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<td>Joseph Mabry</td>
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Sulfur Speciation and Extraction in Jet A

16 August 2015

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Outline

• Background
• Experimental Setup
  – Extraction of sulfur compounds from fuel to alcohol/water extraction fluid
  – Each rinse is continuous mixing followed by phase separation
  – Multiple rinses, each with fresh extraction fluid
• Results and Conclusions
  – Sulfur levels after each rinse determined by GC-SCD analysis
  – Components grouped by elution times and removal rates compared
  – Regressions applied to predict required number of rinses to meet 15 ppm threshold
  – Extraction efficiencies were different across compound spectrum
Background

- Example sulfur compounds present in Jet A:
  - Mercaptans (Thiols)
  - Thiophenes and Benzothiophenes
  - Sulfides

- Detrimental to engine performance: coking, clogging, fouling, and deposits possible
- \( \text{SO}_x \) emissions are an environmental concern
Experimental Setup

• Materials and Data Sources
  – Extraction fluid: denatured ethanol from Fisher Scientific and deionized water
  – Jet A fuel, approximately 500-800 ppm sulfur by weight
  – Data collected with Agilent Technologies 6890N Gas Chromatography System and Agilent Technologies 355 Sulfur Chemiluminescence Detector attachment

• Method of Analysis
  – GC-SCD tests per ASTM D 5623 with slight edits to meet application-specific requirements
  – Calibration of SCD using known-concentration, single-component sulfur compound standards
  – Samples of treated Jet A taken after 1, 2, 3, 4, and 5 consecutive rinses and compared with untreated Jet A
  – Resulting chromatograms analyzed as 7 distinct sections and collectively
Extraction Apparatus

Extraction Fluid Inlet Spray

Hydrophobic / Oleophillic Membrane

Jet A Inlet Spray

Oleophobic / Hydrophillic Membrane

Jet A Outlet

Fuel Phase

Emulsion Phase

Extraction Fluid Outlet

Water (Extraction Fluid) Phase

Figure 1
Sulfur Chemiluminescence Detector

Sulfur compound → SO + H₂O + other products

SO + O₃ → SO₂ + O₂ + hv

Figure 2
Typical Jet A Chromatogram

Figure 3
Rinsed Jet A Chromatogram Overlay

Figure 4
Relevant Calibration Standards

Figure 5

- Diethyl Disulfide
- Benzothiophene
- 3- and 5-methylbenzothiophene
- Diphenyl Sulfide
Partition of Jet A Chromatogram

Figure 6

- Light Component
- Medium-Light Group
- Medium Component
- Medium-Heavy Group
- Heavy Component
- Heavy Group
Benzothiophene Calibration Curve

Figure 7

y = 1458.8x

R² = 0.9823
Methylbenzothiophene Calibration Curve

Figure 8

\[ y = 2458.8x \]
\[ R^2 = 0.9775 \]

SCD Response: Peak Area (15 µVs)
Concentration (ppm by mass)

- 3-methylbenzothiophene
- 5-methylbenzothiophene
Diphenyl Sulfide Calibration Curve

Figure 9

$y = 1029.4x$

$R^2 = 0.9769$

SCD Response: Peak Area (15 µVs) vs. Concentration (ppm by mass)

Concentration (ppm by mass):
- Run 1
- Run 2
- Run 4

Figure 9
Light (Benzothiophene-like) Group Extraction Profile

![Graph showing the extraction profile of light benzothiophene-like groups over multiple passes. The graph plots the equivalent benzothiophene concentration (ppm) against the pass number. The data points are differentiated between treated fuel and shake test results.](image)

**Figure 10**
Heavy (Diphenyl Sulfide-like) Component Extraction Profile

Figure 11

Equivalent Diphenyl Sulfide Concentration (ppm)

Pass Number

-1 0 1 2 3 4 5 6

Treated Fuel
Shake Test
Overall Extraction Profile

Figure 12

Sulfur Species Concentration (ppm)

Pass Number

-1 0 1 2 3 4 5 6

Treated Fuel
Shake Test
# Select Regression Results

<table>
<thead>
<tr>
<th>Light Component</th>
<th>Shake Test Raffinate Ratio</th>
<th>Standard Error</th>
<th>$R^2$</th>
<th>Stages Required for 15 ppm Sulfur</th>
<th>95% Upper Limit</th>
<th>95% Lower Limit</th>
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<tr>
<td></td>
<td>0.82</td>
<td>0.039</td>
<td>0.92</td>
<td>68</td>
<td>110</td>
<td>26</td>
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<tr>
<td>Medium Component</td>
<td>0.60</td>
<td>0.99</td>
<td>0.87</td>
<td>51</td>
<td>71</td>
<td>32</td>
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<tr>
<td>Heavy Component</td>
<td>0.94</td>
<td>0.015</td>
<td>0.98</td>
<td>94</td>
<td>114</td>
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<tr>
<td>Light Group</td>
<td>0.76</td>
<td>0.058</td>
<td>0.88</td>
<td>69</td>
<td>109</td>
<td>28</td>
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<tr>
<td>Medium-Light Group</td>
<td>0.25</td>
<td>0.28</td>
<td>0.87</td>
<td>14</td>
<td>21</td>
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<tr>
<td>Medium-Heavy Group</td>
<td>0.86</td>
<td>0.10</td>
<td>0.86</td>
<td>31</td>
<td>42</td>
<td>19</td>
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<tr>
<td>Heavy Group</td>
<td>0.82</td>
<td>0.21</td>
<td>0.52</td>
<td>26</td>
<td>87</td>
<td>5</td>
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<tr>
<td>Total</td>
<td>0.55</td>
<td>0.13</td>
<td>0.88</td>
<td>34</td>
<td>47</td>
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Table 1
Extraction Models

Figure 13

RMS Relative (Log) Errors:
Speciated + Saturating: 2.4%
Saturating: 3.4%
Speciated: 8.8%
Neither: 10.6%

Total Sulfur (ppm)

Pass Number
Extraction Models

Figure 14

![Graph showing Total Sulfur (ppm) vs. Pass Number for Speciated + Saturating, Saturating, Speciated, and Neither extraction models.](image)

**Figure 14**

**Legend:**
- Blue line: Speciated + Saturating
- Red line: Saturating
- Green line: Speciated
- Purple dotted line: Neither
Summary

To analyze sulfur content, GC-SCD was used. Calibration standards were developed to relate signal output of the device to sulfur concentration, and this relation was then used to quantify the sulfur in samples of Jet A. Samples of the fuel were tested prior to rinsing and after up to 5 consecutive rinses. With consecutive alcohol/water extraction fluid rinses, the sulfur content of Jet A fuel was shown to be reduced significantly.

The resulting Jet A chromatograms were partitioned into seven components and groups to study relative rates of extraction. It is apparent that the spectrum of sulfur-containing compounds in Jet A are not removed at the same rate; generally, the lighter components (those with lower elution times) are more prone to removal than the heavier ones. Saturation also appears to be occurring, restricting extraction efficiency further, especially in higher quantities of consecutive rinses.