GC Analysis of Sulfur Compounds

Emphasis on refinery processes

Phil Streemple Ph.D.
Why is There a Focus on Sulfur?

Sulfur compounds are ubiquitous in refining and petrochemical products.

- Variable in crude oils ranging from ppb level components to wt.% level S
- Sweet vs. Sour Crude oil
- Levels of sulfur in crude oil grow approximately 500 ppm per year, making sulfur management an ever increasing burden.

Sulfur compounds create processing problems for refiners, natural gas, companies, and petrochemical plants and have a negative impact on product quality.
Why Focus on Sulfur Analysis 2

• Sulfur species cause corrosion
  – Higher maintenance costs for pipelines, reactors and furnaces

• Sulfur compounds in intermediates poison catalysts
  – May drastically reduce yield of final product
  – Higher costs for catalysts
  – Higher costs in catalysts regeneration
  – High costs in refinery down time

• All fuel sulfur pollutes the air. Environmental regulations aimed at reducing pollution are requiring lower levels of sulfur in fuels.

• Value of HPI products is related to the presence or absence of sulfur compounds.
Challenges for Sulfur Analysis

- Low levels often require maximum sensitivity
- Matrix interference from the hydrocarbons present
- Highly reactive and polar molecules
Detectors for Sulfur Analysis

Why not use an FID or MSD?
## Sulfur Detection Portfolio

<table>
<thead>
<tr>
<th>Detector</th>
<th>GC-FPD</th>
<th>GC-PFPD</th>
<th>GC-SCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier</td>
<td>Agilent</td>
<td>OI</td>
<td>Agilent</td>
</tr>
<tr>
<td>MDL Sulfur</td>
<td>3.6 pg/sec</td>
<td>1 pg/sec</td>
<td>&lt;0.5 pg/sec</td>
</tr>
<tr>
<td>Selectivity</td>
<td>$10^6$</td>
<td>$10^6$</td>
<td>$10^7$</td>
</tr>
<tr>
<td>Dynamic Range</td>
<td>$10^3$</td>
<td>$10^3$</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Quenching</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Equimolar response</td>
<td>No</td>
<td>No</td>
<td>yes</td>
</tr>
<tr>
<td>Packed Col Compatible</td>
<td>yes</td>
<td>No, &lt; 1ml/min</td>
<td>yes</td>
</tr>
<tr>
<td>Other Elements</td>
<td>P, Sn</td>
<td>P</td>
<td>N</td>
</tr>
<tr>
<td>Cost</td>
<td>$</td>
<td>$$</td>
<td>$$$</td>
</tr>
</tbody>
</table>
## Sulfur Related Analyzers Based on PFD or SCD

<table>
<thead>
<tr>
<th>Method Description</th>
<th>Configuration for Published Methods</th>
<th>How to choose the right solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile sulfur in C2, C3, C4 monomers and LPG</td>
<td>ASTM D6228</td>
<td>• If the matrix is reasonably simple and sulfur levels are in the low ppm to 100 ppb range then the FPD will usually be a good choice.</td>
</tr>
<tr>
<td>Analyzer by FPD</td>
<td></td>
<td>• Ease-of-use</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• The lowest cost of all detectors</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Quenching can be an issue</td>
</tr>
<tr>
<td>Volatile sulfur in NGA, Fuel Gas Analyzer by FPD</td>
<td>ASTM D6228</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur in gas fuels by SCD</td>
<td>ASTM D5504</td>
<td>• For samples where it is not feasible to completely separate sulfur components from the hydrocarbon matrix and low ppb sensitivities are required, the SCD can be considered if experienced users are available.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• A good detector for low-level sulfur, reaching 10 ppb in ideal cases.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• No quenching</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Equimolar response</td>
</tr>
<tr>
<td>Sulfur in light petroleum liquids by SCD</td>
<td>ASTM D5623</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All are available as pre-configured analyzers from Agilent
Sulfur Specific Detectors and Quenching

- **PFPD**
  - Strong disturbance of carrier gas extinguishes flame
    - i.e. by large matrix peak
  - Sensitivity to sulfur is reduced to zero

- **SCD**
  - Detection based on emission of Sulfur specific light
    - Emitted by excited Sulfur dioxide
  - Light is in UV range
    - Potentially absorbed by co-eluting peak
  - Sensitivity is reduced, but not to zero
    - Typically 10-50% reduction

\[
\begin{align*}
R-S-R+ O_2 & \rightarrow SO + Other \text{ Products} \\
SO + O_3 & \rightarrow SO_2 + O_2 + \text{Light (h}, 300-400 \text{ nm)}
\end{align*}
\]
SCD/NCD Components

- Air or Oxygen
- Hydrogen
- Burner
- 7890A GC

Diagram:
- Ozone Generator
- Reaction Cell
- Optical Filter
- Photomultiplier Tube
- Vacuum Pump
Burner Gas Flow Dynamics

Current SCD/NCD

Dual Plasma SCD

Problems can arise here!
SCD for Sulfur Analysis

Basis for several ASTM methods

Very sensitive but….

