Interpreting Additive and Contaminants Results In Oil Analysis Testing
Elemental Spectroscopy (ASTM D5185)

• **Scope**
  
  – Covers the determination of additive elements, wear metals and contaminants in used and unused lubricating oil by inductively coupled plasma atomic emission spectrometry (ICP-AES)

• **Significance**
  
  – Difference in additive concentrations may indicate incorrect fluid
  
  – Increase in wear metals can be indicative of abnormal wear
  
  – Can be used to monitor equipment condition to define when corrective action are needed

Elemental Spectroscopy

- **Principle**
  - Sample is diluted with solvent and injected into a plasma where it is ionized (“burned”) at 10,000 K
  - Each element produces a unique spectra of light, intensity determines elemental concentration
Atomic Emission Spectrum Examples

- Aluminum
- Tin
- Lead
Elemental Spectroscopy

**Limitations**

- Measures 0-5 µm particles accurately, essentially blind beyond 8-12 µm range*
  - Supplemental testing is available for larger particle analysis

**Interferences**

- Samples must dissolve in solvent for accurate measurement
- High water content samples may require different preparation

*Various sources in general agreement that spectrometers lose their ability to detect particles in the 5-10 micron range.
Particle Detection Efficiency in Used Oil

Detection Efficiency, %

Particle Size, µm

Spectrometry

Large Particle Detection Methods
e.g. AF, WPC, Patch

Courtesy Spectro Inc.
Repeatability versus Reproducibility

• **Repeatability Conditions**
  - the same method
  - on identical test items
  - in the same laboratory
  - by the same operator
  - using the same equipment
  - within short intervals of time

• **Reproducibility Conditions**
  - the same method
  - on identical test items
  - in different laboratories
  - with different operators
  - using different equipment

• “As close as possible”

• “Real World” comparison

These values will only be exceeded 1 case in 20 (i.e. 95% confidence)

Ref: ASTM E177-14, Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods, ASTM International, West Conshohocken, PA, 2014
## Precision and Bias

### TABLE 5 Calculated Repeatability (µg/g) at Selected Concentrations (mg/kg)

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Aluminum</td>
<td>...</td>
</tr>
<tr>
<td>Barium</td>
<td>...</td>
</tr>
<tr>
<td>Boron</td>
<td>...</td>
</tr>
<tr>
<td>Calcium</td>
<td>...</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.2</td>
</tr>
<tr>
<td>Copper</td>
<td>...</td>
</tr>
<tr>
<td>Iron</td>
<td>...</td>
</tr>
<tr>
<td>Lead</td>
<td>...</td>
</tr>
<tr>
<td>Magnesium</td>
<td>...</td>
</tr>
<tr>
<td>Manganese</td>
<td>...</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>...</td>
</tr>
<tr>
<td>Nickel</td>
<td>...</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>...</td>
</tr>
<tr>
<td>Potassium</td>
<td>...</td>
</tr>
<tr>
<td>Silicon</td>
<td>...</td>
</tr>
<tr>
<td>Silver</td>
<td>0.2</td>
</tr>
<tr>
<td>Sodium</td>
<td>...</td>
</tr>
<tr>
<td>Sulfur</td>
<td>...</td>
</tr>
<tr>
<td>Tin</td>
<td>...</td>
</tr>
<tr>
<td>Titanium</td>
<td>...</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.1</td>
</tr>
<tr>
<td>Zinc</td>
<td>...</td>
</tr>
</tbody>
</table>

