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## **ZDDPlus™ Tech Brief #4**

### **Oil & Additive Testing**

There are many laboratories and oil analysis services which offer VOA (Virgin Oil Analysis) or UOA (Used Oil Analysis). In order to correctly utilize a testing lab and ensure optimum accuracy in the results, pay attention to exactly what testing services are advertised. Laboratories, like most businesses, concentrate on a certain set of services, and have internal procedures and equipment dedicated to these services. That means if a lab is advertising: "Quick Used Oil Analysis for only \$4.99!" they may be capable of accurately analyzing regular engine oil, but don't expect to send in your concentrated oil supplement or other oil additive and get an accurate test. With a bit of additional information and dialog between you and the lab, a successful test may indeed be possible, but the point is that the lab's specialization makes them less adaptable to a wide range of testing. With this in mind, let's look at the two major types of laboratories at which an oil analysis can be obtained, and see how to successfully utilize each of these laboratory types to get the oil and additive analysis we require.

#### **Consumer Oil Testing Laboratories**

The type of laboratory most commonly utilized by the classic and high-performance car industry primarily deals directly with consumers, and is often set up with a single type of machine designed to analyze engine oil or other normal vehicle fluids quickly and inexpensively. These laboratories are often dedicated to consumer VOA or UOA and usually offer a high level of customer service, supplying the customer with sampling bottles, shipping materials, and delivering a full elemental report on the sample oil. Some of these laboratories will supply traceability documentation on request, some will not. These laboratories offer the very highest value to someone who is primarily interested in VOA or UOA. The only information they may ask for is the vehicle type and mileage, and possibly the oil condition (new or used) and if used, how many miles on the oil. Their procedures are primarily set up to perform speedy, efficient processing of vehicle oils, and as such they do not necessarily test additives or concentrates accurately without additional information. A lab tailored to consumer oil analysis will usually assume that a substance sent to them has elemental levels in the range found in normal oil. This can be the cause of erroneous results, especially when testing concentrates which may contain elemental levels 40 times higher or more than those found in engine oil.

#### **Petrochemical Industry Laboratories**

The other main type of laboratory is primarily dedicated to testing for the petrochemical industry. These labs usually assume their customers have greater familiarity with oils and testing than does a typical consumer. They have a wide range of equipment to test a wide range of substances, as well as specially trained people to perform the testing. They are most familiar with testing to an established standard method, such as one of the ASTM (originally the American Society of Testing and Materials, now ASTM International) methods, and usually expect the customer to know which ASTM tests need to be run on the sample, such as ASTM D4951, ASTM D5185, etc. Industrial laboratory procedures and equipment are under closer scrutiny than is standard at consumer oil labs. Industrial laboratories can always provide documentation showing ASTM or other standard methodology and trace their calibration back to NIST (National Institute of Standards and Technology) standards.

All of these factors associated with industrial testing inevitably drive up the testing cost, to as much as \$200 per element tested. Although it may be unintuitive at first, these industrial labs may actually need to be given more up-front information than a consumer lab. This is because they don't test just automotive engine oils; they regularly test a wide range of petrochemicals. In order to accurately test your sample, they usually need to know the expected elemental types and concentrations. This allows them to tailor the specific tests to obtain accurate results. We will discuss the methodology industrial labs use to ensure accurate results later in this paper.

### ***Standard Techniques for Testing Engine Oil***

The ASTM has developed many standardized methods of analyzing oils and other petroleum substances, as well as just about anything else! The most commonly used tests for automotive engine oil analysis are based on ICP (Inductively Coupled Plasma) Spectroscopy and are identified as:

D4951, "Standard Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry"  
and

D5185, "Standard Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)."

In each of these test methods, the oil sample is vaporized and fed into a high-energy plasma to excite the constituent atoms. An atom in this state is unstable, so it will quickly drop back down to its normal energy state and in doing so, emit the excess energy as light. Each element emits light at a characteristic set of wavelengths as well as unique emission intensities at each wavelength. This set of emission characteristics are often called an element's spectral emission "fingerprint." These elemental emission characteristics are extremely stable and repeatable, and form the basis for identifying elements in many sciences. The ASTM standard methods D4951 and D5185 both identify wavelengths unique to each specific element for use in identifying the concentration of that element in oil.

In modern ICP analysis, a computer compares the emission spectrum fingerprint of an oil sample against stored reference fingerprints. Individual elements are identified by their fingerprints and levels are quantified by comparison to stored calibration standards.

### ***The Difference Between the ASTM D4951 and D5185 Methods***

The two ASTM methods call for different calibration methodologies, which affect the speed and accuracy of the measurement:

D4951 calls for the mixing of calibrated standard solutions into the actual sample being tested. This technique gives a calibration point reading simultaneously with the substance being tested. This delivers very high accuracy when performed correctly, but due to the extra steps required, offers slower throughput and higher testing labor and material costs. D4951 is only intended to test for levels of 9 elements: barium, boron, calcium, copper, magnesium, molybdenum, phosphorus, sulfur and zinc.

