

What Oil Analysis Tests Tell Us

This article reviews tests specific to various sample test classes, as well as additional tests that are triggered in extraordinary circumstances. The first part of this two-part series appeared in the March-April 2006 issue of *Practicing Oil Analysis*.

Debris Analysis

To confirm the results of the ferrous density discussed in the previous article, two other tests are commonly performed to analyze wear debris. These include particle counting and patch microscopy.

Particle Counting

Particle counting is actually a test for particle contaminant levels and not specifically wear debris. It does not distinguish between wear and dirt particles, but if it can be determined that nonferrous contamination has remained stable, then an increase in the particle count must be attributable to wear.

A magnet can be used to modify the particle count to count ferrous debris only. There are various ways of doing this, but essentially a magnet holds back the ferrous debris while the nonferrous debris is flushed from the sample, after which a ferrous debris particle count is performed.

Particle counts are invariably reported according to ISO 4406:99. Other standards do exist, but they are not as commonly used. ISO 4406:99 returns a three-digit solid contamination code.

The method of particle counting is not as important as performing the

test properly. It is important to note that only results from the same method should be compared.

The particle count is an easy test to interpret, assuming the test has been correctly performed. (This point is made because there are many factors which can negatively affect a particle count.) An increasing count is an indication of an increased number of particles in the oil. Exception tests such as analytical ferrography or patch microscopy would then be used to qualify the type and source of the particle contamination.

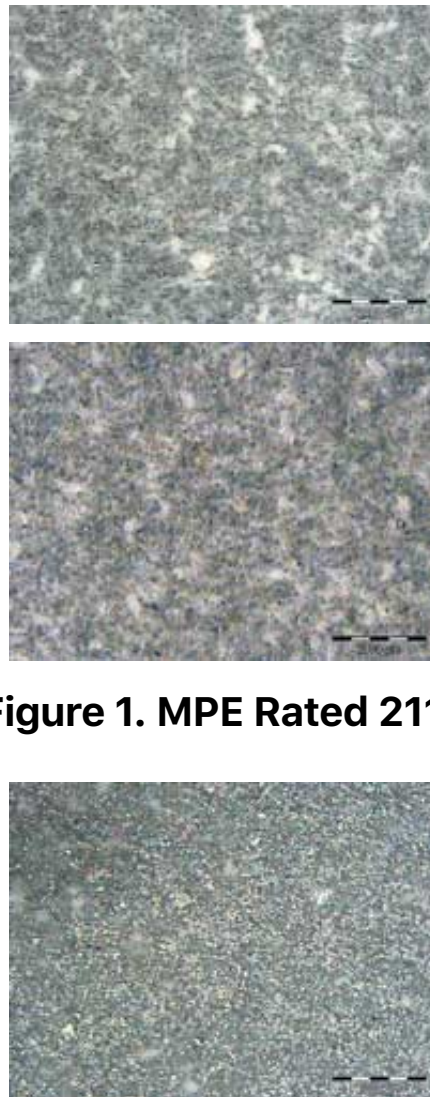


Figure 1. MPE Rated 2111

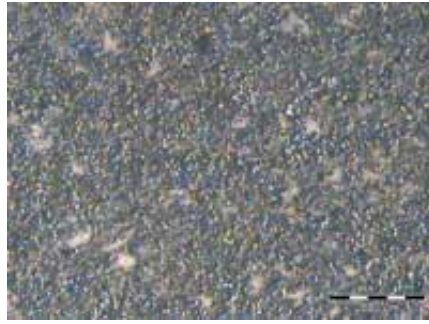


Figure 2. MPE Rated 4111

Analytical Microscopy

Analytical microscopy is a technique used to qualify contaminants, including wear debris, in an oil sample. There are two commonly performed variations of this technique: analytical ferrography and patch microscopy.

Analytical ferrography uses magnetic fields to separate ferrous debris according to particle size. As the name suggests, this technique is biased to ferrous particles, but some nonferrous particles are typically deposited on the substrate either via entrapment or by magnetic effects imparted to them by impaction of ferrous particles.

Patch microscopy, on the other hand, does not demonstrate a bias to ferrous particles. All particles above the membrane pore size are presented on a piece of filter paper, the filtergram, for examination. However, patch microscopy does not have the size-separation attributes of the ferrography, so particle deposition is random.

A modification of the patch test can be performed to analyze both ferrous and nonferrous debris separately. A magnet is used to hold back magnetic particles while a filtergram of nonferrous debris is prepared. Then a filtergram of the remaining magnetic debris is made.

