

### HYDROGEN SULFIDE (H<sub>2</sub>S) AWARENESS PROGRAM

#### PURPOSE

This safety awareness program is intended to provide information to Winger Companies, herein referred to as Winger, employees regarding the potential health effects of Hydrogen Sulfide (H<sub>2</sub>S). Our goal is to ensure our employees have the knowledge they need to work safely and adequate measures can be taken to limit exposures through safe work procedures in the workplace.

#### WHAT IS HYDROGEN SULFIDE (H<sub>2</sub>S)?

Hydrogen sulfide is the chemical compound with the formula  $H_2S$ . It is slightly (20%) heavier than air, has a tendency to settle in low-laying areas, and is readily dispersed by wind movements or currents.  $H_2S$ dissolves in water forming a weak acid (hydro sulfurous acid).  $H_2S$  will be released when in water when agitated making it a dangerous hidden hazard. A mixture of  $H_2S$  and air is explosive. When ignition occurs, the combustion produces irritants and toxic gases, including sulfur dioxide (SO2) which can have an irritating effect on the eyes and lungs and can be fatal.  $H_2S$  attacks most metals, especially in the presence of water, forming sulfides that are usually insoluble precipitates. It is also very corrosive to plastics and tissue.

Hydrogen sulfide is a colorless, very poisonous, flammable, extremely hazardous gas with the characteristic odor of "rotten egg". It occurs naturally in crude petroleum, natural gas, biogas, LPG, volcanic gases, some well waters, and hot springs. Natural gas can contain up to 90%. Hydrogen sulfide often results from the bacterial breakdown of organic matter in the absence of oxygen, such as in swamps and human and animal sewers (e.g., sewage); this process is commonly known as anaerobic digestion. Bacteria found in your mouth and gastrointestinal tract produce hydrogen sulfide from bacteria decomposing materials that contain vegetable or animal proteins. The human body produces small amounts of H<sub>2</sub>S and uses it as a signaling molecule.

Industrial activities that can produce the gas include petroleum/natural gas drilling and refining, wastewater treatment, coke ovens, food processing, tanneries, and kraft paper mills. Hydrogen sulfide can also exist as a liquid compressed gas.

Other names for hydrogen sulfide:

- Dihydrogen monosulfide
- Dihydrogen sulfide
- Hydrosulfuric acid
- Manure gas
- Rotten egg gas
- Sewer gas
- Sour gas
- Stink damp
- Sulfane
- Sulfur Hydride
- Sulfurated hydrogen
- Sulfur hydride
- Swamp gas



Verv Toxic





Dangerous for the Environment



Hydrogen sulfide was used by the British Army as a chemical agent during World War I. It was not considered to be an ideal war gas, but, while other gases were in short supply, it was used on two occasions in 1916.

A dump of toxic waste containing hydrogen sulfide is believed to have caused 17 deaths and thousands of illnesses in Abidjan, on the West Africa coast, in the 2006 Côte d'Ivoire toxic waste dump.

#### PARTICIPANT IN THE SULFUR CYCLE

Hydrogen sulfide is a central participant in the sulfur cycle, the biogeochemical cycle of sulfur on Earth. In the absence of oxygen, sulfur-reducing and sulfate-reducing bacteria derive energy from oxidizing hydrogen or organic molecules by reducing elemental sulfur or sulfate to hydrogen sulfide. Other bacteria liberate hydrogen sulfide from sulfur-containing amino acids; this gives rise to the odor of rotten eggs and contributes to the odor of flatulence.

Sludge from a pond; the black color is due to metal sulfides. As organic matter decays under low-oxygen (or hypoxic) conditions (such as in swamps, eutrophic lakes or dead zones of oceans), sulfate-reducing bacteria will use the sulfates present in the water to oxidize the organic matter, producing hydrogen sulfide as waste. Some of the hydrogen sulfide will react with metal ions in the water to produce metal sulfides, which are not water soluble. These metal sulfides, such as ferrous sulfide FeS, are often black or brown, leading to the dark color of sludge.



