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# CONNECTING ELEMENTAL ANALYSIS TO PARTICULATE COUNT: A NEW TECHNIQUE TO DETECT FAILURES

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## Synopsis

This paper describes a new machine condition measurement system which combines particle count data and elemental analysis information in two closely interlinked measurement phases. This machine condition tool is part of a new portable product that also measures lubricant condition using viscosity and IR to complete the overall condition monitoring picture. The focus of this paper is to describe the new methodologies that apply to the machine condition aspect of the new tool. The paper compares existing analytical techniques used to quantify wear conditions and contrasts them with the new techniques and methodologies the device uses. Finally, this paper presents case studies that use the device to show how the measurements compare to other analytical techniques in different machine condition monitoring applications.

## Introduction

Particle count and elemental identification answers two of the most important questions in oil analysis: "How many?" and "Where is it coming from?" These two measurements are the most critical in any machine condition monitoring application. Using current technologies, the particle count is often a pre-screen for conducting root cause analysis using SEM/EDX , XRF and in some cases ferrography. These techniques have proven to be expensive, time consuming and very labor intensive. Other routine elemental tests are used but they are particle size sensitive towards the small fines, and they do not offer the best solution for detecting normal to abnormal wear transition.

Machine condition through oil analysis is typically monitored by quantifying the number, size and elemental composition of wear particles produced at the extremities of lubricated machine parts. The size and quantity of these wear particles has a direct correlation to a benign versus an abnormal wear state (Figure 1).

It is important to understand that a benign wear state in one type of machine will be different compared to another. In these cases, the type of wear mechanism coupled with the contact area, load, speed and lubricant condition all govern the size and quantity of the normal benign wear. This makes limit and alarm settings difficult compared to cleanliness control applications where the overall contamination level must meet a maximum threshold. This threshold is a fixed limit (often specified by the OEM) and it is often small enough to be easily quantified by light blocking laser particle counters. Particle count standards like ISO 4406 and NAS1638 were developed specifically for these applications.

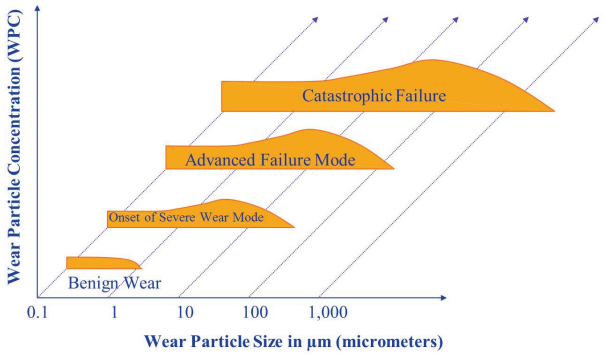



**Figure 1:** Progressions to Failure

Filtration and other loss mechanisms in lubricant systems, which readily generate wear, also play an important role in the overall particle picture. Filters are primarily responsible for the condition of dynamic equilibrium for a given particle size [1] and set baselines and alarms for large particles. Very fine particles do not work well in this model because they are diluted into the system, making any baseline measurement impossible. The transition from a normal benign wear mode to an abnormal wear mode also creates fewer small particles because the forces acting on the shear mixed layer are now greater, and fine rubbing wear substitutes for much larger wear particles produced from beneath the shear mixed layer [2]. Machines produce different types of wear particles depending on the wear mode. These are explained in greater detail in the Wear Particle Atlas [3].

## 2. Existing Machine Failure Measurement Techniques

### 2.1. P article Count

Particle count is a good indicator of the severity of a wear situation and the transition from small to large particles can easily be detected. Particle count is usually performed using one of the following techniques: laser light blockage, direct imaging or pore blockage.

Laser light blocking suffers from coincidence effects (particle overlap) and from the ability to see through dark sooted samples. Therefore, this process is limited to clean translucent fluids used in the contamination control industry where internal machine contact is minimal.

Direct imaging counters the coincidence effect by processing particles over a larger area using a CCD sensor. The sample illuminates by a pulsed laser diode which can increase light throughput and overcome dark sooted samples, to about 2% before dilution.

Traditional pore blockage devices are like optical particle counters because they saturate at relatively low levels and are not ideally suited to accurately quantify heavily contaminated machine wear samples. However, they have no difficulty processing oils containing soot or water because these contaminants can pass through the pores without increasing the signal output. This is the primary advantage that pore blockage techniques have over light blocking and direct imaging techniques.

