When the Oil and Grease test just isn't enough.
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Brett Ward, UT-MTAS
Joe Brock, Clinton Utility Board

Testing for oil and grease is common in municipal and industrial wastewater systems but often the results are surprising and frequently they only add confusion to a challenging situation. Oil and grease and petroleum testing are all "method defined" results. The results you get depend on the test method used. Adding to the confusion there are many names and abbreviations that are used interchangeably and sometimes incorrectly.

This paper will discuss the basic Oil & Grease test, petroleum hydrocarbon tests and variations of each of these and how they relate to each other. Additionally, there is a section on synthetic products.

Regulatory Testing

Any testing for Clean Water Act requirements must follow methods approved in 40 CFR 136. There is only one method approved for testing fat-oil-grease, called Total Recoverable Oil and Grease. It is found in two reference documents. EPA Method 1664 A&B and Standard Method 5520 B&F. Method 1664 A and 5520 B use n-Hexane as a solvent so the methods are also called hexane extracted material or HEM. The numbers in the results represent only those materials extracted by and then separated from the hexane including non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soap, some dyes and sulfur. Very light and volatile materials like gasoline will evaporate with the hexane and will not be reported. On the other end some very heavy high boiling point petroleum materials will not be extracted by the hexane and will not be reported.

Method 1664 B and 5520 F are hexane extractions with silica-gel treatments to remove the "polar" materials, which are generally the animal and vegetable oil and grease. These results are often called silica-gel treatment hexane extracted materials or SGT-HEM or SGT-HEM-NPM meaning the results represent non-polar materials, which are the petroleum oil and grease materials. To quantify the "polar" animal and vegetable oil and grease simply subtract the SGT-HEM from the total HEM. These tests are generally quite accurate in quantifying the animal and vegetable oil and grease.

Total Recoverable Oil & Grease, HEM mg/L
(Subtract) Petroleum SGT-HEM-NPM mg/L (hydrocarbons)
(Equals) Animal & Vegetable Oil & Grease mg/L (triglycerides)

These basic tests have numerous interferences such as: elemental sulfur, complex aromatic compounds, hydrocarbon derivatives with chlorine, sulfur and nitrogen, certain organic dyes and some surfactants. Check the methods for pretreatment steps to reduce interferences and discuss these with knowledgeable laboratory personnel. Some pretreatment steps may not be approved for regulatory reporting, but they can be used in trouble shooting or prescreening situations. Keep all sampling and testing supplies and equipment free from interferences and use blanks to document that these items do not contribute to interference.

Each of these "approved" methods uses n-hexane as a solvent. Hexane has a carbon chain length of six which is commonly abbreviated as C_6. Petroleum based materials with molecular length less than and close to this C_6 cannot be quantified with the test because they evaporate along with the hexane during the test procedure. Anything that volatilizes at ≤85°C such as gasoline, kerosene, or jet fuel will be lost with the hexane. Standard Methods reports, "Significant portions of petroleum distillates from gasoline through #2 fuel oil are lost in the process." Also, some petroleum materials will not dissolve in the hexane and are not quantified. These would be long chain materials, C_{50} and longer in molecular length. So generally, hydrocarbons in the C_7-C_{50} range are captured and quantified by these tests.

The silica gel modification, 1664 B and 5520 F add an extraction step to remove polar animal and vegetable oil and grease. Theoretically what are left are the non-polar materials or mineral oils such as petroleum products. These results sometimes are called Total Petroleum Hydrocarbons or TPH. This name is not accurate and should not be used; it should be SGT-HEM-NPM (Silica Gel Treated-Hexane Extractable Materials-Non Polar Materials. There can be significant error in the test, so the lab's quality control tests should be checked so the reliability of test results can be known. Steric acid is used as a spike or standard for animal or vegetable material and n-hexadecane for petroleum materials.

The Science & Technology section of the EPA web site states: "One should test for this removal [of polar materials] by demonstrating removal of the Steric Acid component of the Precision and Recovery standard in initial precision and recovery tests and the matrix and duplicate test. If this removal is demonstrated, use of repetitive treatments of extracts of environmental samples with Silica Gel for determination of non-polar materials should be allowed…." Basically, before you trust the SGT-HEM-NPM test results, check the labs quality assurance. If there is poor removal of the steric acid spike, the reliability for those non-polar materials is not high.