#### HOW CAN I BE EXPOSED TO HYDROGEN SULFIDE (H<sub>2</sub>S) GAS?

The main way you can be exposed to hydrogen sulfide gas is by breathing it. You also can be exposed to hydrogen sulfide gas through skin and eye contact. You are also exposed to hydrogen sulfide by the small amount that is produced by bacterial in your mouth and gastrointestinal tract.

Exposure to hydrogen sulfide gas can occur in the home and in the workplace. In the home, exposure may occur because of faulty plumbing. Sewer drains that have dry traps can allow hydrogen sulfide gas to enter the home.

Winger employees can be exposed to hydrogen sulfide while working in areas such as:

- water or waste water treatment plants,
- city manholes and sewers
- sludge lagoons
- > pits, underground shafts and tunnels
- electrical utility vaults
- underground utilities and pipelines
- industrial facilities
- food producing facilities
- piping and corroded pipe repairs (H<sub>2</sub>S is a primary contributor to corrosion in refinery processing units and piping)
- preheat exchangers
- tanks and vessels
- confined spaces
- poorly ventilated spaces
- excavations deeper than 4 feet
- > petroleum and natural gas drilling and refining



> farms with manure storage pits or landfills can be exposed to higher levels of hydrogen sulfide.

Individuals living near a wastewater treatment plant, a gas and oil drilling operation, a farm with manure storage or livestock confinement facilities, or a landfill may be exposed to higher levels of hydrogen sulfide. If you live in a neighborhood near these types of industry, you could be exposed to hydrogen sulfide by breathing the gas released into the air or drinking contaminated water from activities at these facilities.

#### HEALTH EFFECTS OF H<sub>2</sub>S EXPOSURE

Hydrogen sulfide is considered a broad-spectrum poison, meaning that it can poison several different systems in the body, although the nervous system is most affected. The toxicity of  $H_2S$  is comparable with that of hydrogen cyanide. It is both an irritant and a chemical asphyxiant with effects on both oxygen utilization and the central nervous system. Its health effects can vary depending on the level and duration of exposure. The effects can be delayed for several hours, or sometimes several days, when working in low-level concentrations. Repeated or prolonged exposures may cause eye inflammation, headache, fatigue, irritability, insomnia, digestive disturbances and weight loss. Repeated exposure can also result in health effects occurring at levels that were previously tolerated without any effect. In many individuals, permanent or long-term effects such as headaches, poor attention span, poor memory, and poor motor function may occur. No health effects have been found in humans exposed to typical environmental concentrations of hydrogen sulfide at levels of 0.00011 - 0.00033 ppm. Hydrogen sulfide has not been shown to cause cancer in humans and has not been classified for carcinogenicity.

You can smell hydrogen sulfide gas at lower levels than may cause health effects, so smelling the gas does not always mean that it will make you sick. *However, at higher levels (100 ppm – 150 ppm), your nose can become overwhelmed by the gas and you cannot smell it.* A person's ability to detect the gas is affected by rapid temporary paralysis of the olfactory nerves in the nose, leading to a loss of the sense of smell. This means that the gas can be present at dangerously high concentrations, with no perceivable odor. These properties make it extremely dangerous to rely totally on the sense of smell to warn of the presence of hydrogen sulfide gas.

Low concentrations irritate the eyes, nose, throat and respiratory system (e.g., burning/ tearing of eyes, coughing, shortness of breath, and fluid in the lungs). Asthmatics may experience breathing difficulties. These symptoms usually go away in a few weeks after exposure ends. Long-term, low-level exposure may result in bronchitis, pneumonia, pulmonary edema, fatigue, loss of appetite, headaches, irritability, poor memory, dizziness and loss of motor coordination.

Moderate concentrations can cause more severe eye and respiratory irritation, including coughing, difficulty breathing, and pulmonary edema (accumulation of fluid in the lungs), headache, dizziness, nausea, vomiting, staggering and excitability.