- Slow to stabilize
- “Tricky” to operate
- Prone to “coking” in the ceramic reaction tubes with resulting costly maintenance and slow recovery (see above)

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D6228</td>
<td>Volatile sulfur in C1, C2, C3 and C4 monomers and LPG</td>
</tr>
<tr>
<td>ASTM D6628</td>
<td>Volatile sulfur in NGA, fuel gas</td>
</tr>
<tr>
<td>ASTM D5504</td>
<td>Sulfur in gas fuels by SCD</td>
</tr>
<tr>
<td>ASTM D5623</td>
<td>Sulfur in light petroleum liquids by SCD</td>
</tr>
</tbody>
</table>
About SCD Maintenance….

Ceramic reaction tube fouling/”coking”

- Price per incident preventative maintenance service call for GC-SCD is expensive.
- Cost of SCD ceramics: G6602-67000, G6602-60037 is also pricey. *Plus* the self repair time of 4 hours and several days to stabilize.
What is Required of GC Column for Sulfur Analysis?

**Response**
- Linearity of response from ppm – ppb
- 100% sulfur recovery

**Stationary phase selectivity**
- Minimal detector quenching
- Low detection limits

**Loadability**
- Large injection volumes
- Low detection limits

**Robust**
- No detector fouling
Introducing DB-Sulfur SCD

A novel optimized low polarity column with low bleed and exceptional inertness to sulfur.

Developed with Dow Chemical and other leading companies in these markets.

Excellent for a broad range of sulfur compounds from light sulfur gasses to sulfur containing hydrocarbons out to C24.

Designed for trace analysis

Optimized for the lowest possible contribution to SCD reaction tube fouling.
Introducing DB-Sulfur SCD Cont.

Easy to change from existing columns but with:

- Greatly improved SCD performance
- Increased stability
- Less frequent burner tube maintenance

<table>
<thead>
<tr>
<th>Part number</th>
<th>Description</th>
<th>Temperature limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3903-63001</td>
<td>DB-Sulfur SCD 60 m, 0.32 mm, 4.2 μm</td>
<td>250-270 °C</td>
</tr>
<tr>
<td>G3903-63002</td>
<td>DB-Sulfur SCD 40 m, 0.32 mm, 0.75 μm</td>
<td>270-290 °C</td>
</tr>
<tr>
<td>G3903-63003</td>
<td>DB-Sulfur SCD 70 m, 0.53 mm, 4.3 μm</td>
<td>250-270 °C</td>
</tr>
<tr>
<td>G3903-63004</td>
<td>DB-Sulfur SCD 40 m, 0.32 mm, 3 μm</td>
<td>250-270 °C</td>
</tr>
</tbody>
</table>

Other configurations are also available by request
DB-Sulfur SCD:
Sulfur standards in Toluene
Good resolution of H$_2$S and COS at room temperature

Thiophene and 2-Methyl-1-propanethiol can be baseline separated

1  Hydrogen sulfide
2  Carbonyl sulfide
3  Methanethiol
4  Ethanethiol
5  Dimethyl sulfide
6  Carbon disulfide
7  2-Propanethiol
8  2-Methyl-2-propanethiol
9  1-Propanethiol
10 Ethyl methyl sulfide
11 Thiophene
12 2-Methyl-1-propanethiol
13 Diethyl sulfide
14 1-Butanethiol
15 Methyl disulfide
16 2-Methylthiophene
17 3-Methylthiophene
18 Diethyl disulfide
19 5-Methylbenzo thiophene
20 3-Methylbenzo(b)thiophene
21 Diphenyl sulfide (Int Std)

Column: Agilent J&W DB-Sulfur SCD, 60 m x 0.32 mm, 4.2 μm (p/n G3903-63001)
Typical Chromatogram of Sulfur Compounds in Light Petroleum Liquids by ATSM D5623