<u>EPA Method 8015, Nonhalogenated Organics using GC/FID</u>

So, there is a name only an organic chemist can understand. The test will quantify many materials such as acetone, alcohols, ethers and petroleum products. There are a variety of names and abbreviations associated with the test. Total Petroleum Hydrocarbons (TPH) is often used though somewhat in error. Volatile Petroleum Hydrocarbons (VPH), Purgable Hydrocarbons (PHC), Extractable Petroleum Hydrocarbons (EPH), Gasoline Range Organics (GRO) and Diesel Range Organics (DRO) are also used when the test results are reported. Some states will actually define these names in their test regulations (often associated with underground storage tanks), but these names may not fit well in a troubleshooting situation when the goal is to determine what is in the sample. Discuss with your lab the test to be performed and what will be quantified in the results. The results may be quite vague.

The test is performed in two parts. One quantifies the short chain (C_6-C_{10}) volatile materials and is often called VPH (Volatile Petroleum Hydrocarbons), GRO (Gasoline Range Organics) or PHC (Purgable Hydrocarbons) because the test process uses a purge and trap or vacuum distillation step prior to the Gas Chromatograph. The second step quantifies the long chain (C_{10}-C_{40}) of semi volatile materials and is often called EPH (Extractable Petroleum Hydrocarbons) or DRO (Diesel Range Organics) because there is an extraction step prior to the Gas Chromatograph.

There will be some overlap of the materials in the C_{10} range. Each will capture some of the same material so the addition of GRO and DRO results to get a Total Petroleum Hydrocarbon value does not truly represent what is actually in the sample.

Viewing the chromatograph will give general indication of what type of products are in the sample. Petroleum materials are all volatile to some degree. Fresh products will have a slightly different chromatograph than the same product that has aged or has been open to the environment because of the evaporation of the volatile components and possibly because of biological breakdown in the environment. Gasoline for example, is a mixture of C_4-C_{12} length hydrocarbon materials and generally contains over 150 separate hydrocarbons. The common alkenes are benzene, tolulene, ethylbenzene, and xylene (BTEX). There are also alkanes like isopentane, butane, pentane, and n-hexane. Kerosene is in the C_6-C_{16} range; Jet fuel C_4-C_{16}; dry cleaning fluid, paint thinner, and naptha C_6-C_{12}; diesel #1C_8-C_{17} & Diesel #2 C_8-C_{26}; motor oil C_{18}-C_{34}. Fuel Oils C_{20}-C_{40}, lubricating oils C_{20}-C_{45}, mineral oils C_{15}-C_{50}, crude oils can go as high as C_{100}. For these heavy materials there are specialized gas chromatographs so a discussion with your testing lab is recommended.

Testing Wastewater Samples for Unknown Materials

If you are testing a wastewater sample for unknown materials, a combination of several tests can add insight. Hexane Extractable Materials (HEM), or Silica Gel Treated Hexane Extractable Materials (SGT-HEM) are always a good starting point. The basic Volatile Organic Compounds (EPA 624) and Semi Volatile Organic Compounds (EPA 625) can be initial screening tests. If petroleum products are indicated such as benzene, toluene and ethylbenzene, progress to more complete tests such as Purgeable Hydrocarbons (PHC), or Extractable Petroleum Hydrocarbons (EPH). If the lab has demonstrated good quality assurance with the silica gel treatment associated with the HEM test, the Silica Gel Treatment could be performed prior to the PHC and the EPH in order to remove animal and vegetable product interference. When collecting these samples in a troubleshooting situation, collect samples for all of the possible tests in the appropriate containers even if the tests are not performed. If the HEM and SGT-HEM test are unhelpful, you will have a sample from the exact day and waste stream to later perform the PHC and EHC tests. Discuss your needs and objectives with your lab before sampling. They can often make recommendation that can be helpful.

Additional samples could also be collected so that different pretreatment steps can be performed on the sample to remove interferences. For example, the silica gel treatment can be done with the PHC and EHC test to remove the effects of animal and vegetable oils.