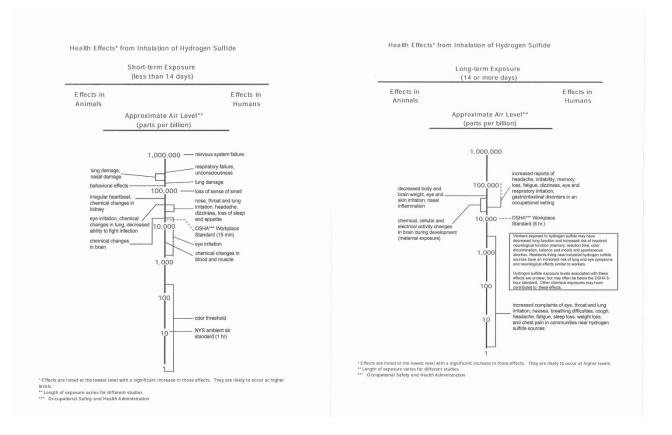
High concentrations (greater than 500 ppm) can cause shock, convulsions, inability to breathe, extremely rapid unconsciousness, coma and death. Effects can occur within a few breaths, and possibly a single breath. This high level of exposure would not be expected in a home, but could occur in a workplace.

Health effect at different exposures:

- 0.00047 ppm or 0.47 ppb is the odor threshold, the point at which 50% of a human panel can detect the presence of the compound.
- 0.0047 ppm is the recognition threshold, the concentration at which 50% of humans can detect the characteristic odor of hydrogen sulfide, normally described as resembling "a rotten egg".
- OSHA has established a permissible exposure limit (PEL)(8 hour time-weighted average(TWA)) of 10 ppm.
- 10–20 ppm is the borderline concentration for eye irritation.



- 20 ppm is the acceptable ceiling concentration established by OSHA.
- 50 ppm is the acceptable maximum peak above the ceiling concentration for an 8 hour shift, with a maximum duration of 10 minutes.
- 50–100 ppm leads to eye damage.
- At 100–150 ppm the olfactory nerve is paralyzed after a few inhalations, and the sense of smell disappears, often together with awareness of danger.
- 320–530 ppm leads to pulmonary edema with the possibility of death.
- 530–1000 ppm causes strong stimulation of the central nervous system and rapid breathing, leading to loss of breathing.
- 800 ppm is the lethal concentration for 50% of humans for 5 minutes exposure (LC50).
- Concentrations over 1000 ppm cause immediate collapse with loss of breathing, even after inhalation of a single breath.
- Although respiratory paralysis may be immediate, it can also be delayed up to 72 hours.



# IS THERE A MEDICAL TEST TO SHOW WHETHER I'VE BEEN EXPOSED TO HYDROGEN SULFIDE?

Hydrogen sulfide can be measured in exhaled air, but samples must be taken within 2 hours after exposure to be useful. A more reliable test to determine if you have been exposed to hydrogen sulfide is the measurement of the sulfate levels in urine. This test must be done within 12 hours of exposure. Both tests require special equipment, which is not routinely available in a doctor's office. Samples can be sent to a special laboratory for the tests. These tests can tell whether you have been exposed to hydrogen sulfide, but they cannot determine exactly how much hydrogen sulfide you have been exposed to or whether harmful effects will occur.



A simple diagnostic clue of extreme poisoning by  $H_2S$  is the discoloration of copper coins in the pockets while working. Treatment involves immediate inhalation of amyl nitrate, injections of sodium nitrite, inhalation of pure oxygen, administration of bronchodilators to overcome eventual bronchospasm, and in some cases hyperbaric oxygen therapy.

#### HOW CAN I REDUCE MY EXPOSURE TO HYDROGEN SULFIDE (H<sub>2</sub>S) GAS?

Exposure to hydrogen sulfide gas can be reduced or prevented by ensuring that plumbing fixtures and pipes are installed and maintained properly. In homes where hydrogen sulfide gas is present, you can reduce the level of gas by locating and eliminating the source. If you live in a neighborhood impacted by industrial emissions of hydrogen sulfide, go inside and close doors and windows when odors are strong outside. When outdoor odors are high, you also may want to avoid outdoor activities such as jogging or yard work.