### TABLE 6 Calculated Reproducibility (µg/g) at Selected Concentrations (mg/kg)

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Aluminum</td>
<td>...</td>
</tr>
<tr>
<td>Barium</td>
<td>...</td>
</tr>
<tr>
<td>Boron</td>
<td>...</td>
</tr>
<tr>
<td>Calcium</td>
<td>...</td>
</tr>
<tr>
<td>Chromium</td>
<td>...</td>
</tr>
<tr>
<td>Copper</td>
<td>...</td>
</tr>
<tr>
<td>Iron</td>
<td>...</td>
</tr>
<tr>
<td>Lead</td>
<td>...</td>
</tr>
<tr>
<td>Magnesium</td>
<td>...</td>
</tr>
<tr>
<td>Manganese</td>
<td>...</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>...</td>
</tr>
<tr>
<td>Nickel</td>
<td>...</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>...</td>
</tr>
<tr>
<td>Potassium</td>
<td>...</td>
</tr>
<tr>
<td>Silicon</td>
<td>...</td>
</tr>
<tr>
<td>Silver</td>
<td>...</td>
</tr>
<tr>
<td>Sodium</td>
<td>...</td>
</tr>
<tr>
<td>Sulfur</td>
<td>...</td>
</tr>
<tr>
<td>Tin</td>
<td>...</td>
</tr>
<tr>
<td>Titanium</td>
<td>...</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.3</td>
</tr>
<tr>
<td>Zinc</td>
<td>...</td>
</tr>
</tbody>
</table>

Measured Elements

• Wear Metals
  – Iron
  – Copper
  – Lead
  – Aluminum
  – Tin
  – Nickel
  – Chromium
  – Titanium
  – Vanadium
  – Silver

• Additives
  – Calcium
  – Magnesium
  – Phosphorus
  – Zinc
  – Barium
  – Molybdenum

• Contaminants
  – Silicon
  – Boron
  – Lithium
  – Sodium
  – Potassium
Calcium – Common Cause

• Additive
  – Calcium soaps are commonly used in detergent additives
    • More than 25% deviation from new oil baseline typically represent mixing or top-up with a different product
    • Unless a degraded additive drops out of solution, it will still be present and measured
Calcium – Exceptions

- **Clay-based absorbents**
  - Common oil absorbents are made from Fuller’s Earth (a.k.a. kitty litter), as are some acid scavenging filters
    - Contains a magnesium- and calcium-based clay, with iron contaminant; generally increases particle count

- **Water and/or salt**
  - Calcium and magnesium represent the hard in water
    - May not correlate with water content if water is being driven off
  - Calcium is present in road dust
    - May correlate with an increase in particle count
Calcium – Pitfalls

• Masked by additive chemistry
  – Calcium as an additive may be present at levels of 100-3000 ppm, making it difficult to identify small increases due to contamination
  • Seek correlations with magnesium, water and/or particle count to confirm
Magnesium – Common Cause

• Additive
  – Magnesium soaps are commonly used in detergent additives
    • More than 25% deviation from new oil baseline typically represent mixing or top-up with a different product
    • Unless a degraded additive drops out of solution, it will still be present and measured
**Magnesium – Exceptions**

- **Clay-based absorbents**
  - Common oil absorbents are made from Fuller’s Earth (a.k.a. kitty litter), as are some acid scavenging filters
  - Contains a magnesium- and calcium-based clay, with iron contaminant; generally increases particle count

- **Water and/or salt**
  - Calcium and magnesium represent the hard in water
    - May not correlate with water content if water is being driven off
  - Magnesium is present in road dust
    - May correlate with an increase in particle count
Magnesium – Pitfalls

• Masked by additive chemistry
  – Magnesium as an additive may be present at levels of 100-1000 ppm, making it difficult to identify small increases due to contamination
    • Seek correlations with magnesium, water and/or particle count to confirm
Phosphorus – Common Cause

• Additive
  – Phosphorus is used in both anti-wear (AW) and extreme pressure (EP) additive chemistries

• More than 25% deviation from new oil baseline typically represent mixing or top-up with a different product
  – AW oils contain relatively equal phosphorus and zinc levels
  – EP oils contain phosphorus only
  – R&O oils have neither
Grease contamination

- Greases also use both anti-wear (AW) and extreme pressure (EP) additive chemistries

  • Some systems have greased seals protecting oil lubricated bearings, it is possible excess grease will migrate into the oil

  • Some mechanics/millwrights apply grease to parts to aid in reassembly, it is possible residual grease will be measurable
Phosphorus – Pitfalls

• Cleaning agents
  – Phosphate-based degreasers and cleaners are still allowed in industrial applications
Zinc – Common Cause

• Additive
  – Zinc is used in anti-wear (AW) additive chemistries
    • More than 25% deviation from new oil baseline typically represent mixing or top-up with a different product
      – AW oils contain relatively equal phosphorus and zinc levels
      – EP oils contain phosphorus only
      – R&O oils have neither
Zinc – Exceptions