D5185 calls for calibration using a standard solution before testing, and again after each fifth sample test run. This method does not result in as high a guaranteed measurement accuracy, but is quicker and offers higher throughput. It is for this reason that most oil testing laboratories use a procedure such as ASTM D5185. The D5185 testing method will deliver data in a few minutes for 22 elements: aluminum, barium, boron, calcium, chromium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, phosphorus, potassium, sodium, silicon, silver, sulfur, tin, titanium, vanadium and zinc.

## ***ASTM D5185 Repeatability and Reproducibility***

By definition, repeatability is the precision with which two measurements can be made with the same sample, machine, and operator. Reproducibility is the comparison of results obtained when the same sample is tested at different laboratories. ASTM D5185 specifies a different degree of repeatability and reproducibility for each element, but we will look at the limits set for phosphorus and zinc at the 1000 ppm (parts per million) concentration, a level similar to that found in current oils. ASTM ICP testing terminology specifies mass measurements in grams, with the elemental levels expressed per gram of total mass to be analyzed. Since the repeatability and reproducibility are within the range of one millionth of the sample mass per gram, they are expressed in µg per g ratios, which can also be stated as ppm of mass.

For phosphorus, repeatability is specified to be less than 71 ppm and reproducibility is 140 ppm. For zinc, repeatability is specified to be less than 65 ppm and reproducibility is 170 ppm.

D5185 calls for reporting precision to three significant figures for calcium, magnesium, zinc, barium, phosphorus, and sulfur. Reporting of results in mg/kg is required to two significant figures for aluminum, boron, chromium, copper, iron, lead, manganese, molybdenum, nickel, potassium, sodium, silicon, silver, tin, titanium and vanadium.

Most laboratories report the resulting elemental levels in ppm and some report in percentage. The conversion between percentage and ppm is: 1% = 10,000 ppm, 0.1% = 1,000 ppm, and 0.01% = 100 ppm.

## ***Upper and Lower Sensitivity Limitations of the Common Methods for Zn and P***

Depending on the particular brand, model and age of the ICP unit being employed, the upper limit can range from less than 10,000 ppm to over 100,000 ppm. In order to get accurate results, solutions with elemental concentrations above this equipment limit must be diluted with an inert dilutant before analysis. This is necessary to bring the concentration of the element being quantified within range of the equipment. This is another area where the commercial testing labs more closely follow the ASTM methodology than do the consumer labs; in order to minimally affect the accuracy of the test, the dilutant must be soluble in, and as close in density as possible to the oil being tested. The standard dilutant is white oil, available in differing densities to match the sample, although lighter fractions can be diluted using xylene. Many consumer labs use a more inexpensive dilutant, such as kerosene or other solvent. Properly done, this should cause minimal error when testing engine oil. With denser concentrates, it can become a source of dilution and measurement error.

The lowest detectable reading available from an ICP unit is dependent on two factors: inherent noise in the electronics of the unit and the background reading level due to contamination of the unit's ICP plasma generator and mass detector.

## ***Testing Substances Above the Concentrations the Equipment Can Analyze***

As with virtually all test equipment, there is a lower and upper measurement limit to any equipment used for analyzing oil.

The lower limit is defined as the "sensitivity" of the equipment, and is usually due to the basic noise of the equipment itself. With no sample present in the equipment, the electronic noise floor of the equipment will be displayed. At extremely low elemental levels, a sample fingerprint will be totally masked by this noise floor. At some slightly higher level, the spectral peaks from the sample being measured will begin to rise from this equipment noise. If the levels of the spectral peaks are read at this time, an erroneously high reading will be obtained, since the noise will substantially contribute to the peak level.

The upper measurement limit is usually expressed as the point where the inherent upper limit of the measurement technique results in an erroneously low reading.

The difference between the upper limit and the lower limit is expressed as the "dynamic range" of the equipment.

An analogy to these two error conditions can be made using a car's speedometer. If you are creeping along in gear at idle, the speedometer may still read "0" mph, but you are certainly moving, just at a rate below the minimum sensitivity of the speedometer, so it is in error. If you are one of the lucky people who have a car with an 85 mph speedometer, then you may have experienced the needle stopping at 85 mph while you accelerated, even though your tachometer continued to rise. This means that you have exceeded the upper limit of the speedometer, and it is reading an erroneously low speed. These two errors can occur with virtually any measuring instrument; therefore basic laboratory technique must include the knowledge of how to scale readings.

In a chemical testing laboratory, scaling a measurement is the step taken after a dilution. As an example, if the basic dynamic range of an ICP analyzer is from 10 ppm to 10,000 ppm, it will not be capable of accurately resolving an elemental level below 10 ppm or above 10,000 ppm. If an oil sample has elemental levels within these limits, no dilution will be needed to get accurate results. The equipment most commonly sold into the oil analysis testing market is specifically designed to have a dynamic range which allows for accurate testing of almost all commonly used oils and oil/additive mixes with a simple 2:1 or similar dilution. Using these ICP units to test anything other than common vehicle oils, without the more time-consuming multiple dilution procedure, can cause measurement error.