Workers who may be exposed to hydrogen sulfide gas should follow the guidelines established by the U.S. Occupational Safety and Health Administration (OSHA). OSHA has established confined space entry standards to prevent death from exposure to chemicals like hydrogen sulfide gas.

OSHA has set an acceptable ceiling limit for hydrogen sulfide of 20 parts hydrogen sulfide per 1 million parts of air (20ppm) in the workplace.

The National Institute for Occupational Safety and Health (NIOSH) recommends a 10 minute ceiling of 10 ppm in the workplace.

#### SAFE WORK PRACTICES

Wherever possible, exposure should be minimized by implementing adequate engineering controls and safe work practices. Our projects are typically multi-employer worksites. Communication must be made with the host facility to ensure our employees are not exposed to the above recommended levels. This will be performed during pre-job meetings, pre-job hazard identification, and at the direction of customer facilities. The job supervisor must access the work site to determine the risks associated with the work tasks. All Winger employees must be aware of site specific contingency and emergency plans.

Before entering areas where hydrogen sulfide may be present:

- 1. Air must be tested for the presence and concentration of hydrogen sulfide by a qualified person using air monitoring equipment, such as hydrogen sulfide detector tubes or a multi-gas meter that detects the gas. Testing should also determine if fire/explosion precautions are necessary.
- 2. The space/area must be ventilated continually to remove the gas.
- 3. If the gas cannot be removed, the person entering the space/area must use appropriate respiratory protection and any other necessary personal protective equipment, rescue and communication equipment.

OSHA's Confined Spaces standard contains specific requirements for identifying, monitoring and entering confined spaces. Follow the Winger Confined Space Program.

Extra precautions must be made in any area that would qualify for low lying areas such as below ground levels of waste water treatment buildings. Even though these areas are not confined spaces, we must make every attempt to ensure our employees do not succumb to over exposure of hydrogen sulfide. One



of the ways we achieve this is to have an employee monitor the air while other employees are in the basement performing their work task.

Should an alarm sound on an H<sub>2</sub>S detector, immediately evacuate the area and notify your supervisor. Also, immediately notify your foreman and safety director if you feel you have been exposed to or are developing potential signs or symptoms of hydrogen sulfide exposure.

Procedures in the event of a hydrogen sulfide release that requires evacuation:

- 1. Hold your breath and quickly leave the area containing H<sub>2</sub>S. Do NOT inhale.
- 2. Move quickly upwind. Always be conscious of the wind and constantly monitor wind direction. Wind socks and streamers show which direction the wind is blowing so that you can determine the proper safe breathing area.
- 3. Report to the designated muster point for head count.
- 4. Do NOT return to work area until it has been determined safe for re-entry.

## ENTERING DANGEROUS H<sub>2</sub>S ATMOSPHERES A LEVEL OF H<sub>2</sub>S GAS AT OR ABOVE 100 PPM IS IMMEDIATELY DANGEROUS TO LIFE AND HEALTH (IDLH)

No entry into and IDLH atmosphere will be made by a Winger employee. Winger employees are not trained in the use of self-contained breathing apparatus (SCBA) or rescue training.

NEVER attempt a rescue in an area that may contain hydrogen sulfide without using appropriate respiratory protection and without being trained to perform such a rescue. Many would be rescuers have died as a result to the same high levels as their downed co-workers. Do not become a casualty.

Entry into IDLH atmospheres can only be made using:

- 1) a full facepiece pressure demand self-contained breathing apparatus (SCBA) with a minimum service life of thirty minutes, or
- 2) a combination full facepiece pressure demand supplied-air respirator with an auxiliary selfcontained air supply.