## 3. LNF Compared to Traditional Ferrography

### 2.2. A tomic Emission Spectroscopy

Elemental identification of wear particles has traditionally been performed using atomic emission spectroscopy by either Rotating Disc Electrode (RDE) or Inductively Coupled Plasma (ICP). Both these techniques are limited when it comes to identifying large particles. As a result, other complementary techniques have been developed to help increase the large particle detection capability of atomic emission. These techniques include Rotrode Filter Spectroscopy (RFS) and acid digestion. These additional techniques are time consuming and require a lot of special sample preparation and, in the case of acid digestion, dangerous chemicals are used.

### 2.3. X-ray Fluorescense (XRF)

XRF is a common technique that quantifies individual chemical elements in used oil samples.

Samples are typically analyzed by taking an x-ray of a small oil sample (1-2 ml) in a cup. Similar to atomic emission techniques, the large particles associated with abnormal failure modes are not suited to the analysis technique using a cup because the focused XRF beam spot does not statistically represent the large particle distribution in only 1-2ml of oil. These results do correlate well with RDE and ICP; however, the overall elemental signal is much lower. Again, this is expected based on the small XRF beam spot compared to the overall oil volume being examined. Interference from small sub micron carbonaceous soot particles also creates issues for heavily sooted diesel engine oil samples using this technique. These types of samples require some form of baseline calibration to compensate for the soot interference.

You can achieve better sensitivity for large wear particles by focusing the beam onto the particulate itself. This is essentially what occurs when you examine particles from magnetic chip detectors using a piece of sticky tape. The RAF early failure detection centers (EFDCs) in the United Kingdom extensively use this technique.

### 2.4. Ferrography and Filter Patch Analysis

Microscopy is a powerful technique for identifying root causes of wear mode and mechanism failures. More advanced ferrography techniques for substrate preparation also identify ferrous from non-ferrous metals and crystalline from non-crystalline materials. Ferrogram

analysis is an in depth and conclusive test since it uses heat treatment to identify different types of steel along with particle color, surface, morphology and use of polarized light. The more advanced substrate preparation, such as using a ferrogram maker, differs from straight filter patch analysis in this regard.

The biggest downside to performing ferrography is that it is time consuming and requires an expert to perform the analysis. This skill demands many years of analyzing multiple ferrograms to become skilled in the art. Microscopy techniques need to be coupled with other quicker screening techniques for them to be successful. It is not feasible to run a routine sample history using microscopy alone.

### 2.5. SEM EDX

The SEM EDX technique is used for visually examining particles at very high magnifications and performing spot elemental analysis on the particle using an EDX device. The depth of field is much larger on an SEM compared to conventional metallurgical microscopes. This depth of field enhancement means the complete particle can remain in focus at high magnifications and you can achieve greater detail. Like standard wear particle analysis, using an optical microscope SEM EDX is not suitable for routine sample analysis. The instruments are expensive and the technique involves some sample preparation, such as applying a conductive coating to the sample to help increase resolution.tivity of a complete ferrographic analysis. However, if identification of the root cause of the problem is required or further corroboration is needed, we recommend a complete Ferrography analysis.

## 3. A New Technique - Filtration Particle Quantification Combined with EDXRF

[In this unique system design, machine failure and root cause analysis is interpreted by using a two-step process combining a modified pore blockage technique with an XRF analyzer. Figure 2 shows the tower which encompasses the FPQ and XRF device in the overall oil monitor system. The figure also shows the filter being inserted into the XRF. This relatively quick process can screen out samples with high particle counts and perform a complete 13 element XRF analysis on the resultant sample filter.