Sulfur Compounds in Gasoline

1. Ethanethiol
2. Dimethyl sulfide
3. Carbon disulfide
4. 2-Propanethiol
5. 2-Methyl-2-propanethiol
6. 1-Propanethiol
7. Ethylmethyl sulfide
8. Thiophene/2-Methyl-1-propanethiol
9. Dimethyl Disulfide
10. 2-Methylthiophene
11. 3-Methylthiophene
12. C2-thiophenes
13. Diethyl disulfide
14. Benzo thiophene
15. C1-benzo thiophenes
16. C2-benzo thiophenes
17. Diphenyl sulfide (Int Std)

... the industry standard
Chromatogram of Sulfur Standards in Toluene with Better Resolution

Oven: 35 °C (3 min), 35 -250 °C @ 5 °C /min, 250 °C (10 min)

1 Hydrogen sulfide
2 Carbonyl sulfide
3 Methanethiol
4 Ethanethiol
5 Dimethyl sulfide
6 Carbon disulfide
7 2-Propanethiol
8 2-Methyl-2-propanethiol
9 1-Propanethiol
10 Ethyl methyl sulfide
11 Thiophene
12 2-Methyl-1-propanethiol
13 Diethyl sulfide
14 1-Butanethiol
15 Methyl disulfide
16 2-Methylthiophene
17 3-Methylthiophene
18 Diethyl disulfide
19 5-Methylbenzothiophene
20 3-Methylbenzo(b)thiophene
21 Diphenyl sulfide
Cracked Gasoline Sample

4A
Cracked gasoline

4B
Sulfur standards
## Individual Sulfur Compounds and Total S in Cracked Gasoline

### Major individual sulfur compounds in cracked gasoline

<table>
<thead>
<tr>
<th>Major Sulfur compounds</th>
<th>Average content (mg/kg)</th>
<th>RSD% (n = 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon disulfide</td>
<td>3.58</td>
<td>2.74</td>
</tr>
<tr>
<td>Thiophene</td>
<td>30.75</td>
<td>4.08</td>
</tr>
<tr>
<td>2-Methylthiophene</td>
<td>8.72</td>
<td>4.34</td>
</tr>
<tr>
<td>3-Methylthiophene</td>
<td>6.98</td>
<td>3.75</td>
</tr>
</tbody>
</table>

### Repeatability data of total sulfur in cracked gasoline

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total sulfur (mg/kg)</th>
<th>Mean</th>
<th>RSD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cracked gasoline</td>
<td>91.46 91.60 100.60 94.89 100.88</td>
<td>95.89</td>
<td>4.84</td>
</tr>
</tbody>
</table>
**DB-Sulfur-SCD: Sulfur Sensitivity**

| Peak No. | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    | 14    | 15    | 16    | 17    | 18    | 19    | 20    |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| S/N      | 3.0   | 3.1   | 2.7   | 4.4   | 2.8   | 2.1   | 2.9   | 3.3   | 3.5   | 3.0   | 3.8   | 3.5   | 6.3   | 3.2   | 4.4   | 6.3   | 3.1   | 2.9   |

