Hydrogen Sulfide (H$_2$S)

Hydrogen Sulfide (H$_2$S) is a very dangerous, toxic, explosive, colorless and transparent gas which can be found naturally in coal pits, sulfur springs, gas wells and as a product of decaying sulfur-containing organic matter. It is also a by-product of crude and other petroleum products.

It can be generated during refining processes, and be released during handling, storage, and distribution. At very low levels (0.0047 PPM), the gas has the characteristic smell of rotten eggs. If the concentration is between 10 – 50 PPM, H$_2$S causes loss of smell, headaches, and dizziness. At concentrations above 300 PPM, exposure to H$_2$S may be fatal.

**TESTING - H2S**

These are the most common methods that AmSpec uses to determine Hydrogen Sulfide Content:

- **D5705** – Hydrogen Sulfide in the *Vapor Phase* above Residual Fuel Oils
- **D7621 (IP 570)** – Hydrogen Sulfide in Fuel Oils – Rapid Liquid Phase Extraction Method
- **UOP 163** – Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration

<table>
<thead>
<tr>
<th>Method</th>
<th>Products</th>
<th>Scope</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>D5705</td>
<td>Residual Fuel</td>
<td>5 to 4000 PPM H$_2$S</td>
<td>Only applicable to liquids with a viscosity of 5.5 mm$^2$/s at 40°C to 50 mm$^2$/s at 100 °C</td>
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<tr>
<td>D7621 (IP 570)</td>
<td>Marine Residual Fuels and Blend Stocks</td>
<td>0.40 – 15.0 PPM H$_2$S</td>
<td>Only applicable to liquids with viscosities up to 3000 mm$^2$/s at 50°C</td>
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<tr>
<td>UOP 163</td>
<td>Gasoline, Naphtha, Light Cycle Oils, and Similar Distillates</td>
<td>1.0 PPM H$_2$S and above</td>
<td>Only applicable to products that are liquid at ambient temperature</td>
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**D5705** – A 1 liter H$_2$S-inert glass test bottle is filled 50% with the fuel oil from a filled H$_2$S-inert glass sample bottle just prior to testing. In the test container, the vapor space above the fuel oil sample is purged with nitrogen to displace air. The test container with sample is heated in an oven to 60°C, and agitated on an orbital shaker at 220 RPM for 3 minutes. A “length of stain” detector tube and hand operated pump are used to measure the H2S concentration in the vapor phase of the test container.
D7621 (IP 570) – A weighed test portion is introduced into a heated test vessel containing a diluent base oil. Air is bubbled through the oil to extract the H₂S gas. The H₂S is passed, with the air, over a detector to enable the H₂S content of the air to be measured and the amount of H₂S in the liquid phase to be calculated.

UOP 163 – The liquid hydrocarbon sample is weighed into isopropyl alcohol containing a small amount of ammonium hydroxide. The solution is titrated potentiometrically with alcoholic silver nitrate using a glass reference and silver-silver sulfide indicating electrode system.

** Please note below, Turnaround Time is defined as the actual length of time, on average, it takes to perform a particular method once the sample has arrived and logged in the lab, and prepared for testing.

<table>
<thead>
<tr>
<th>Method</th>
<th>Phase Tested for H₂S</th>
<th>Turnaround Time</th>
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</thead>
<tbody>
<tr>
<td>D5705</td>
<td>Vapor Phase</td>
<td>10 Minutes</td>
</tr>
<tr>
<td>D7621 (IP 570)</td>
<td>Liquid Phase</td>
<td>30 Minutes</td>
</tr>
<tr>
<td>UOP 163</td>
<td>Liquid Phase</td>
<td>30 Minutes</td>
</tr>
</tbody>
</table>

**Vapor Phase**
The vapor headspace above the liquid that is generated by heating and shaking the sample as described in the method.

**Liquid Phase**
The sample that is treated in accordance with the method.

Residual fuel oils that contain H₂S in the liquid phase can result in hazardous vapor phase levels of H₂S in storage tank headspaces. The vapor phase levels can vary significantly according to the headspace volume, fuel temperature and agitation. Measurement of H₂S levels in the liquid phase provides a useful indication of the residual fuel oil’s propensity to form high vapor phase levels, and lower levels in the residual fuel oil will directly reduce risk of H₂S exposure. The measurement of H₂S in the liquid phase is appropriate for product quality control, while the measurement of H₂S in the vapor phase is appropriate for health and safety purposes.

**TREATMENTS - H₂S Reduction Additives**
The H₂S content of fuels and crude oils can be reduced with chemical additives (such as “H₂S Scavengers”) during transport and blending operations to address safety and product quality concerns. H₂S Scavengers are widely used due to their ability to quickly and irreversibly react H₂S into a safe non-volatile sulfide molecule.

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The fast reaction of H2S Scavengers make them an excellent fit for treatments to reduce H2S during vessel loading / discharges or tank transfers. The irreversible nature of a scavenger reaction is key to ensure the continued safe handling of the treated fuel as it undergoes additional heating and/or transportation.

There are multiple types of chemistries / products available that fall under the “H2S Scavenger” umbrella. The actual chemistry type used will depend on the particular oil being treated and its end use.

The most common H2S treatments occur in residual fuel oils and sour crude oils. In these cases, a triazine-type chemistry is typically used to provide fast reactions at the lowest relative scavenger cost.

Some refineries request that a non-triazine scavenger be used for treated crude oil coming into their facility due to potential corrosive salt formation in the crude distillation unit. In these cases, a glyoxal-based scavenger may be a good solution to provide fast / irreversible H2S reduction and no refinery impacts in terms of corrosive salt formation or nitrogen input to the naphtha hydrotreaters.

A wide variety of other specialized H2S scavengers are also available for naphtha, asphalt or sour water applications.

HANDLING H2S

As previously mentioned, H2S has a very low odor threshold, with its smell being very perceptible at concentrations below 1 part per million (ppm) in air. The odor increases as the gas is more concentrated, with the strong rotten egg smell recognizable up to 30 ppm.

Above this level the gas is reported to have a sickeningly sweet odor up to around 100 ppm. However, at concentrations above 100 ppm, a person’s ability to detect the gas is affected by rapid temporary paralysis of the olfactory nerves in the nose, leading to loss of the sense of smell. This means the gas can be present at dangerously high concentrations with no perceivable odor.

H2S is classed as a chemical asphyxiant, similar to carbon monoxide and cyanide gases. It inhibits cellular respiration and uptake of oxygen, causing biochemical suffocation.

AmSpec issues personal gas detectors to all employees who might encounter H2S. When calibrated correctly and worn properly the detectors will ensure employee safety alerting them to the presence of H2S. They are set to alarm at 10 ppm and must be worn close to the nose and mouth to be effective.

Need more information? Feel free to contact the following AmSpec specialists

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