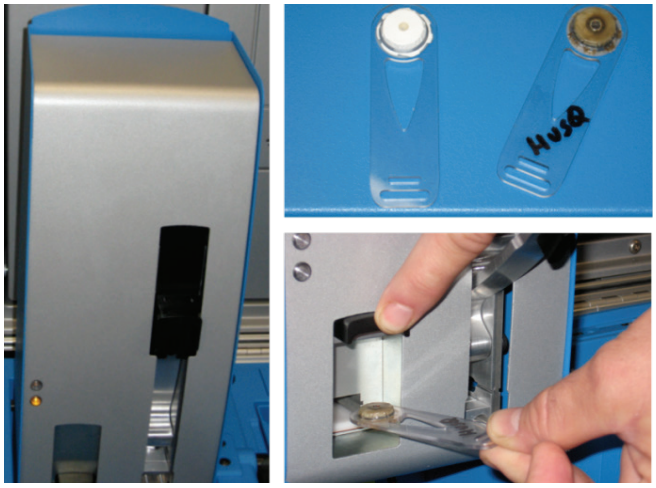


**Figure 2:** FPQ and XRF tower assembly

### 3.1. Combined Particle Quantifier (FPQ) and XRF Device

The modified pore blockage technique has been termed "Filtration Particle Quantification" or FPQ. The FPQ uses constant flow by driving a 3 ml oil sample using a syringe through a polycarbonate filter with ~ 30,000 4um diameter holes. The resultant pressure drop across the filter, measured with reference to atmospheric pressure is used to quantify particles >4um up to ~1million particles/ml. This is achieved primarily by using a modified filter design compared to a conventional pore blockage instrument. This new patent pending dual dynamic design allows a much greater particle count range ( x50) beyond the point where particle swapping and saturation occurs (Figure 3).

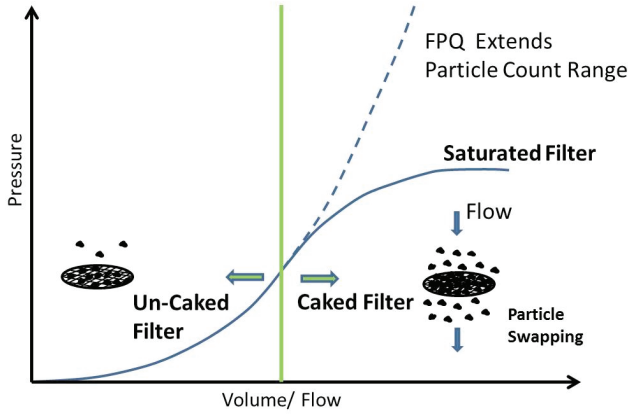



**Figure 3:** FPQ Filter vs Conventional Pore Blockage Filter

Once the analysis is complete, the filter passes from the FPQ to the XRF device. The FPQ and XRF are closely linked in terms of calibration because of the particle swapping phenomenon. The FPQ and XRF instruments use a series of unique rules and calibrations to ensure accurate elemental quantification of particles up to 1 million particles /ml. This technique combined with the patented filter overcomes the problem with the oil cup analysis which XRF devices typically use. This unique filter design is able to corral the particles into a small area on the filter so the focused X-ray beam can concentrate its energy on those particles. The instrument uses 40kev and 15kev to quantify 13 elements with an average limit of detection of ~ 1ppm.

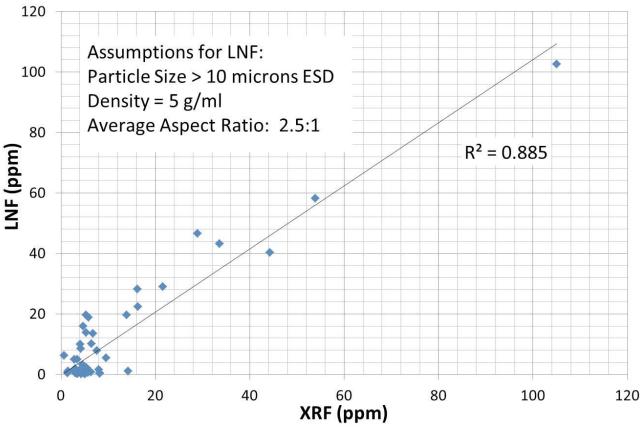



**Figure 5:** LaserNet Fines® vs. XRF – Total ppm

## 4. FPQ / XRF Device Case Studies

The case studies that follow demonstrate how the FPQ/XRF device correlates to existing analytical techniques for measuring particles in various real word applications.

### 4.1. FPQ and X-Ray Correlation to Established Measurement Techniques

The following data set from a series of marine diesel vessels was used to evaluate the FPQ and XRF technology. Samples were analyzed on the FPQ device and XRF and were shown to correlate to LaserNet Fines® and acid digestion using the ICP. A model using an assumed wear particle size aspect ratio and particle mass was used to further correlate the aggregate elemental concentration on the FPQ filter using the LaserNet Fines® and XRF data. Figure 4 and Figure 5 show how the FPQ and XRF correlate to the LaserNet Fines® direct imaging particle counter.

