MERCURY in U.S. CRUDE OIL

Crude Oil Quality Group
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U.S. Environmental Protection Agency
National Petrochemical and Refiners Association
American Petroleum Institute
Mercury Technology Services
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PURPOSE

- Data will be acquired to estimate the upper limit to atmospheric emissions attributable to petroleum.

- The industry is also interested to develop the science necessary to understand mercury in hydrocarbons and its fate in processing.
OBJECTIVES

- Determine the mean concentration and range of concentrations of mercury in crude oil processed in the U.S.
- Data must be statistically significant
- Sampling and analysis methods must reflect the best science currently available
LABORATORIES

- CEBAM ANALYTICAL (Combustion CVAF)
- FRONTIER GEOSCIENCES (Digestion CVAF)
- U.S. EPA (Combustion CVAF)
- TEXAS A&M (Neutron Activation)
TECHNICAL APPROACH

- Phase 1 – Analytical Methods
- Phase 2 – Sampling Methods and Oil Variability
- Phase 3 – Statistical Sampling and Analysis
170 market-named oils were sampled and analyzed. Oils come from both domestic and foreign sources. Each oil is sampled and analyzed a minimum of 3 times. Inter-laboratory replication - 20%
Mercury in US Crude

Laboratory Comparison

The graph shows a comparison of THg (μg/kg) versus Interlaboratory Mean (μg/kg) for different methods.

- Black circles represent Digestion - AF
- Red circles represent Combustion - AF
Mercury in US Crude

Standard Deviation

\[ s^{os} = 0.44C^{os} + 0.013 \]
\[ (R = 0.85) \]

\( n > 2 \)
Mercury in US Crude

Mean Concentration and Range

Oil Streams
170 data points
Mean - 7.3 μg/kg
Median - 1.5 μg/kg
SD - 46.1 μg/kg
Range - 593 μg/kg
# Mercury in U.S. Crude

<table>
<thead>
<tr>
<th>Country</th>
<th>Country Volume (1000 barrels)</th>
<th>% US Supply</th>
<th>(µg/kg)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Africa</td>
<td>705,714</td>
<td>11.75</td>
<td>2.7</td>
<td>21</td>
</tr>
<tr>
<td>Asia</td>
<td>50,333</td>
<td>0.84</td>
<td>220.1</td>
<td>4</td>
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<tr>
<td>Canada</td>
<td>591,489</td>
<td>9.845</td>
<td>2.1</td>
<td>32</td>
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<tr>
<td>Europe</td>
<td>198,389</td>
<td>3.30</td>
<td>8.7</td>
<td>9</td>
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<tr>
<td>Mexico</td>
<td>585,023</td>
<td>9.74</td>
<td>1.3</td>
<td>9</td>
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<tr>
<td>Middle East</td>
<td>883,946</td>
<td>14.71</td>
<td>0.8</td>
<td>24</td>
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<tr>
<td>S. America</td>
<td>677,169</td>
<td>11.27</td>
<td>5.3</td>
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<tr>
<td>US</td>
<td>2,315,760</td>
<td>38.55</td>
<td>4.3</td>
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<tr>
<td>Total</td>
<td>6,007,823</td>
<td></td>
<td>3.5</td>
<td>170</td>
</tr>
</tbody>
</table>

3.5 ± 0.6
Mercury in U.S. Crude
Volatile Species

Henry’s Constant for Hg⁰ and DMHg in Toluene

\[ K_H = \text{ng/mL (gas)} / \text{ng/mL (liq.)} \]

- \( K_H \) for DMHg (slope = 3372 +/- 191)
- \( K_H \) for Hg (slope = 2539 +/- 1236)
Asphaltene Hg by Differential Solubility

Sediment Mercury
THg Oil – THg Filtered Oil

Asphaltene Mercury
C7 Insoluble & Toluene Soluble

Insoluble Mercury (HgS, HgSe)
C7 Insoluble & Toluene Insoluble
Asphaltene Mercury

Mostly Asphaltene
Asphaltene Mercury

Mostly Soluble (Elemental)
Asphaltene Mercury

Balanced Species

Concentration (µg/kg)

$\theta = 0.78$
Asphaltene Mercury
Asphaltene
Processing Mercury-Laden Crudes

- Water
- Product Quality
- Catalysts
- Waste
- HSE