On-site Additive Depletion and Oxidation Monitoring in Turbine Oils by FTIR Spectroscopy

By Christopher Sasso
Out of Lab Product Specialist
Agilent Technologies
FT-IR Spectroscopy Fundamentals

Overview of Antioxidants and Oxidation

Measuring Phenolic and Aminic Antioxidants in Turbine Oil

Relationship Between AO Depletion and Oxidation

Remaining Useful Life Results

- Portable FT-IR
- Other Methods

Contaminant Detection
Portable FT-IR Spectrometers
What is Spectroscopy?

- “Spectroscopy” is the study of how electromagnetic radiation interacts with the atoms and molecules that compose matter.

- “Infrared” spectroscopy is specifically the study of how infrared light (heat) is absorbed by the bonds between atoms that form molecules.
Wavelengths of light in the infrared (heat) region have energies that are on the same order of magnitude as *vibrating bonds* in molecules.

<table>
<thead>
<tr>
<th>Infrared (Molecule Vibration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelengths:</td>
</tr>
<tr>
<td>770 nm – 50 µm</td>
</tr>
<tr>
<td>Wavenumbers:</td>
</tr>
<tr>
<td>12,900 – 200 cm⁻¹</td>
</tr>
</tbody>
</table>

- X-ray (Nuclei)                  
- Ultraviolet (Electron States)  
- Visible (Electron States)      
- Microwave (Rotation)           
- Radio Wave (Nuclear Spin)
Infrared Spectrum

A spectrum is a graph of how much infrared light is *absorbed* by molecules at each *wavenumber* of infrared light.
Infrared Spectrum of Water (H2O)

Antisymmetric stretch: ~3400 cm⁻¹
Symmetric stretch: ~3300 cm⁻¹
Bend: ~1600 cm⁻¹

Wavenumber (cm⁻¹)

Absorbance

Hydrogen
Oxygen

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Simple IR Group Frequency Chart
Hexane

[C – H stretch]

[H – C – H bend]

Wavenumber (cm⁻¹)

Absorbance
Hexanol

![Hexanol molecule](image)

**Absorbance**

**Wavenumber (cm⁻¹)**

- **O – H stretch**
- **C – O stretch**
Hexanal
Hexanoic acid

O – H stretch

C = O stretch

C – O stretch
Specificity of Infrared Spectra

Ephedrine

Pseudoephedrine

![Graph showing infrared spectra of (1R, 2S)-(-)-ephedrine HCl and (1S, 2S)-(+)pseudoephedrine HCl](image)
IR Spectral Overlay of an Additive in an Aromatic Solvent
Calibration Curve for Additive in Aromatic Solvent

R²=1.000
Overview of Antioxidants

Aminic and Phenolic Based Additives

Sulfur based, ZDDP

Function as preservatives

- Prevent oxidation
- Inhibit the oxidation mechanism

Will not reverse oxidation damage

Once consumed oxidation skyrockets
Antioxidants

Phenolic Antioxidants (AO)

- Common in most mineral based lube oils
- Similar in function to natural antioxidants such as vitamin E, (tocopherols)
- Efficient free radical scavengers
- Terminate the oxidation chain reaction
- Sacrificial additive, first to be consumed
- Better performance at low temperatures
Antioxidants

Aminic Antioxidants

- Also common in most mineral based lube oils
- Functions similarly to phenolics, quenches oxidation free radicals
- Synergistic Relationship with phenolic AO
  - Can be recharged by phenolic AO
- High thermal stability
- Performs better than phenolics at high temperatures
Oxidation

Conditions that lead to oil oxidation

- Heat
- Extreme Pressures
- High sheer conditions
- Water
  - Accelerates oxidation by forming peroxides
  - Can cause wash out of antioxidants and other additives
- Metal wear particles
  - Acts as a catalysts that accelerate oxidation
- Electrostatic sparking
  - Introduces nitrates
Oxidation

The Oxidation Chain Reaction

- Held in check by AO
- Skyrockets without AO
  - Exponential growth
  - Hockey stick model
  - Reaches a critical saturation point before taking off

Point of no return

- Adding AO after critical saturation point has little benefit

Varnish consists of mostly oxidation products

- Observed increase in varnish as AO’s are consumed
Measuring Phenolic and Aminic Antioxidants in Turbine Oil

IR bands are distinctive for aminic and phenolic functional groups.