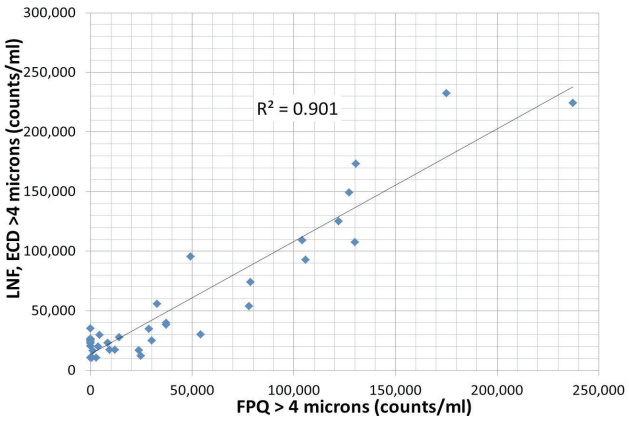



**Figure 4:** LaserNet Fines® vs. FPQ (counts/ml >4um)

### 4.2. XRF vs. Acid Digestion

LaserNet Fines® direct imaging and spectroscopy are well established techniques to quantify particle count and elemental concentration respectively. RDE and ICP spectrometers lack good sensitivity to detect large particles and they are used as trending tools for fine particles based on a dissolved elemental calibration. An accepted methodology to quantify large particles is to "acid digest" the entire sample by dissolving particles into a liquid which can be quantified using a standard ICP calibration. However, corrosive chemicals, time, cost and effort make acid digestion impractical.

The data in Table 1 shows a selection of marine samples analyzed on the ICP before and after acid digestion. This method is commonly known as differential acid digestion.

Figure 6 shows how the differential ICP results (large particles) for

| | Before Acid Digestion -ICP (ppm) | | | | | | After Acid Digestion - ICP (ppm) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | A | B | C | D | E | F | A | B | C | D | E | F |
| Ag | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Al | 0 | 0 | 0 | 10 | 10 | 21 | 0 | 0 | 0 | 0 | 13 | 28 |
| Cr | 6 | 0 | 0 | 0 | 6 | 7 | 6 | 0 | 0 | 0 | 6 | 8 |
| Cu | 0 | 0 | 0 | 0 | 11 | 11 | 0 | 0 | 0 | 0 | 10 | 10 |
| Fe | 10 | 7 | 0 | 0 | 33 | 67 | 11 | 10 | 0 | 0 | 35 | 86 |
| Mo | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ni | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Pb | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Sn | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ti | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| V | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Total ppm | 16 | 7 | 0 | 10 | 60 | 106 | 17 | 10 | 0 | 0 | 64 | 132 |

**Table 1:** Differential Acid Digestion Sample Result (Sample E=10-1151, SampeF=10-1149)

samples E and F compare to the XRF data for the same samples. Note that the XRF data is not shown in Table 1 above. The large particle portion correlates very well (within 3ppm) to the filtered XRF results (Figure 6).