Sample: 400 ppb sulfur standard  
Inj. Vol: 1 uL  
Split ratio: 160:1

**Approximately 2.5 pg for each compound on column (calculated)**

Low bleeding at 250 °C
<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>10 ppm RSD%</th>
<th>1 ppm RSD%</th>
<th>0.1 ppm RSD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methyl mercaptan</td>
<td>2.94</td>
<td>4.46</td>
<td>5.12</td>
</tr>
<tr>
<td>2</td>
<td>Ethyl mercaptan</td>
<td>2.53</td>
<td>3.00</td>
<td>4.38</td>
</tr>
<tr>
<td>3</td>
<td>Methyl sulfide</td>
<td>2.53</td>
<td>2.79</td>
<td>4.79</td>
</tr>
<tr>
<td>4</td>
<td>Carbon disulfide</td>
<td>2.13</td>
<td>3.29</td>
<td>5.43</td>
</tr>
<tr>
<td>5</td>
<td>2-Propanethiol</td>
<td>2.49</td>
<td>3.98</td>
<td>4.85</td>
</tr>
<tr>
<td>6</td>
<td>2-Methyl-2-propanethiol</td>
<td>2.89</td>
<td>4.47</td>
<td>4.41</td>
</tr>
<tr>
<td>7</td>
<td>1-Propanethiol</td>
<td>2.81</td>
<td>3.88</td>
<td>4.91</td>
</tr>
<tr>
<td>8</td>
<td>Ethyl methyl sulfide</td>
<td>2.34</td>
<td>4.17</td>
<td>5.24</td>
</tr>
<tr>
<td>9</td>
<td>Thiophene</td>
<td>2.24</td>
<td>3.06</td>
<td>3.49</td>
</tr>
<tr>
<td>10</td>
<td>2-Methyl-1-propanethiol</td>
<td>1.87</td>
<td>2.31</td>
<td>5.86</td>
</tr>
<tr>
<td>11</td>
<td>Diethyl sulfide</td>
<td>2.00</td>
<td>2.97</td>
<td>4.80</td>
</tr>
<tr>
<td>12</td>
<td>1-Butanethiol</td>
<td>2.46</td>
<td>3.36</td>
<td>6.47</td>
</tr>
<tr>
<td>13</td>
<td>Methyl disulfide</td>
<td>3.62</td>
<td>4.15</td>
<td>4.23</td>
</tr>
<tr>
<td>14</td>
<td>2-Methylthiophene</td>
<td>3.59</td>
<td>4.62</td>
<td>5.95</td>
</tr>
<tr>
<td>15</td>
<td>3-Methylthiophene</td>
<td>2.85</td>
<td>3.90</td>
<td>4.90</td>
</tr>
<tr>
<td>16</td>
<td>Diethyl disulfide</td>
<td>2.74</td>
<td>3.16</td>
<td>6.34</td>
</tr>
<tr>
<td>17</td>
<td>3-Methylbenzothiophene</td>
<td>2.48</td>
<td>4.87</td>
<td>5.29</td>
</tr>
<tr>
<td>18</td>
<td>5-Methylbenzo(b)thiophene</td>
<td>2.42</td>
<td>4.25</td>
<td>7.37</td>
</tr>
</tbody>
</table>
DB-Sulfur-SCD: Sulfur Sensitivity

H₂S

COS

2 ppm

<table>
<thead>
<tr>
<th>Compound</th>
<th>S/N</th>
<th>RSD% (N=5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>9.5</td>
<td>3.14</td>
</tr>
<tr>
<td>COS</td>
<td>5.3</td>
<td>3.25</td>
</tr>
</tbody>
</table>
## Linearity

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration Range</th>
<th>Linearity ((R^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulfide</td>
<td>2 - 25 ppm</td>
<td>0.9976</td>
</tr>
<tr>
<td>Carbonyl sulfide</td>
<td>2 - 25 ppm</td>
<td>0.9990</td>
</tr>
<tr>
<td>Methanethiol</td>
<td>0.1 - 10 ppm</td>
<td>0.9987</td>
</tr>
<tr>
<td>Ethanethiol</td>
<td>0.1 - 50 ppm</td>
<td>0.9998</td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td>0.1 - 10 ppm</td>
<td>0.9991</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>0.1 - 10 ppm</td>
<td>0.9990</td>
</tr>
<tr>
<td>2-Propanethiol</td>
<td>0.1 - 50 ppm</td>
<td>0.9999</td>
</tr>
<tr>
<td>2-Methyl-2-propanethiol</td>
<td>0.1 - 10 ppm</td>
<td>0.9989</td>
</tr>
<tr>
<td>1-Propanethiol</td>
<td>0.1 - 10 ppm</td>
<td>0.9990</td>
</tr>
<tr>
<td>Ethyl methyl sulfide</td>
<td>0.1 - 50 ppm</td>
<td>0.9998</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration Range</th>
<th>Linearity ((R^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiophene</td>
<td>0.1 - 50 ppm</td>
<td>0.9997</td>
</tr>
<tr>
<td>2-Methyl-1-propanethiol</td>
<td>0.1 - 10 ppm</td>
<td>0.9991</td>
</tr>
<tr>
<td>Diethyl sulfide</td>
<td>0.1 - 10 ppm</td>
<td>0.9992</td>
</tr>
<tr>
<td>1-Butanethiol</td>
<td>0.1 - 10 ppm</td>
<td>0.9990</td>
</tr>
<tr>
<td>Methyl disulfide</td>
<td>0.1 - 10 ppm</td>
<td>0.9987</td>
</tr>
<tr>
<td>2-Methylthiophene</td>
<td>0.1 - 50 ppm</td>
<td>0.9991</td>
</tr>
<tr>
<td>3-Methylthiophene</td>
<td>0.1 - 50 ppm</td>
<td>0.9996</td>
</tr>
<tr>
<td>Diethyl disulfide</td>
<td>0.1 - 10 ppm</td>
<td>0.9990</td>
</tr>
<tr>
<td>5-Methylbenzothiophene</td>
<td>0.1 - 10 ppm</td>
<td>0.9984</td>
</tr>
<tr>
<td>3-Methylbenzothiophene</td>
<td>0.1 - 50 ppm</td>
<td>0.9988</td>
</tr>
</tbody>
</table>
General SCD System Configuration for Chemical Analysis