Sample	Mg	Ca	Zn	P	B	S	Vis@40	Ox
1	549	3,627	1,136	967	5	10,838	94.7	15
2	524	3,295	1,086	934	4	10,708	92.5	13
3	667	4,516	1,431	1,222	7	11,112	129.7	17

Table 1. Overheating with Regular Oil Top-up

In deciding on the correct microscopy test to perform, one must make some judgment on the machine metallurgy and the nature of the contaminant being sought. It is not a good idea to perform ferrography on a worm-and-wheel gearbox where the majority of wear particles are likely to be cupric (thus nonmagnetic) in origin. Similarly, if a wear situation is suspected on a reducer with helical gear sets, then analytical ferrography will probably provide far better resolution than the patch.

It is worth mentioning that for filtered oil systems, a ferrogram or patch which does not show abnormalities should be treated with suspicion. Assuming that there was a reason to proceed with the analytical microscopy in the first place, one would then expect to see problems. A good approach to filtered systems is to remove a section of the filter medium, wash it out in solvent and perform the microscopy on the extract.

Each laboratory will have its own system for quantifying and reporting wear and contaminants in each of these tests. Interpretation is subjective and can be expensive to perform because it is labor-intensive.

Analytical microscopy is a powerful technique which should be used to confirm and qualify contamination and wear situations identified by the routine tests.

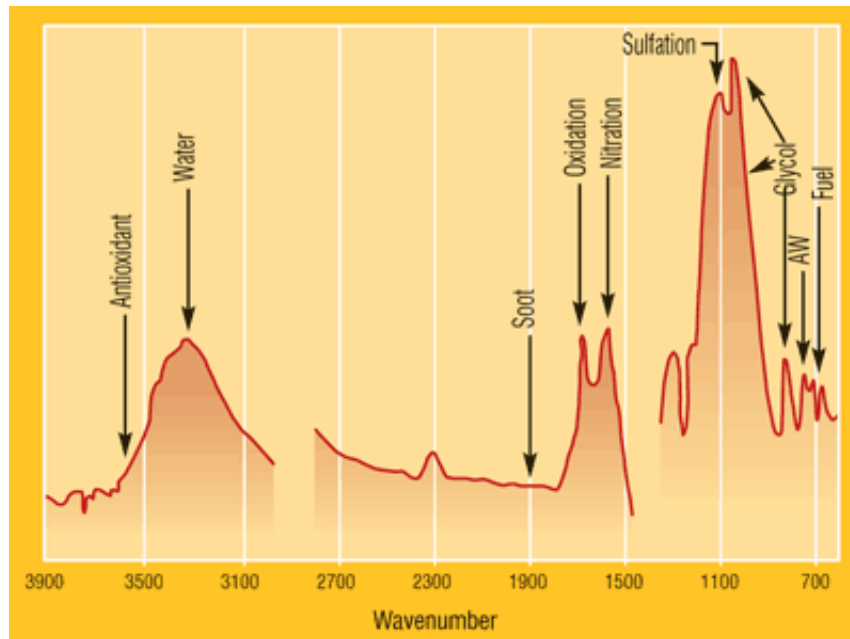


Figure 3. Example of an FTIR Spectrum

Fourier Transform Infrared (FTIR) Spectroscopy

Infrared analysis is the second type of spectroscopy commonly found in a laboratory. Unlike elemental analysis, FTIR provides information on compounds, rather than elements, found in an oil. FTIR measures several useful degradation parameters, so is particularly useful in engine oil samples. Infrared analysis detects the presence of water and can also be used to identify oil base stocks.

While the ICP spectroscopy measures emissions of radiation of specific wavelength in the visible and ultraviolet regions of the electromagnetic spectrum, infrared analysis measures the specific wavelengths of radiation in the infrared region. The various degradation by-products and contaminants found in the oil cause characteristic absorptions in specific regions of the infrared spectrum. The higher the level of contamination in the sample, the higher the degree of absorption in the characteristic region.

A plot of absorbance, transmittance, or concentration versus wave-number is generated during the analysis of an oil sample, called the infrared spectrum. This spectrum is subsequently analyzed by specialized oil analysis software that yields measurements most commonly for soot, oxidation, sulfates, nitrates and water. Other compounds, such as additives, fuel and glycol can also be measured, but for these an accurate sample of the new oil is needed as a reference. If no such reference sample has been supplied then readings of the latter parameters should be regarded with suspicion. The most commonly measured parameters are examined below.