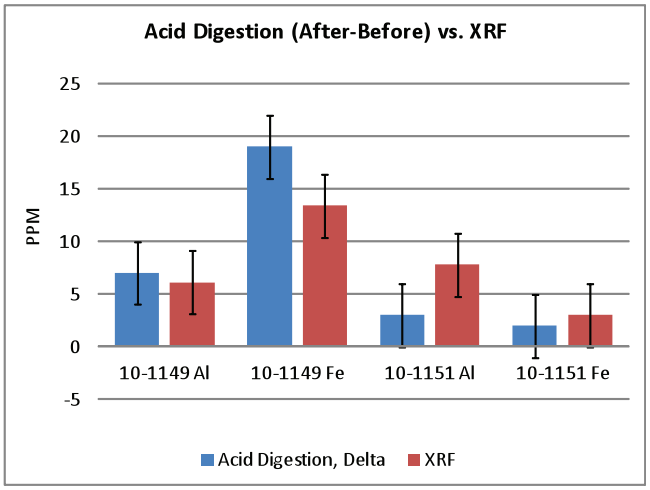



**Figure 6:** Differential ICP vs XRF (Sample E=10-1151, Sample F=10-1149)

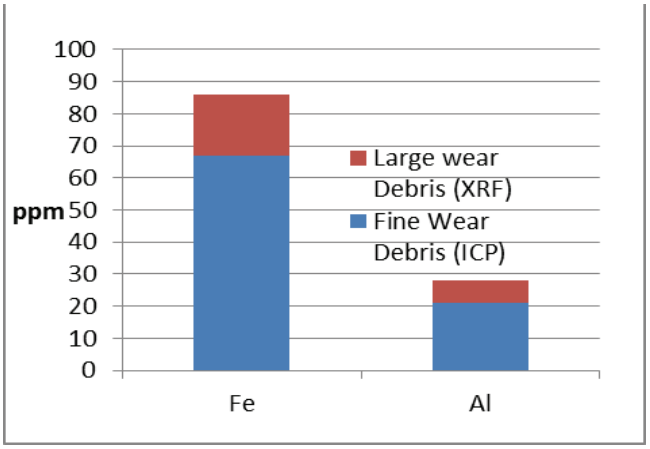
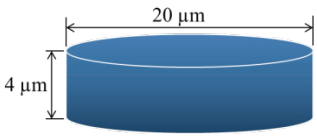



**Figure 7:** Typical ratio of large to small particles observed between XRF and ICP (Sample F)

Figure 7 shows the difference in ppm between the ICP and XRF readings for Fe and Al in Sample F. This is an expected result based on how large and small particles behave in a closed loop lubricating system. Large particles get lost and filtered out far more easily compared to fine debris which never gets lost and continues to grow in concentration.

## 4.3. PPM (mass) vs Particle Concentration (quantity) on the FPQ Filter

Based on the density of iron, it would take ~100 particles of the illustrated dimensions in 1ml of oil to raise the elemental concentration by just 1ppm. For lighter metals such as Aluminum, it takes approximately three times the amount of particles. This explains why the differential elemental ICP and XRF readings are relatively low when compared to the fine and dissolved particle readings using routine spectroscopy. In this example, the Fe and Al wear particles are most likely caused by cylinder/piston wear. This is a common failure mode in the application and shows how the XRF is able to identify root causes of problems.




## 4.4. Wear Progression to Failure

When a machine enters an abnormal wear mode there is always an increase in the size and production of severe large wear particles. They are identified as an increase from a known equilibrium level in the system. As the abnormal wear progresses, the size and rate of production of these particles increases until the system eventually fails.

Note that fine wear particles detected by RDE spectroscopy and ICP continue to rise in the lube system and are unaffected by filtration or other system loss mechanisms. Take care when changing the oil and subsequently interpreting fine and dissolved wear metal data vs. XRF data. Limits based on rate of change apply in this case. For larger particles measured by FPQ and XRF, a static limit applies after the system reaches equilibrium. This is demonstrated in Figure 8.

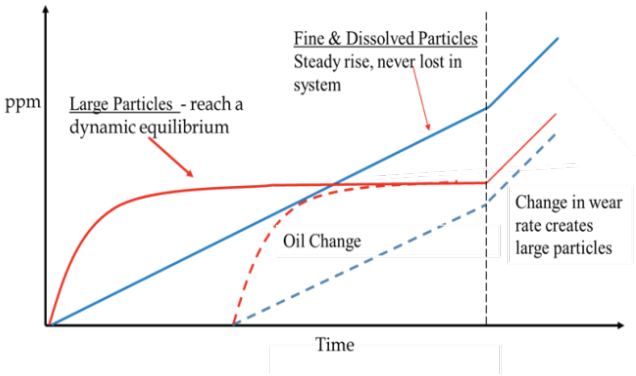



**Figure 8:** Behavior of large vs fine particles

Unlike existing optical particle counter and pore blockage technologies, the FPQ can handle a wide range of applications with relatively high wear rates (up to 1.0 million p/ml). Table 2 shows FPQ and XRF data for a wide range of components that are typically found in heavy duty industrial vehicle equipment such as engines, transmissions, final drives, and front differentials. The data shows pairs of components with corresponding high and low wear rates.