Inlet

Pulsed SCD

CFT splitter

FID 710 torr

60 m x 0.32 mm id x 4.3 μm DB-Sulfur SCD

Data courtesy of Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical
Last Three Runs of the Day (n=20, 100 ppmv std)

1. H$_2$S
2. COS
3. CH$_3$SH
4. C$_2$H$_5$SH

Data courtesy of Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical
Sulfides and Thiophenes (n=5)

1. Dimethyl sulfide (100 ppm)
2. Ethyl methyl sulfide (50 ppm)
3. Thiophene (100 ppm)
4. Diethyl sulfide (75 ppm)
5. Dimethyl disulfide (25 ppm)
6. 2-Methyl thiophene (75 ppm)
7. 3-Methyl thiophene (100 ppm)
8. Diethyl disulfide (20 ppm)
9. Benzothiophene (75 ppm)
10. 3-Methylbenzothiophene (100 ppm)

Data courtesy of Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical
Overlay of Chromatograms of 50 ppm $v$ Each of Hydrogen Sulfide, Carbonyl Sulfide, Methyl mercaptan, Ethyl mercaptan and 500 ppm $v$ Each of Hydrocarbons from Methane to Hexane in Nitrogen

1. Hydrogen sulfide
2. Carbonyl sulfide
3. Methyl mercaptan
4. Ethyl mercaptan
5. Methane
6. Ethane
7. Propane
8. Butane
9. Pentane
10. Hexane

Data courtesy of Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical
Chromatogram of Carbon Disulfide and Alkyl mercaptans

Data courtesy of Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical
Chromatogram of Sulfides, Disulfides, Thiophene, Alkyl Thiophenes, Benzothiophene, and Alkyl Benzothiophenes

1. Dimethyl sulfide (100 ppm)
2. Ethyl methyl sulfide (50 ppm)
3. Thiophene (100 ppm)
4. Diethyl sulfide (75 ppm)
5. Dimethyl disulfide (25 ppm)
6. 2-Methyl thiophene (75 ppm)
7. 3-Methyl thiophene (100 ppm)
8. Diethyl disulfide (20 ppm)
9. Benzothiophene (75 ppm)
10. 3-Methylbenzothiophene (100 ppm)

Data courtesy of Jim Luong, Rorida Gras, Myron Hawryluk of Dow Chemical
Chromatogram Volatile Sulfur Odorants in Commercially Available Natural Gas

1. Hydrogen sulfide
2. Methyl mercaptan
3. Tert-butyl mercaptan
4. Methyl ethyl sulfide

1. Methane
2. Propane
3. Iso-butane
4. n-Butane
5. Iso-pentane
6. n-Pentane
7. Hexanes
8. Heptanes

Data courtesy of Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical
Long Term SCD Performance with DB-Sulfur SCD

No observable SCD sensitivity change in subsequent runs

Data courtesy of Jim Luong, Ronda Gras, Myron Hawryluk of Dow Chemical with permission
# DB-Sulfur SCD

<table>
<thead>
<tr>
<th>Feature</th>
<th>Advantage</th>
<th>Customer Benefit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCD Optimized lower bleed</td>
<td>Less ceramic tube fouling</td>
<td>• Increased detector uptime and less maintenance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Lower costs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Improved S response and more accurate data</td>
</tr>
<tr>
<td>High column inertness</td>
<td>Improved linearity and sensitivity</td>
<td>Reliable and accurate ppb level measurements</td>
</tr>
<tr>
<td>Methyl silicone phase selectivity</td>
<td>Identical to standard columns</td>
<td>Easy method upgrade</td>
</tr>
</tbody>
</table>
Application Notes and Literature:

Applications for ASTM D5623 and ASTM D5504
Brochure

“The Analysis of Sulfur Compounds in Petroleum Fraction by Agilent J&W DB-Sulfur SCD Column”
Publication number: 5991-3108EN

Brochure number 5991-2977EN
Inert Flow Path for Trace Analysis with GC-SCD

The opportunity to sell the whole solution

Proprietary innovation in every component
DB-Sulfur SCD Summary

The new Agilent J&W DB-Sulfur SCD with low bleed and inertness can provide:

- Excellent resolution and peak shape
- Excellent linearity at ppm to ppb levels
- Best repeatability
- High sensitivity

All of which are required for dependable sulfur analysis.
Sulfur in Refinery Feeds and Propylene

The boiling point range of the hydrocarbon matrix determines the scope of the sulfur species present.