Synthetic Oils and Lubricants

There are two major types of synthetic oils and lubricants. Polyalphaolefins (PAO's) are highly refined mineral oil based or alkanes. They have a very narrow molecular length and have had common contaminants like sulfur removed. The second type of synthetic lubricant is called a synthetic ester or vegetable ester and are a non-mineral oil base. These are made from other organic materials than petroleum oil. Synthetic oils are becoming more popular in industrial lubrication for several reasons. They biodegrade more quickly than mineral oils and have good machining properties. They can be manufactured for specific purposes with specific characteristics. Another lubricant that is gaining popularity is the group known as polyalkylene glycols. These materials are water soluble polymers and are being called "environmental acceptable lubricants" as are the ester-based oils.

The PAO oils and lubricants should be quantified by the various test methods as well as any petroleum product. Ester based oils and lubricants appear to be *inaccurately* quantified by the HEM or SGT-HEM test method but should be quantified by the 8015 method. Phthalate esters will be quantified by the Semi Volatile Organic Compound (EPA-625) method.

Fat, Oil, and Grease testing are method determined results. The result you get depends on the test method used. No test will quantify the full spectrum of all fats, oils and greases and there is always overlap with the various methods. To determine the "best" method, utility personnel must use their knowledge, senses, and observations to pre-screen the sample to determine the appropriate test. The initial test may not be the correct method. It is a process of observing, testing, evaluating the test, and then possibly retesting. Regulatory tests must use 40 CFR 136 approved methods but troubleshooting or testing to build knowledge or insight may use non-approved methods. Always discuss your testing strategy with your testing lab.

References

David Smith, Chemist, Environmental Express Inc.
EPA-Total Petroleum Hydrocarbon Working Group
Microbac Laboratory
Standard Methods for the Examination of Water and Wastewater

Animal fats and Vegetable oils are triglycerides. The molecule contains glycerin with three fatty acids attached. The different fatty acids and structure changes the properties of the oil or fat.

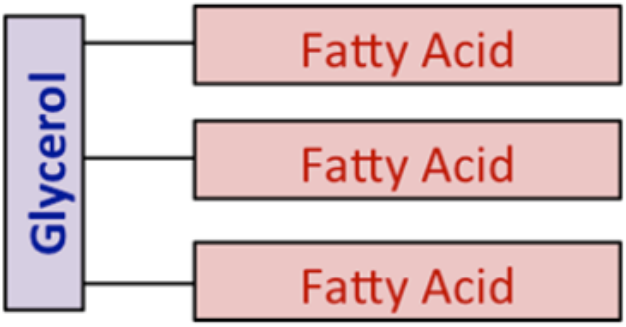
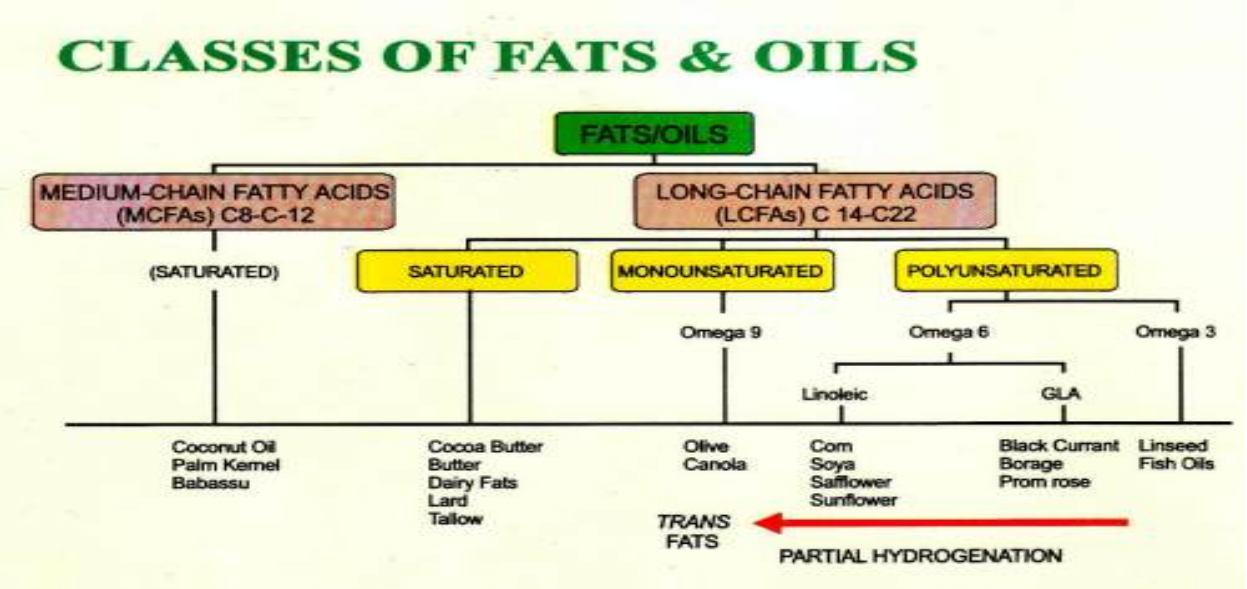