| | Particles >4um (/ml) | | Application | ITS Q5800 XRF (ppm) | | | |
|---|---|---|---|---|---|---|---|
| Sample | LaserNet Fines | FPQ data | | Al | Cu | Fe | Si |
| E1 High wear | 180209 | 141795 | Engine | 2.0 | 0.0 | 0.8 | 1.4 |
| E2 Low Wear | 26802 | 44188 | Engine | 0.5 | 0.6 | 0.6 | 0.7 |
| T1 High Wear | 46618 | 50390 | Transmission | 0.4 | 2.2 | 2.2 | 1.7 |
| T2 Low Wear | 5346 | 9664 | Transmission | 0.0 | 0.0 | 0.2 | 0.3 |
| F1 High wear | 213674 | 226222 | Final Drive | 4.3 | 0.0 | 8.4 | 7.0 |
| F2 Low Wear | 17185 | 26948 | Final Drive | 0.1 | 0.0 | 2.0 | 0.5 |
| D1 High Wear | 88193 | 62259 | Front Diff | 1.2 | 0.0 | 4.2 | 1.9 |
| D2 Low Wear | 37613 | 34773 | Front Diff | 0.9 | 0.7 | 2.9 | 1.2 |
| E3 High Water | 1025329 | 31686 | Engine | 0.5 | 0.0 | 1.0 | 0.4 |

**Table 2:** Normal and abnormal FPQ & XRF data for various applications

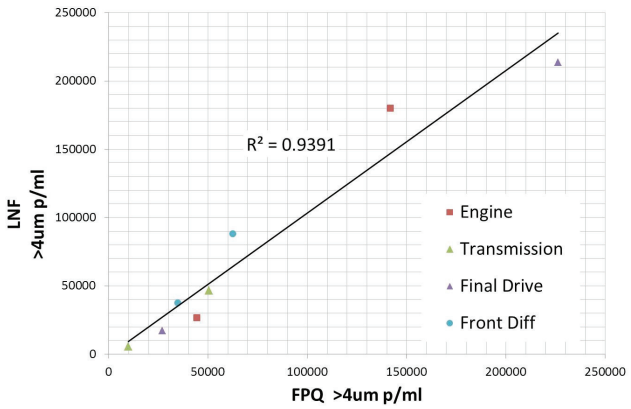



**Figure 9:** FPQ vs LaserNet Fines®, normal and abnormal wear in different applications

As expected, the particle count on the FPQ correlates well with direct imaging particle counting (Figure 9). In addition,the elemental XRF readings can differentiate between low wearing systems and more critical high wearing systems. This data shows that it is possible to make a recommendation on the root cause of the increased wear rates based on a material map of the lube system.

This data set also demonstrates a unique advantage that the FPQ has when analyzing emulsions and other sample types that contain "phantom" particles included in the overall particle count. Water and other liquids pass through the polycarbonate filter pores and the results are unaffected. Sample E3 contains a significant amount of free water ingestion that produced a highly elevated particle count reading on the LaserNet Fines®. The real particle count in this sample was only ~ 31k p/ml and the elemental level was low.

## 5. Conclusion

The FPQ, with its patent pending dual dynamic filtration system, handles a wide range of lubricant applications with varying wear levels. The particle count using the FPQ filter correlates with existing direct imaging particle counting. The subsequent elemental concentration from the FPQ filter using XRF analysis correlates well with ICP differential acid digestion, demonstrating that the methodology is valid. The combined particle count and elemental concentration identifies changing wear rates and isolates potential root causes of problems in lube systems. Particle count and elemental concentration provides the real elemental break down of particles captured and quantified on the filter. This methodology eliminates many of the problems associated with other techniques such as particle size detection and the impervious nature of many used oils found in heavy duty industrial applications.

## References

[1] Daniel P. Anderson and Richard D. Driver. "Equilibrium particle concentration in engine oil" Wear, Volume 56, Issue 2, October 1979, Pages 415-419

[2] Reda, A.A., Bowen, E.R., and Westcott, V.C. "Characteristics of Particles Generated at the interface Between Sliding Steel Surfaces" Wear, Volume 34 (1975) Pages 261-273

[3] Anderson, D.P., "Wear Particle Atlas (Revised)" prepared for the Naval Air Engineer¬ing Center, Lakehurst, NJ 08733, 28 June 1982, Report NAEC-92-163, Approved for Public Release; Distribution Unlimited – Pages 125-134



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