Hydrogen Sulfide in Petroleum

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Hydrogen Sulfide

- Toxic, Colorless Gas
- Rotten Egg Odor
  - Detectable at >10 ppb
  - Paralyzes olfactory system
  - LC50 = 713 ppm
- Weak Acid, Air Oxidized, Absorbs On Metals
- Solubility Depends On Temperature, Fuel, & Henry’s Law
# Hydrogen Sulfide Toxicity

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Health Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.02</td>
<td>Olfactory Detection Limit</td>
</tr>
<tr>
<td>10</td>
<td>8 Hr Exposure Limit</td>
</tr>
<tr>
<td>15</td>
<td>15 Min. STEL</td>
</tr>
<tr>
<td>100</td>
<td>Common Ship Headspace Spec.</td>
</tr>
<tr>
<td>300</td>
<td>Considered Immediately Hazardous</td>
</tr>
<tr>
<td>713</td>
<td>LC50 Concentration</td>
</tr>
<tr>
<td>1000</td>
<td>Common Tank, Ship Headspace Concentration</td>
</tr>
</tbody>
</table>
Hydrogen Sulfide Concerns

- **Toxic**
  - Employee exposure
    - Storage tanks
    - Barges, ships
- **Corrosive**
  - Fuel specs.
  - Tank roof
  - Pipelines
- **Odor Control**
  - Storage tank vents
  - Sewers
# Odor Issues

## Detection Limits for Common Odorants

<table>
<thead>
<tr>
<th>Odorant</th>
<th>Detection Limit (PPM V/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl Mercaptan</td>
<td>0.0003</td>
</tr>
<tr>
<td>Methyl Mercaptan</td>
<td>0.0008</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>0.002</td>
</tr>
<tr>
<td>Dimethyl Sulfide</td>
<td>0.002</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.05</td>
</tr>
<tr>
<td>P-Xylene</td>
<td>0.05</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.0</td>
</tr>
<tr>
<td>Ammonia</td>
<td>50</td>
</tr>
</tbody>
</table>
**Hydrogen Sulfide**

**Petroleum Streams Where H₂S Found**

- Crude Oil
- Asphalt
- Residual Fuel & Components
- Mid-Distillates & Blend Components
- Gasoline & Blend Components
- Natural Gas, Propane, LPG
Crude Oil

High Sulfur Crudes

- Mexico
  - Maya 100ppm liquid
  - Olmeca 116ppm liquid

- Middle East
  - Eocene 90ppm liquid
  - Ratawi 80ppm liquid

- Africa
  - Soyo 16ppm liquid
H2S Partitioning

- Fuel A: 200 ppm Headspace H2S
- Fuel B: 800 ppm Headspace H2S

- 2 ppm liquid phase H2S content
- 60 F with sample mixing
Partition Coefficients

- **Crude Oil**
  - 80-300 vppm per 1lppm

- **Residual Oil**
  - 80-400 vppm per 1lppm

- **Gas Oil**
  - 30-150 vppm per 1lppm

- **Gasoline**
  - 50-200 vppm per 1lppm
Partitioning of $H_2S$

- 1 ppm in liquid can equate to > 50 ppm in vapor space
- 100 ppm in liquid can equate to 20,000 ppm in vapor space
Hydrogen Sulfide Concentrations

- Levels of H2S Can be Extremely High if Cargoes Are Over Heated
- Eocene Crude H2S Production After Heating 1 Hour @ Specified Temperature
  - 100 Deg. F 400 ppm
  - 200 Deg F 16,000 ppm
  - 300 Deg F >80,000 ppm
Factors Affecting Partitioning

- Temperature
- Viscosity
- Pressure
- Agitation
- Basic compound in oil
HEAD SPACE H2S VARIATION WITH TIME

TIME (HOURS)

VAPOIR SPACE H2S (PPM)
**$H_2S$ Specifications**

- **Regulatory Bodies**
  - LA harbor, < 70 ppm in liquid

- **Terminals**
  - Variable
  - None to 0 ppm
  - 50-200 ppm in vapor typical

- **Processing Facilities**
  - Variable
  - < 50 ppm in Can Test to None

- **Pipelines**
  - Only one encountered, < 50 ppm in can test
Hydrogen Sulfide Test Methods

- **Vapor Space**
  - Gas detection tubes
  - Monitor Electronically

- **Fuel Sample**
  - ASTM D-5705 “Can Test”

- **Liquid**
  - Sparge test,
  - ASTM D-3227, UOP-163
  - New ASTM method
"Can Test" Method