Phenolic functional group creates a sharp band at 3650 cm\(^{-1}\).

Aminic functional group is at 3430 cm\(^{-1}\) (broad), and sharp \(p\)-aromatic at 1510 cm\(^{-1}\).

Multiple bands in the IR spectra for both AO.
Measuring Phenolic and Aminic Antioxidants in Turbine Oil

Phenolic DBPC, di-tertiary-butyl paracresol

Aminic aDPA, alkyl di-phenylamine
Infrared Spectrum of Turbine Oil
Measuring Phenolic and Aminic Antioxidants in Turbine Oil

Quant Validation Plot for Phenolic (ppm)
$R^2=1.000$

Concentration

Absorbance

Wavenumber

Peak Area

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Measuring Phenolic and Aminic Antioxidants in Turbine Oil

Beer’s Law (Absorbance Law): IR absorbance is directly proportional to concentration

$A = abc$

A is Absorbance, $b=$ thickness, $c=$ concentration, $a=$ absorptivity constant

FT-IR measures each AO separately

FT-IR measures all compounds in a mixture at the same time (one spectrum can yield concentrations for dozens of components)
Relationship Between Antioxidant Depletion and Oxidation

Goal: Predict oxidation before the critical saturation point is reached

Performed a modified thermal oxidation stability test (TOST D943)

- Universal Oxidation Test (D6514, D5846)
- Similarity to RPVOT (D2272)
Oxidation Experiment

Started with 250mL used Chevron ISO 32 turbine oil

- heated in a lab oven at 135°C
- Cu and Fe catalysts added

2mL removed and tested every 2-3 days

- Experiment lasted 26 days
- Trended phenolic, aminic and oxidation FT-IR measurements over time
Relationship Between Antioxidant Depletion and Oxidation

Critical Saturation of Oxidation Products
Relationship Between Antioxidant Depletion and Oxidation

Phenolic Diminishes 40% right away

- Evaporation, Low molecular weight flash off
- Aminic stays above 80% until near the end of useful life

Aminic Stages of depletion

- Stage 1: Initial slight increase to 110%
- Stage 2: Mid-way point in oil lifespan, 25% depletion
- Stage 3: Decent from 80% to 40% after phenolic reaches 30%
Relationship Between Antioxidant Depletion and Oxidation

AO levels give a larger window of warning than oxidation alone

- TAN tracks oxidation
- Viscosity tracks oxidation
Relationship Between Antioxidant Depletion and Oxidation

1 Day in the Lab Experiment = 3-6 months in real world oil life (assuming 6-10y oil life)

Rapid oxidation spiked on day 22

- Day 20-21
  - Aminic Rapid decrease
  - Phenolic modest decrease
  - Slight growth in oxidation

Day 22-23 = 1200% increase in Oxidation

- Equal to 400% increase in one month real world in-service oil life
Re-additize, bleed & feed, or top-off at day 19

• Outcome greatly delayed by preventive measures

Aminic perhaps the best indicator for Oxidation

Varnish layer in Day 22 and later samples

• 65-80% more oxidation products in varnish compared to free flowing oil
Oxidation products are complex mixtures

Oxidation carbonyls are the most visible

- 1700-1720 cm⁻¹ region of IR spectrum
  - Ketones
  - Carboxylic Acids
  - Aldehydes
- All contribute to the strong band at 1713 cm⁻¹

\[ \text{Oxidation products} \rightarrow \text{Oxidation carbonyls} \]
Relationship Between Antioxidant Depletion and Oxidation

Oxidation,
Perester,
Organic Carbonate,
Cyclic Anhydride,
Acid Chloride

Oxidation,
Ester

Oxidation Carbonyl,
Ketone, Carboxylic Acid,
Aldehyde

Day 23,
Oxidation

Aminic Antioxidant

Oxidation at Critical Saturation Point (Day 22)

Preventive Action Zone

Wavenumber

Absorbance
Relationship Between Antioxidant Depletion and Oxidation

Ester Oxidation products absorb at 1720-1745 cm\(^{-1}\)

- Shoulders on main COOH and ketone components

1778 cm\(^{-1}\) band likely a perester and/or an organic carbonate
Best practice to save new oil to compare to used in-service oil