Sulfur components of concern:
- $\text{H}_2\text{S}$, COS, mercaptans, thiophenes, sulfides, disulfides,

Example: $\text{H}_2\text{S}$, COS and methyl mercaptan in propylene

Polypropylene catalysts are highly sensitive to sulfur poisoning:

Manufactures pay attention to sulfur components at few ppb in propylene.
Introducing the Agilent J&W Select Low Sulfur GC Column

New PLOT column, especially engineered for trace level sulfur in Propylene matrix:

**Inertness**: 100% response for H2S, methyl mercaptan

**Selectivity**: No quenching for COS because of the resolution from propylene

**Stability**: Zero particle shedding. Compatible with FPD, PFPD, SCD, AED

**Dimensions**: one dimension, 60 m x 0.32 mm id  (p/n CP8575)

The new Select Low Sulfur PLOT column is designed to offer high inertness, sensitivity and linearity for low level detection of active sulfur and mercaptans in the HPI market.

The Select Low Sulfur improves data accuracy and can significantly improve propylene yields and reduce catalyst costs providing strong economic value and quality results for lab and process management.
Sulfurs & Propylene on Select Low Sulfur

Select Low Sulfur – 60 m*0.32 mm
Overlay of $\text{H}_2\text{S}$, COS and methyl mercaptan with hydrocarbons

Conditions:
- Column: Select Low Sulfur, 60 m x 0.32 mm
- Temperature: 65 °C
- Carrier Gas: Helium, constant flow 2 mL/min
- Injector: 200 °C
- Detector: PFPD

Note that the hydrocarbon peaks are from the FID
Detector quenching but not interfering with COS quantification

500 ppbv H$_2$S and COS same peak height
High response of H$_2$S

Sulfur Components in Propylene Using PFPD

Technique: GC-PFPD
Column: Agilent J&W Select Low Sulfur, 60 m x 0.32 mm (p/n CP8575)
Oven: 65 °C isotherm
Carrier gas: Helium, constant flow, 2.0 mL/min
Injector: 200 °C, split 1:20
Detector: PFPD, 200 °C
Sample: Propylene matrix containing ~500 ppb H$_2$S, COS, and CH$_3$SH
Injection volume: 1 mL
Injection: Gas sampling valve
Linearity on Select Low Sulfur, PFPD

Linearity on the Select Low Sulfur column of active sulfurs using GC-PFPD

$R^2 = 0.9981$

$R^2 = 0.9977$

$R^2 = 0.9972$

Select Low Sulfur Landing Page:
### Benefits of the Agilent J&W Select Low Sulfur GC Column

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<th>Feature</th>
<th>Advantage</th>
<th>Benefit</th>
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| Inert sulfur column coating                  | Near 100% response for H2S and methyl mercaptan | • Improved accuracy at low ppb levels for active sulfur compounds  
• More control of polymerization and refinery processes |
| Optimized separation between propylene and sulfur compounds | No quenching problems for S specific detectors | Better data for all sulfur compounds in propylene.                                          |
| Every column is tested                       | Consistent column to column performance        | • Reliable and repeatable performance  
• Less system downtime                                                                   |
Summary

Sulfur compounds present challenges, even at low levels, for petroleum processors and downstream chemistry.

Agilent Technologies has introduced two new GC column technologies to improve trace level sulfur analysis:

1. Agilent J&W DB-Sulfur SCD. A column engineered to improve sensitivity and linearity at very low levels while increasing uptime and reducing maintenance for the very selective and sensitive SCD.

2. Agilent J&W Select Low Sulfur. A PLOT column optimized for Propylene analysis with optimized selectivity and inertness to deliver reliable results at low levels.
Select Low Sulfur Resources

Select Low Sulfur landing page


SCD application note:

5990-6989EN

http://www.chem.agilent.com/Library/applications/5990-6989EN.pdf

PFPD application note:

5990-6990EN

http://www.chem.agilent.com/Library/applications/5990-6990EN.pdf

Flyer 5990-7243EN


Workshop talk on Select Low Sulfur

Sulfur Chemiluminescence Detector


Pulsed Flame Photometric Detector

http://www.tau.ac.il/chemistry/amirav/pfpd.shtml