• **Wear metal**
  - Zinc is a component of brass, used in some solders and in plating and galvanizing
  - Differentiates brass from bronze, but both contain copper, lead and tin
  - Increase in zinc, lead and tin, often with an increase in Acid Number indicates solder attack
  - Increase in zinc with larger amounts of iron suggests galvanized metal wear
  - Proportional increase in zinc, chromium and/or nickel suggest plating wear
Zinc – Pitfalls

• Masked by additive chemistry
  – Zinc as an additive may be present at levels of 100-800 ppm, making it difficult to identify small increases due to wear

  • Seek correlations with other relevant elements
Barium – Common Cause

• Additive
  – Barium soaps are rarely used in detergent additives
    • More than 25% deviation from new oil baseline typically represent mixing or top-up with a different product
    • Unless a degraded additive drops out of solution, it will still be present and measured
Barium – Exceptions

• **Grease contamination**
  
  – Barium can be used as a thickener system for grease
    
    • Some systems have greased seals protecting oil lubricated bearings, it is possible excess grease will migrate into the oil
    
    • Some mechanics or millwrights apply grease to parts to aid in reassembly, it is possible residual grease will be measurable
Barium – Pitfalls

- Often ignored
  - Since it hardly ever appears on the majority of sample reports it often is skipped when reading
  - Any new appearance of barium suggests contamination with another product
Molybdenum – Common Cause

• Additive
  – Molybdenum is commonly used in friction modifiers or anti-slip additives
    • More than 25% deviation from new oil baseline typically represent mixing or top-up with a different product
    • Unless a degraded additive drops out of solution, it will still be present and measured
Molybdenum – Exceptions

- **Wear metal**
  - Molybdenum may be used in piston rings and some alloys of steel
    - Proportional increase of molybdenum and iron suggest alloyed part wear
    - Disproportional increase of molybdenum and iron suggest ring/cylinder wear

Courtesy Hot Rod Magazine
Molybdenum – Pitfalls

• **Bad assumption**

  – At one point it was safely assumed that oils with an API Donut that did not indicate “Resource Conserving” were free from friction modifiers, and therefore safe for use in motorcycles and other wet-clutch applications.

  – The requirement is now more complex, so it is possible they still contain friction modifiers.
Silicon – Common Cause

• Dust and/or dirt
  – Silicon is present in dust (silicon dioxide) and dirt (aluminum silicate)
    • Proportional increase of silicon and aluminum is an ~3:1 ratio is indicative of dirt
    • May not correlate with particle depending on manner ingested and system filtration
    • Anomalous silicon without corresponding wear can be due from improper sample taking procedure
Silicon – Exceptions

- **Gasket maker sealant**
  - Silicon is commonly used in sealant
    - Increase in silicon immediately after maintenance activity without corresponding wear

- **Grease contamination**
  - Silicon can be used as a thickener system for grease
    - Some mechanics or millwrights apply grease to parts to aid in reassembly, it is possible residual grease will be measurable
Silicon – Pitfalls

• Contaminant particle size
  – Severe contamination, such as ingestion through missing or loose fill cap or breather, may produce particles too large for detection

• Decreases viewed too positively
  – Without a maintenance activity, such as fluid change or <5 µm filtration, lower than typical values may indicate particle size has increased, suggesting worsening of problem
Boron – Common Cause

- **Additive**
  - Boron soaps are commonly used in detergent additives, and some EP or AW additive chemistries
  - More than 25% deviation from new oil baseline typically represent mixing or top-up with a different product
  - Unless a degraded additive drops out of solution, it will still be present and measured
Boron – Exceptions

• Coolant leak
  – Borate-based inhibitors are used in some coolant formulations
    • Increase in boron, sodium and/or potassium indicates a likely coolant leak
    • Glycol and/or water may not be detected, this suggests a small leak or a top-end (cracked head or head gasket) leak
Boron – Pitfalls

• Cleaners
  – Borate-based cleaners are used in drum and tote recycling programs
    • Inconsistent, yet low, level of boron from new
Lithium – Common Cause

