H$_2$S Measurement in Crude

COQA Meeting
March 1, 2012
Houston, TX
H₂S Measurement in Crude

- Project Objectives
  - Testing framework for analysis and sampling
    - Provide most accurate H₂S values
    - Reduce analytical error, technician variability
  - Educate transportation operators
    - H₂S potential of crudes in system
    - Health and safety issues
  - All operators using the same test method and comparing the same data
H$_2$S Measurement in Crude

- Available Testing Methodologies
  - ASTM D5705
    - Easy to perform, low equipment costs
    - Only measures vapor phase H$_2$S
H₂S Measurement in Crude

- Available Testing Methodologies, cont.
  - ASTM D5623
    - Provides speciation between (sulfur compounds)
    - High equipment costs ($80K)
    - Requires experienced technician to operate.
    - Not practical for most terminal operators
H₂S Measurement in Crude

- Available Testing Methodology, cont.
  UOP 163
  - Easy to perform, low equipment costs
  - Data interpretation requires skilled technician
  - Only measures liquid phase H₂S

[Graph showing sulfur measurements: 17ppm and 34ppm]
H₂S Measurement in Crude

- Available Testing Methodology, cont. IP 570
  - Modified for use with Crude Oils
  - Operator independent, little technical training required. NO interpretation required.
  - Measures both liquid and vapor phase H₂S
Method Scope Comparison

- **D5623** – Applicable to distillate, gasoline motor fuels and other petroleum liquids with a FBP <230°C. Range 0.1-100mg/kg

- **D5705** – Applicable to residual fuel oil. Applicable to liquids 5.5 @ 40°C to 50 and 100°C. Range 5-4000ppmv.

- **UOP 163** – Applicable to gasoline, naphtha, light cycle oils, and similar distillates that are liquid at ambient temperature and pressure. Lower quantitation limit is 1.0 mg/kg.

- **IP 570** – Applicable to marine fuels. Range 0-50 mg/kg (Note: Method and instrument has been modified to accommodate for the volatile nature of crude/condensate products to limit the interference from light end components.)
H$_2$S Measurement in Crude

- **Analysis Protocol**
  - As each sample was opened the full set of tests was completed immediately, prior to opening the next sample.
  - Samples were refrigerated until opened.
## Analysis Data

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>ASTM D445</th>
<th>ASTM D5002</th>
<th>ASTM D5191</th>
<th>UOP 163</th>
<th>ASTM D5705</th>
<th>ASTM D5623</th>
<th>IP 570</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Viscosity@20°C</td>
<td>Density @ 15°C</td>
<td>Vapor Pressure</td>
<td>H₂S</td>
<td>Mercaptan</td>
<td>H₂S - Vapor</td>
<td>H₂S</td>
</tr>
<tr>
<td></td>
<td>cSt</td>
<td>kg/m³</td>
<td>DVPE (kPa)</td>
<td>mg/kg</td>
<td>ppmv</td>
<td>mg/kg</td>
<td>mg/kg</td>
</tr>
<tr>
<td>WTS</td>
<td>19.65</td>
<td>877.6</td>
<td>35.1</td>
<td>36</td>
<td>0</td>
<td>1</td>
<td>24.2</td>
</tr>
<tr>
<td>TK 1106</td>
<td>13.82</td>
<td>856.9</td>
<td>16.7</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>15.0</td>
</tr>
<tr>
<td>Peace Sour</td>
<td>4.91</td>
<td>816.2</td>
<td>54.9</td>
<td>110</td>
<td>0</td>
<td>&gt;2000</td>
<td>74.9</td>
</tr>
<tr>
<td>Peace Sour</td>
<td>126</td>
<td>0</td>
<td>&gt;2000</td>
<td>67.6</td>
<td>108.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peace Sour</td>
<td>127</td>
<td>0</td>
<td>&gt;2000</td>
<td>70.8</td>
<td>126.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OSA</td>
<td>6.311</td>
<td>865.2</td>
<td>20.6</td>
<td>0</td>
<td>8</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>Koch</td>
<td>9.392</td>
<td>839.4</td>
<td>57.3</td>
<td>104</td>
<td>0</td>
<td>&gt;2000</td>
<td>76.7</td>
</tr>
<tr>
<td>Koch</td>
<td>105</td>
<td>0</td>
<td>&gt;2000</td>
<td>61.0</td>
<td>247.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Koch</td>
<td>104</td>
<td>0</td>
<td>&gt;2000</td>
<td>52.3</td>
<td>204.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRL-403</td>
<td>1.345</td>
<td>749.7</td>
<td>85.5</td>
<td>26</td>
<td>237</td>
<td>241</td>
<td>17.2</td>
</tr>
<tr>
<td>CRL-403</td>
<td>27</td>
<td>248</td>
<td>295</td>
<td>19.1</td>
<td>16.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRL-403</td>
<td>28</td>
<td>234</td>
<td>268</td>
<td>17.7</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPM-781</td>
<td>1.279</td>
<td>762.2</td>
<td>72.3</td>
<td>16</td>
<td>40</td>
<td>0.5</td>
<td>14.2</td>
</tr>
<tr>
<td>CPM-781</td>
<td>17</td>
<td>38</td>
<td>1</td>
<td>14.2</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPM-781</td>
<td>11</td>
<td>56</td>
<td>2</td>
<td>12.2</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPR-025</td>
<td>1.028</td>
<td>750.3</td>
<td>80.7</td>
<td>34</td>
<td>222</td>
<td>11</td>
<td>17.2</td>
</tr>
<tr>
<td>CPR-025</td>
<td>34</td>
<td>220</td>
<td>12</td>
<td>11.9</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPR-025</td>
<td>34</td>
<td>225</td>
<td>11</td>
<td>13</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
H2S Measurement in Crude

• Potential Interferences
  – Chlorides (halides?)
  – UOP-163 inflection point interpretation
    🌺 Dave to provide copies of inflection curves to all
    🌺 Curves were actually very “clean” and relatively easy to interpret
  – Corrosion inhibitors (nitrogen based)
  – Mercaptans? – D5623 segregates the mercaptans and IP570 VPP development was based on removing mercaptan and light hydrocarbon interferences
  – Scavengers – water based cations? (HS- scavengers retaining partial H2S in “ionic” state)
Follow Up Discussions

- Agreed that future testing would include SAPA (saturates, aromatics, polars, asphaltenes), C30+ compositional analysis, Karl Fischer titration, and nitrogen testing by D4629
- Agreed that future testing would be done on one only sample from the triplicate sample sets
- Agreed that samples to be tested would be CPR (Peace condensate [Enbridge EP], CPM (Pembina Drayton Valley condensate [Enbridge EP]), CRL (Plains Midstream Rangeland condensate [Enbridge EP]), PEM (Pembina sweet crude [Kinder Morgan]), and TK1106 [Coffeyville Resources, KS],
- Agreed to proceed with testing matrix ASAP based on Dave Murray’s estimate of ~$5,000 analytical costs and end of February completion estimate
H2S Measurement in Crude

• Does anyone in COQA audience have any experience/insight that could streamline or focus our efforts??
  – Example: H2S scavengers
    ◆ Are there naturally occurring varieties??
    ◆ Would amine based corrosion inhibitors, “bug killers”, or something else be interfering??

• Please contact Bill Lywood
  ◆ 780-991-9900 or lywood@crudequality.com