Soot

The soot index is a linear measurement that measures the extent to which the oil has become contaminated by fuel soot, an unwanted by-product of combustion. The units reported depend on the spectrometer manufacturer. The measurement really applies only to diesel engines because the soot measurement on gasoline engines is expected to be very low. In diesel engines, excessive amounts of soot can be generated by overfueling (air to fuel ratios), incorrect combustion temperatures, low operating revolutions, restricted intake and exhaust systems, and faulty turbochargers.

Dispersant additives are formulated in engine oils to hold soot in suspension. Unfortunately, there is a limit to how much soot a lubricant can carry. When the maximum amount is exceeded, sludge deposits start to form, which can harm the engine. The effects of severe sludging manifest themselves as increasing oil viscosity. These usually occur rapidly to the point where the oil can no longer be pumped and engine failure ensues.

When interpreting the severity of the soot index measurement, one should take into account the soot readings on previous samples from the engine as well as the magnitude of the change in the oil's viscosity. It should also be noted that high soot loading can negatively affect the accuracy of other infrared measurements.

Oxidation

As oil oxidizes, its ability to lubricate diminishes and, in cases of severe oxidation, noticeable changes occur: it becomes darker and emits odor; varnishes, lacquers and resins are formed; and in the advanced stages viscosity increases, often rapidly. Fortunately, the chemical reaction between oxygen and lubricant molecules at room temperature is slow and oxidative degradation is not an issue under these conditions. The situation changes when reaction conditions are altered to favor a more rapid reaction rate.

Engine lubricants are formulated with a hostile environment in mind. Many conditions promoting accelerated oxidation co-exist in an engine, such as high temperatures, high pressures, a good air supply, agitation, the presence of metal catalysts and thin film exposure.

The most significant of these conditions is the operating temperature, because rate of oxidation doubles for every 10°C increase in temperature. Excessively high operating temperature (overheating) is generally accompanied by increased wear (lead, copper, tin and iron) and increased baseline viscosity.

Sometimes overheating leads to the evaporation of volatile fractions in the oil, making regular top-ups necessary. In this case, the sump oil will exhibit increased additive levels (concentration of nonvolatile

components) and an increased viscosity as a direct result of light end loss. As this lost oil is replaced with fresh oil, the antioxidants are replaced and oxidation is often not immediately evident. This is shown in Table 1, with sample No. 3 being the most recent.

Oxidation is also of use with industrial oil samples. Results should be compared with acid number and possibly viscosity for confirmation.

Sulfation

The combustion by-products formed by burning diesel fuel, sulfur oxides and water, readily combine to form sulfur-based acids. The bulk of these corrosive acids is removed as part of the engine's exhaust, but some remain and escape into the engine cavity in blow-by gas where they are neutralized by additives in the oil, or proceed to attack the thin oil films providing lubrication for piston rings and cylinder liners.

The sulfate index from infrared analysis is a measurement of the amount of sulfur-based acids that have reacted with the oil and reflect the amount of sulfation that has occurred. If fuel sulfur levels remain constant, the sulfate index would be expected to increase continuously with use until the oil reaches the end of its useful service life, for which the sulfation level or sulfate index can be an important determinant.

At normal operating temperatures, acids remain in a gaseous state in the blow-by gas with minimal contact with reactive surfaces. However, when an engine experiences lower-than-normal operating temperatures (such as just after start-up, at shutdown, or when a faulty cooling system results in continuous overcooling) the acids

condense and come in contact with the oil in the sump, causing the oil to film on exposed metal surfaces. This places an extra burden on the lubricant because it must neutralize more acid than would be expected during normal operation. Thus, high sulfation early in the oil's life often indicates abnormally low operating temperatures.

Nitration

As with sulfation, nitration is the reaction of the oil with combustion by-products of nitrogen. These reactions tend to become more pronounced at higher temperatures. Therefore, increased nitration is often an indication of increased blow-by, as the hot combustion gases react with the oil. Nitration is rarely mentioned because other problems, such as high top-end wear associated with blow-by, will manifest themselves first.

Nitration in industrial oil samples is an indication of a thermal breakdown of the oil. This can occur when the oil comes into contact with extremely hot surfaces, or where excessive aeration, particularly in hydraulic systems, leads to microdieselling. Though not often seen, an increase in nitration should be taken seriously.