If the elemental levels are higher than the upper limit of the ICP equipment, or the elemental content is unknown, then a dilution and retesting procedure must be used to get accurate results. This procedure is not called out in a standard D5185 test such as that performed by consumer labs, so the lab would have to have been advised in advance that a dilution may be necessary. This is where industrial labs have a procedural difference from consumer labs; they usually have a standard dilute-and-repeat methodology in order to ensure the equipment range is not a factor in the accuracy of the test. In order to do this, a dilutant is added and thoroughly homogenized with the unknown in a carefully measured mass ratio (usually 2 or 10 parts dilutant to 1 part unknown oil). This sample is then tested, and if the elemental analysis shows readings of 1/2 (in the case of a 2:1 dilution) or 1/10 (for a 10:1 dilution) of the initial undiluted test, then both tests are valid. However, if the readings are proportionally higher on the diluted measurement, then the initial undiluted test was above the upper dynamic range limit of the equipment.

### ***Some Common Pitfalls at Laboratories Performing Oil Analysis***

Error in an ICP measurement can be caused by infrequent calibration, as well as old or degraded calibration standards. Calibration is done on a two-point basis; the first point with a solution containing none of the elements in question called a "blank" solution, and the second with a "standard" solution containing a known amount of the calibration elements. When performing a test on an unknown sample, the ICP unit will determine the intermediate value by performing a straight-line interpolation between the blank and standard calibration points. If either the blank or calibration solution is not tested correctly, error will be introduced at all levels. Frequent cleaning of the plasma generation unit is required to minimize background contamination and resulting erroneous reading of the blank solution. Also, most ICP units require a 30-minute or longer warm-up in order to stabilize. Any readings taken before this period would be of questionable accuracy.

There are procedural or human errors unrelated to the equipment which can occur despite everyone's best intentions. We have seen labs fail to perform a correct dilution, even after being given a desired dilution, as well as scaling error by the operator after a dilution. Each of these errors resulted in reported values which were off by a factor of 5 or 10. To each laboratory's credit, after contacting them and informing them of a problem, corrections were made which resulted in test reports of adequate accuracy.

It is the responsibility of the customer to make sure adequate information and instructions are provided to a lab to avoid erroneous test results. On the other hand, it is good business practice for a laboratory to understand its capabilities and limitations and to inform their customer before testing. We have found most reputable labs will work with the customer to ensure the sample is tested in a way which optimizes the accuracy of the test results, if they are informed of the challenges in advance.

## **Calibration Standards**

Standard solutions (such as the ASTM standard SRM-1085 calibration solution) for use in calibrating the ICP unit can be obtained commercially from ICP equipment suppliers as well as from the NIST. Commercially prepared calibration solutions are required to prove traceability to the NIST standards and are a cost-effective alternative. Periodic use of standard solutions obtained from NIST is a good way for a laboratory to verify the validity of commercially obtained standards.

## **Should You Trust a Test Report?**

A test report may have impressive amounts of data, and a convincing degree of precision in the recorded values but, in our experience, if you are looking for absolute accuracy you should not rely on a single test report. In the 1000 ppm range of zinc and phosphorus concentrations commonly found in automotive oils, the ASTM D5185 test method calls for a measurement to be repeatable at a lab within 70 ppm. It also calls for a measurement to be reproducible between labs within 140 ppm. Despite this, we have submitted identical samples to a single lab on multiple occasions and received reports which varied by over 100 ppm. We have also seen a several hundred ppm difference from one laboratory to another. Despite the fact this amount of error exceeds the ASTM specification limits, we believe it is adequate for consumer virgin or used oil analysis.

## **Testing ZDDPlus™**

As the astute reader will have deduced by this point, much of the information in this paper was obtained through our own experiences here at ZPlus. We conducted extensive research into ASTM standard testing methods and obtained valuable information from many laboratories and ICP machine manufacturers. As a result, we have settled on a testing procedure we recommend to our customers which will give reliable results from a wide range of laboratories.

Specifically for ZDDPlus™, which has extremely high levels of zinc and phosphorus, most laboratories must be informed that the sample being tested will have phosphorus levels >50,000 ppm and zinc levels >60,000 ppm. The laboratory must dilute the ZDDPlus™ sample by weight at a factor of 40:1 relative to the dilution they use for normal oils. This will allow the laboratory to correctly test the sample just like they test normal oil. If possible, the lab should calibrate the ICP with a 1000-to-2000 ppm calibration standard before testing in order to give the most accurate test result. Giving the lab this information will not bias the test result in favor of any particular test outcome other than an accurate one. This information will help the laboratory quickly set up the correct dilution and scaling necessary to ensure the most reliable results. Conversely, failure to inform the lab of the difference between this product and regular oil will often cause the lab to incorrectly test ZDDPlus™, resulting in an erroneous test report *at your expense*. If the lab is not set up to perform high-ratio dilutions, then a different lab must be found.

In our production environment, we have a high degree of confidence in the exact elemental makeup of our product. To ensure consistent product quality, we currently test incoming materials and finished product both internally and using external testing laboratories. This multiplicity of reported values gives us confidence that our average calculated data is accurate. This guarantees a consistent formula and high-quality content in the ZDDPlus™ product.