If  $H_2S$  levels are below 100 ppm, an air-purifying respirator may be used, assuming the filter cartridge/canister is appropriate for hydrogen sulfide. A full facepiece respirator will prevent eye irritation. If air concentrations are elevated, eye irritation may become a serious issue. If a halfmask respirator is used, tight fitting goggles must also be used. Workers in areas containing hydrogen sulfide must be monitored for signs of overexposure.

#### WINGER MULTIGAS DETECTORS

Winger uses portable MSA Orion and Altair Multigas detectors. These multigas detectors have 4 sensors installed that will detect oxygen (O2), carbon monoxide (CO), lower explosive limits (LEL) and hydrogen sulfide (H<sub>2</sub>S). The MSA Altair 5 Multigas detector also has an additional sulfur dioxide (SO2) sensor. Multigas air monitors will ONLY detect the type of chemical or component of that particular sensor they are installed with. For instance, for ammonia, you would need an air monitor with an ammonia sensor installed in it. Winger MSA Multigas detectors with hydrogen sulfide sensors are designed to alarm at pre-set low alarm levels of 10 ppm.



WARNING: If the Toxic Gas alarm condition is reached while using the instrument as a personal or area monitor, leave the area immediately as the ambient condition has reached a preset alarm level. If using the instrument as an inspection device, do not enter the area without proper protection. Failure to follow this warning will cause over-exposure to toxic gases, which can result in serious personal injury or death.

#### **PERSONAL PROTECTIVE EQUIPMENT & RESPIRATORY PROTECTION**

It is important to know that the respirators that Winger provides, at no cost to the employee, are the MSA 3200 full face respirator with MSA GME P100 cartridges. These cartridges have the warning: "*Do not wear for protection against organic vapors with poor warning properties or those which generate high heats of reaction with the sorbent material in the cartridges and are to be used for escape use only*".

Protective Engineering controls and work practices are generally sufficient to reduce exposures to at or below the PEL/STEL without the use of respirators. Where an area has been determined to be contaminated with hydrogen sulfide, work will be stopped until further evaluation and engineering practices can be implemented to prevent further exposure to Winger employees.

#### FIRST AID

Eye: PERSONS WITH POTENTIAL EXPOSURE TO HYDROGEN SULFIDE SHOULD NOT WEAR CONTACT LENSES. Flush eyes with large amounts of water for at least 15 minutes, holding eyelids open to ensure adequate rinsing. If irritation persists, seek immediate medical attention.

Skin: Remove contaminated clothing and flush affected area with large quantities of water. If irritation persists or symptoms occur, seek medical attention.

Ingestion: Not anticipated; product is a gas.

Inhalation: PROMPT REMOVAL FROM THE CONTAMINATED AREA TO FRESH AIR AND IMMEDIATE MEDICAL ATTENTION IS MANDATORY IN ALL CASES OF OVEREXPOSURE. If breathing has stopped, perform CPR. Keep the affected person warm and at rest until medical personnel arrive.

#### TRAINING DOCUMENTATION

All Winger employees, that perform work activities where the potential of exposure to hydrogen sulfide may be present, will be provided awareness training in this program in order to be familiar with the potential hazards and proper safe work procedures. These standards are designed to protect anyone who could be exposed and suffer serious health consequences. Training records will be kept in the employee's safety training files at the Winger main office in Ottumwa, Iowa.



### **SOURCE CREDITS**

U.S. Department of Labor Occupational Safety and Health Administration (OSHA) <u>www.osha.gov</u> Agency for Toxic Substances and Disease Registry (ATSDR) <u>www.atsdr.cdc.gov</u> Airgas Hydrogen Sulfide Safety Data Sheet <u>http://en.wikipedia.org/wiki/Hydrogen\_sulfidehttp://en.wikipedia.org/wiki/Hydrogen\_sulfide</u> Wagner-Meinert LLC (WMI) Environmental Management Alternatives (EMA Industrial) Safety Directory, <u>www.safetydirectory.com</u> Illinois Department of Public Health, Division of Environmental Health

#### **DOCUMENT CONTROL**

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