil and Grease Methods

The first question that comes up whenever a different oil and grease measurement is mentioned is: "Does it correlate to the existing method?" Oil and grease is a difficult analysis because it is not a unique chemical entity. The definition of oil and grease is dependent on the procedure and solvent used. Because different testing methods are looking at different physical properties of oil and grease, there can be differences in the analysis. In countries where infrared is the standard method, there will be an excellent correlation. For those in the

US still using EPA Methods 413.2 and 418.1 which use infrared analysis, again the correlation will be excellent.

The gravimetric method as used in EPA Method 1664A measures the weight of the oil that is removed from the sample with hexane after the hexane is evaporated off. Infrared looks at the infrared absorbance due to the hydrocarbons present in the extracted oil. At 3.4 μ m infrared is primarily counting CH₂ groups so the infrared absorbance goes up with the length of the hydrocarbon chain which correlates with the weight of the hydrocarbon. Whether the infrared intensity correlates well with the total weight of the material depends on what else is present in the molecule. Petroleum hydrocarbons are various CH groups and the infrared absorbance will correlate well with weight. With fatty acids there is also the carboxyl group that contributes to the weight but is not detected at 3.4 μ m. For example, octane (C₈H₁₈) has a different number of C-H bonds for unit weight than octanoic acid (C₇H₁₅COOH).

Another factor in comparing methods is the solvent used for extraction. Each solvent has a different extraction efficiency meaning some are better at removing the oil from the sample than others. S-316 called for in the new ASTM Method D 7066-04 is comparable to the earlier Freon/infrared methods in extraction efficiency and what is extracted. There is also no evaporation stage in the analysis so extracted light oil and other volatile fractions will remain in the solvent and be measured by infrared analysis. This can be a benefit if on gas condensate platforms or when petroleum fuels such as gasoline or #2 fuel oils are present in a sample and the analyst would like to determine their presence.

As in the days when Freon/infrared and Freon/gravimetric were constantly compared, the discrepancies between the methods were small enough that it did not outweigh the usefulness or cost effectiveness of the infrared method. The EPA 1664A Method and hexane/infrared analysis also typically correlate well with each other.

Conclusion

With the price of oil and gas reaching record high levels, the activity in the oil industry is also nearing historic levels. The produced water section of the industry is testing new technologies for the removal of oil from water. The soil remediation sector also has new innovative technologies available and many refineries are facing stricter limits. All of this activity requires more oil and grease testing. Onsite testing can lower laboratory costs, avoid out-of-compliance fees, and improve remediation efficiency. With the new ASTM method, onsite oil and grease analysis options are increased. While FTIR spectrometers can be used for oil and grease testing in the laboratory, only fixed filter portable IR analyzers provide the onsite quick and accurate measurements necessary to help ensure TOG and TPH concentration levels comply with various regulations -- without having to wait hours or days for results.