Figure 9.1: A generic diagram of oils and fats; a free fatty acid is when the fatty acid separates from the glycerol.

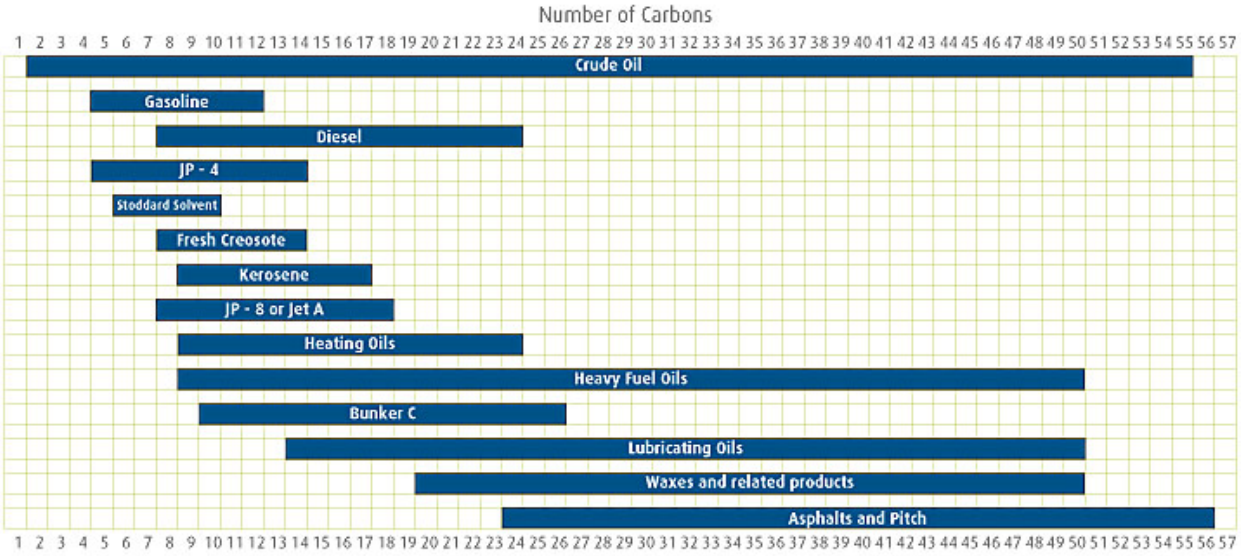
Credit: BEEMS Module B4

e-education.psu.edu, Penn State College of Earth and Mineral Sciences, John A. Dutton

The length of the fatty acid portion of the fat or oil changes the properties as does the amount of saturation.



Petroleum products are mixtures of various hydrocarbon of similar molecule lengths. The following table, which does not exactly match the text, shows common carbon chain lengths.


Number of Carbons
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57
Crude Oil
Gasoline
Diesel
JP - 4
Stoddard Solvent
Fresh Creosote
Kerosene
JP - 8 or Jet A
Heating Oils
Heavy Fuel Oils
Bunker C
Lubricating Oils
Waxes and related products
Asphalts and Pitch
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57