**Advantages**
- Quick & easy
- 1 - 80,000 ppm
- Industry standard

**Disadvantages**
- Loss of H$_2$S
- Poor repeatability & reproducibility
- Results influenced by temp. & shaking

**Steps**
1. Add 500 ml Sample to can
2. Equilibrate Temp. Agitate
3. Measure H$_2$S With Gas Detection Tube
Hydrogen Sulfide Scavengers
D-5705 Test Conditions

- 140 F Test Temp
- 1/2 Full Liter Bottle
- 3 Minutes @ 150 RPM on Orbital Shaker
- Drager Tube Detection
Liquid Phase Sparge Test

- **Multi-step Procedure**
- **Advantages**
  - Results not dependent on temp., vol., etc...
  - Field method
  - Works with a variety of hydrocarbons
- **Disadvantages**
  - Wet chemistry analysis

150°F Water Bath

Nitrogen (150 ml/min.)

GTD* Tube

Stopper

Glass Jar

Total H₂S = (GDT* Reading x 1.42) / Sample wt.

*Gas Detection Tube with n=10 scale
Hydrogen Sulfide Scavengers
Additional Test Methods

- Vapor Space Methods
  - Esso Can Test
  - Shell Can Test
  - Baker Petrolite Can Test

- Liquid Test Methods
  - UOP 163
  - ASTM D-3227
  - ASTM D-6021 (New Method)
H2S Analysis

- Good sampling critical for good results
  - Common mistakes
    - cooling of samples before analysis
    - excessive pouring, transfer of samples
    - storage of oil before analysis
  - Test influences
    - Vapor phase test
      - agitation, temperature, vapor/liquid ratio
    - Liquid phase test
      - coating of electrodes, interferences
Hydrogen Sulfide Scavengers
Hydrogen Sulfide Scavengers
Additive Treatments

- **Chemistry**
  - Oxidizers
  - Neutralizers
  - Reactants

- **Process Considerations**
  - Temperature gradients
  - Weathering
  - Additive mixing
Hydrogen Sulfide Scavengers

Organic Bases

Typically Amines (e.g. MEA)

\[
\text{H}_2\text{S} + \text{Neutralizer} \rightleftharpoons \text{Salt}
\]

- Advantages:
  - Fast reaction
  - No sodium
  - Oil soluble/dispersible

- DISADVANTAGES:
  - Reaction is Reversible
  - Weak acid/base equilibrium
  - Not specific for H\textsubscript{2}S
Hydrogen Sulfide Scavengers
Inorganic Neutralizers

Inorganic Bases: NaOH, KOH Or Blends
\[ \text{H}_2\text{S} + \text{NaOH} \rightarrow \text{Salt} \]

- **Advantages**
  - Fast reaction, cheap
  - Use alone or in combination
  - Thermally stable products (NaHS)

- **Disadvantages**
  - Non-selective for \( \text{H}_2\text{S} \)
    - Ash forming
  - Increases fuel Na content
  - Limited Safe Injection Temperature
H2S REDUCTION WITH CAUSTIC,
50 PPM NaOH

60 MIN REACTION TIME

VAPOR SPACE H2S

FUEL A  FUEL B  FUEL C  FUEL D

INITIAL  FINAL

60 MIN REACTION TIME
EFFECT OF TEMPERATURE AND CONCENTRATION ON CAUSTIC SODA SERVICE APPLICATION

AREA "C"
NICKEL ALLOYS TO BE CONSIDERED IN THIS AREA

AREA "B"
CARBON STEEL
STRESS RELIEVE WELDS & BENDS

AREA "A"
CARBON STEEL
NO STRESS RELIEF NECESSARY

CORROSION DATA SURVEY; NACE, 1968, p 4
**H₂S Scavengers**

**Reactive/Conversion Additives**

**Organic Compounds**

H₂S + Sulfix product → alkyl sulfides (RSR)

**Advantages:**
- Non-reversible
- Selective for H₂S
- Oil Soluble Additives & Rxn. Products
- May be used at high temperature & with caustic

- Rapid reaction
- Wide range of fuels

"Organic Compounds" and "H₂S + Sulfix product → alkyl sulfides (RSR)" refer to the chemical reactions involving H₂S scavengers.
H2S Scavenger Application

- Scavenger/hydrocarbon mixing important
  - Injection quill
  - Injection up-stream of sample point
  - Continuous injection
  - Storage tank mixing, blending

- Transportation vessel effects
  - Steam coils, temperature
  - Compartment seals
  - "Soda bottle" effect