• **Grease contamination**
  
  – Lithium is the most common thickener system for greases
  
  • Some systems have greased seals protecting oil lubricated bearings, it is possible excess grease will migrate into the oil
  
  • Some mechanics or millwrights apply grease to parts to aid in reassembly, it is possible residual grease will be measurable
  
  – No exceptions or pitfalls
Sodium – Common Cause

- Coolant leak
  - Sodium-based inhibitors are used in most coolant formulations
    - Increase in boron, sodium and/or potassium indicates a likely coolant leak
    - Glycol and/or water may not be detected, this suggests a small leak or a top-end (cracked head or head gasket) leak
Sodium – Exceptions

• **Salt**
  - Sodium as a salt may be from nearby saltwater, or possibly from road salt (once dried, can become airborne)
  - Increase in sodium with possible increase in aluminum from salt corrosion

• **Activated Alumina**
  - Some acid scavenging media, e.g. Selexsorb®, is alumina based
  - Proportional increase of sodium and aluminum
  - May not correlate with particle depending on system filtration
Sodium – Pitfalls

• Newer formulations
  – Some newer coolant are formulated without sodium-based inhibitors, therefore a glycol test may not be triggered
Potassium – Common Cause

• Coolant leak
  – Potassium-based inhibitors are used in most coolant formulations
    • Increase in boron, sodium and/or potassium indicates a likely coolant leak
    • Glycol and/or water may not be detected, this suggests a small leak or a top-end (cracked head or head gasket) leak
Potassium – Exceptions

• **Fly ash**
  – Potassium can be found in both wood and coal smoke
    • Potassium particulate is small enough to ingress through breathers

Courtesy Suzy Walton, USDA Forest Service
Potassium – Pitfalls

• **Newer formulations**
  - Some newer coolant are formulated without sodium-based inhibitors, therefore a glycol test may not be triggered

• **Invisible smoke**
  - The source need not be nearby or visible, so long as asset is in fallout zone
## Potential Contaminant Sources

<table>
<thead>
<tr>
<th>Element</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Airborne dirt (correlation ~3:1 Silicon/Aluminum), grease thickener</td>
</tr>
<tr>
<td>Barium</td>
<td>Grease additive</td>
</tr>
<tr>
<td>Boron</td>
<td>Coolant additive, detergent additive, oil drum cleansing agent</td>
</tr>
<tr>
<td>Calcium</td>
<td>Fuller’s earth, dust, gypsum, hard water</td>
</tr>
<tr>
<td>Lithium</td>
<td>Grease thickener</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Fuller’s earth, hard water</td>
</tr>
<tr>
<td>Potassium</td>
<td>Coolant additive, fly ash</td>
</tr>
<tr>
<td>Silicon</td>
<td>Airborne dust or dirt (as above), defoamant additive, sealant</td>
</tr>
<tr>
<td>Sodium</td>
<td>Coolant additive, detergent or dispersant additive, airborne salt</td>
</tr>
<tr>
<td>Titanium</td>
<td>Machinist layout paint, aerosol paint</td>
</tr>
<tr>
<td>Vanadium</td>
<td>Residual fuel contamination (Bunker C)</td>
</tr>
</tbody>
</table>
## Potential Additive Sources

<table>
<thead>
<tr>
<th>Element</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium</td>
<td>Rust Inhibitor, detergent or dispersant additive</td>
</tr>
<tr>
<td>Boron</td>
<td>Anti-wear additive</td>
</tr>
<tr>
<td>Calcium</td>
<td>Detergent or dispersant additive, corrosion inhibitor</td>
</tr>
<tr>
<td>Copper</td>
<td>Anti-wear additive</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Detergent or dispersant additive, corrosion inhibitor</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Friction modifier</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>EP additive, anti-wear additive, corrosion inhibitor</td>
</tr>
<tr>
<td>Silicon</td>
<td>Defoamant additive</td>
</tr>
<tr>
<td>Sodium</td>
<td>Detergent or dispersant additive, corrosion inhibitor</td>
</tr>
<tr>
<td>Zinc</td>
<td>Anti-wear or anti-oxidant additive, rust inhibitor, EP additive</td>
</tr>
</tbody>
</table>