Acid Number (AN)

The measurement of AN involves a titration where the total acid content of the oil dissolved in a mixed solvent is completely neutralized by the gradual addition of an alcoholic solution of potassium hydroxide (KOH). A colorimetric method of determining the end point is effected by the use of a chemical indicator that changes color as soon as the acid is completely neutralized. Alternatively, a potentiometric method may also be used.

The AN test is performed on nonengine oil samples and is used to quantify the acid buildup in these oils. An increased AN is a result of oxidation of the oil, perhaps caused by overheating, overextended oil service, or water or air contamination.

Components within refrigeration systems are particularly susceptible to acid attack. This can occur when air containing water vapor enters the system, or alternatively when the system is subjected to excessive heat and the refrigerant drier releases retained water. When this happens, acids created by the reaction of the air, water, refrigerant and oil cause iron components in the system to become plated with copper, which can cause bearing failure due to copper plating. In refrigerant systems, the acid content of the oil, moisture content and copper level need to be regularly monitored to indicate incipient problems.

AN limits vary enormously and depend both on OEM specifications and on the oil itself. In some cases, an AN exceeding 0.05 is unacceptable; in others ANs of 4.00 and higher remain acceptable. As with all other readings, trend analysis is the best indication of the health of both the oil and the machine.

Base Number (BN)

The measurement of BN involves a complex potentiometric titration where the total alkaline reserve of one gram of oil dissolved in a mixed solvent is reacted with the gradual addition of a known excess of an acid solution. The reaction is monitored using a reference and a measuring electrode, where a graph of voltage (mV) vs. acid added (ml) is then plotted. The end point is detected from a point of inflection on the graph or, in the case of badly degraded oils, from a

predetermined millivolt reading.

This test applies only to engine oil samples because these lubricants are deliberately formulated to contain a reserve alkalinity that enables them to neutralize the corrosive acidic by-products of the combustion process. The BN of an oil is a direct measurement of its alkaline reserve.

Every engine oil has an initial BN that gradually reduces during use.

Typical starting values for diesel engine oils are between 8 and 12. However, marine engines burning heavy fuel oil need a much higher BN, possibly as high as 80, to handle the harsh combustion conditions from fuels containing a high concentration of sulfur. A general rule of thumb is to discard the oil when the BN drops below half its beginning value.

While it may seem logical to assume that oils formulated to have a high BN would be most desirable, this is not always the case because some engines may suffer burnt valves if such an oil is used. This results from the high ash content of the oil and high valve temperatures causing fusion of the valve seats. Using a lubricant specifically formulated for diesel combustion in a gasoline engine could also prove detrimental, highlighting the importance of adhering to equipment manufacturers' lubricant specifications.

BN measurements are performed only on samples from infrared results flagged for analysis. A BN can be predicted through the infrared data and, where this prediction is below the specified limit, a BN test is requested to confirm the degree of degradation evident in the infrared data. All samples having a predicted BN exceeding a safe

limit are reported as having a BN of +6 while the actual result is reported for samples selected for the test.

AN and BN Units of Measurement

The units of BN and AN can be somewhat confusing. Although they are different tests, the results are both expressed in the same units: milligrams of potassium hydroxide per gram of oil, represented as mg KOH/g.

The AN of an oil is defined as the number of milligrams of KOH needed to neutralize the acid constituents in one gram of the oil.

The BN of an oil is the number of milligrams of KOH needed to neutralize the acid needed to neutralize the basic constituents in one gram of the oil.

Gas Chromatography Test for Fuel Dilution

Gas chromatography (GC) is a separation technique used to analyze used engine oils for evidence of fuel dilution. The technique as applied to fuel dilution measurements is used to separate and measure two volatile fractions of specified boiling ranges from used engine oil samples. The first volatile fraction of interest has a boiling range similar to that specified for gasoline, while the second fraction has a boiling range similar to diesel. The instrument is calibrated and measurements are reported as a percentage contamination by mass.

The fuel dilution test is typically performed either when a significant drop in sample viscosity is measured, or when the flash-point test has failed. It is important that the oil brand and grade are correctly described to your laboratory if problematic samples are to be detected. Special care is necessary in interpreting results because

many factors can influence their interpretation. Fuels are complex mixtures of organic compounds that are classified into products based largely on distillation ranges rather than specific chemical data. There are also significant overlaps between various product specifications, making it sometimes difficult to accurately separate and quantify fuel mixtures.

Editor's Note:

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