- Enables % deletion of additives
- Enables top offs and/or bleed and feed

Agilent Technologies MicroLab Software stores the IR spectrum of new oil

- Overlays new oil spectrum with used oil
- Provides weight percent value for aminic and phenolic antioxidants, Oxidation % of upper limit
Relationship Between Antioxidant Depletion and Oxidation

Yellow “Monitor Frequently” warning when AO’s reach critical depletion points

Red “Change Immediately” warning = critical thresholds reached

Phenolic and aminic are red = critical saturation point is imminent

Water is measured in ppm with yellow at 200ppm and red at 400ppm
# Condition Monitoring Alert Levels

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Current Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (ppm) 0-5000ppm</td>
<td>462</td>
</tr>
<tr>
<td>Phenolic Antioxidant (wt.%) x100</td>
<td>10</td>
</tr>
<tr>
<td>Aminic Antioxidant (wt.%) x100</td>
<td>14</td>
</tr>
<tr>
<td>Oxidation (% of upper limit)</td>
<td>23</td>
</tr>
<tr>
<td>Nitration (% of upper limit)</td>
<td>0</td>
</tr>
</tbody>
</table>
Remaining Useful Life Measurements - Portable FT-IR and Other Methods

Remaining Useful Life (RUL)

- Rotating Pressure Vessel Oxidation Test (RPVOT)
  - Specifically designed to measure RUL
  - Overall quality of oil base stock and additives
  - Accelerates oxidation reaction with heat, pressure, and pure oxygen
  - Requires lab set up
    - Pure Oxygen gas cylinders (highly flammable)
    - Significant sample prep and monitoring
    - Expensive initial costs
Remaining Useful Life Measurements - Portable
FT-IR and Other Methods

RUL by Voltammetry

• Measures antioxidants
  – Not a direct measurement, introduces errors
• Electrochemical Technique: electrodes
  – Current flow relative to applied voltage
• Need new oil to compare to used oil
  – Mixed oil and contaminant interference
  – Wear metals, basic detergents, antifoam, and oxidation products (organic salts) cause interference
Remaining Useful Life Measurements - Portable FT-IR and Other Methods

RUL by Voltammetry

 Require Sample Preparation

- Careful Pipetting
- Extraction step with an electrolyte solution
  - Assumes a constant extraction efficiency
  - Extraction efficiencies are variable for additives in oil
  - Some additives remain in oil = not measured

Voltammetric Electrodes need maintenance

- Cleaning and conditioning in buffer solutions
Remaining Useful Life Measurements- Portable FT-IR and Other Methods

RUL by 4500 Portable FT-IR

- Exact direct measurements
  - Aminic antioxidant wt.%
  - Phenolic antioxidant wt.%
  - Oxidation Products: via carbonyl bands
  - Water (ppm), calibrated to Karl Fischer
  - Nitration Products: occur in electrostatic spark conditions and combustion engine oils
- Single drop of neat oil + ~30 seconds to scan
  - KF precision water requires a stabilizer additive
Remaining Useful Life Measurements- Portable FT-IR and Other Methods

RUL by Portable FT-IR

- No interference by wear metals or other contaminants
- New oil comparison is recommended but not necessary
  - Weight percent values are absolute regardless of mixed oils
- Monitors the effectiveness of top-offs, bleed & feed, filtration, re-additization, and dehydration
Contaminant Detection By Portable FT-IR

Detects common contaminations of oil

- Phosphate ester (EHC) hydraulic in turbine, gear, or mineral based hydraulic fluids
- “Fingerprint” IR bands for EHC
- Cross contamination from filtration & dehydration units
- ID and/or Quantify a range of impurities
  - WD-40 in Hydraulics
  - High particulates like Soot, Dirt, and wear metals
Contaminant Detection By Portable FT-IR

EHC, Phosphate Ester Bands
Methods Development – Portable FT-IR

- Other 4500 FT-IR Water Calibrations
  - Gear Oil
  - EHC hydraulic, phosphate ester based
  - Polyester hydraulic, Quintolub
  - Grease
  - Crankcase oil
- ASTM E-2412 method also available for condition monitoring of mineral oil basestocks
- ASTM D2668 Transformer Oil Phenolic
Conclusions

4500 Portable Full Scanning FT-IR Spectrometers Can Provide:

- Independent phenolic and aminic antioxidant concentrations
- Fast results – helps prevent an unscheduled shutdown
- Eliminates calibrating, maintaining, and conditioning other systems require
- Total analysis time per sample less than 3 minutes, immediately ready for the next sample