

Hydrogen Sulfide (H₂S)

Introduction

Hydrogen sulfide (H₂S) presents a potential hazard to workers at the work site. It usually occurs as an unwanted by-product and can result in worker exposure in many different industries or occupations. To ensure protection against exposure to H₂S, Hilscher-Clarke has established this policy and procedure. In order to ensure protection against exposure to H₂S, employees shall be made aware of its properties, how it affects the body and what to do in emergency situations. The Safety Manager shall ensure that all personnel who will, or have the potential for, exposure to H₂S at the job site are properly trained in H₂S awareness and established contingency procedures.

Occurrence of Hydrogen Sulfide

Hydrogen sulfide (H₂S) is a naturally occurring component of crude oil and natural gas. Petroleum oil and natural gas. As a result oil and gas operations may emit hydrogen sulfide, routinely or accidentally during the extraction, storage, transport, or processing stage. During extraction hydrogen sulfide may be released into the atmosphere at wellheads, pumps, piping, separation devices, oil storage tanks, water storage vessels, and during flaring operations. Normally flares burn gases at points in the system where operating problems may occur, as a safety measure. Because it cannot be sold, hydrogen sulfide is routinely flared. Sulfur dioxide (SO₂) is the product of combusting hydrogen sulfide, but in the event of incomplete combustions, H₂S may be emitted into the atmosphere.

The EPA reports that most accidental releases of H₂S (i.e., reported) are a result of well blowouts, line releases, extinguished flares, collection of H₂S in low lying areas, line leakage, and leakage from idle or abandoned wells. These releases may not only affect employees, but the general public. Well blowouts are uncontrolled releases from wells and can occur during drilling, servicing, or production, as a result of a failed "blowout preventer" during drilling or a failed subsurface safety valve during production. Additionally, H₂S may be routinely or accidentally released into the atmosphere at oil refineries and natural gas processing facilities, including desulfurization plants.

Hydrogen sulfide is also a by-product produced by the putrefaction of organic matter and may accumulate in sewers, sewage treatment plants or hide storage pits in the tanning industry. Tunnel workers, as well as miners, may be exposed when underground pockets of hydrogen sulfide.

Hydrogen sulfide may be used in the manufacture of inorganic sulfides, sulfuric acid and mercaptans.

Definitions

Acceptable ceiling concentration: airborne concentration that should not be exceeded at anytime during an 8-hour shift.

Acceptable maximum peak concentration: The maximum airborne concentration allowed over a short time period if there is no other measurable exposure over any 8-hour shift.

Container: any barrel, bottle, can, cylinder, drum, reaction vessel, storage tank, or the like, but does not include piping systems.

Emergency: any occurrence such as equipment failure, rupture of containers, or failure of control equipment that may or does result in an unexpected significant release of hydrogen sulfide.

Employee exposure: exposure to airborne hydrogen sulfide that would occur if the employee were not using respiratory protective equipment.

Permissible Exposure Limit (PEL): the OSHA limit for exposure to airborne hazards.

Route of exposure: the route by which air contaminants enter the body. Exposure routes include inhalation, ingestion or skin absorption.

Short Term Exposure Limit (STEL): airborne concentration measured over any 15 minute time period.

Time-weighted Average (TWA): airborne concentration averaged over an 8-hour time period.

Responsibilities

The **Safety Manager** shall:

- Issue and implement this program and ensure that it meets applicable requirements.
- Implement and enforce Hilscher-Clarke's Confined Space Entry Program according to OSHA CFR 29 1910.146 and host employer requirements and standards.
- Provide Hazard Communication training for hydrogen sulfide.
- Implement engineering and work practice controls to prevent exposure to hydrogen sulfide.
- Provide appropriate personal protective equipment for exposed employees.
- Maintain exposure monitoring records according to the recordkeeping section of this program.

Supervisory Personnel shall:

- Know and understand the hazards of hydrogen sulfide exposure.
- Comply with the Hilscher-Clarke's Confined Space Entry Program
- Comply with all engineering and work practice controls in place to prevent hydrogen sulfide exposure
- Ensure the availability and use of appropriate ANSI & NIOSH approved personal protective equipment for all exposed employees.

Employees will:

- Comply with all aspects of this hydrogen sulfide exposure control program.
- Comply with Hilscher-Clarke's Confined Space Entry Program.
- Attend scheduled Hazard Communication Training and Confined Space Entry training.
- Use engineering and work practice controls in place to prevent hydrogen sulfide exposure.
- Use and maintain all issued personal protective equipment as necessary to prevent hydrogen sulfide exposure.

Characteristics of Hydrogen Sulfide

Hydrogen sulfide (H₂S) is a colorless gas with a powerful nauseating smell of rotten eggs. The odor is a poor warning property because hydrogen sulfide exposure quickly deadens the sense of smell. The gas is heavier than air and may collect in low areas such as sewers, pits, tunnels or gullies. High airborne levels of hydrogen sulfide (between 4.3 and 46.0 percent of gas by volume in the air) may catch fire if there is a source of ignition. If the gas is burned, toxic products such as sulfur dioxide will be formed. Hydrogen sulfide is incompatible with oxidizing agents, such as nitric acid and chlorine trifluoride, and may react violently or ignite spontaneously.

The physical characteristics of Hydrogen sulfide gas are below:

H ₂ S Characteristic	
Chemical Symbol	H ₂ S
Color	Colorless
Odor	"Rotten eggs" (detectable at 10 ppb)
Specific Gravity	1.192 (heavier than air)
Explosive Limits	Lower 4%, Upper 44% volume in air
Toxicity	Highly Toxic
Flammability	Flammable
Solubility	0.4%
Incompatibilities	Strong oxidizers, strong nitric acid, metals

Health Effects on the Body:

Hydrogen sulfide is extremely toxic. It may cause death instantaneously in high airborne concentrations. Low levels may be extremely irritating to the lungs, nose, throat and eyes.

Hydrogen sulfide can be detected by smell at levels as low as 0.13 parts hydrogen sulfide per million parts air (ppm). Odor cannot be used as a warning because the gas can deaden the sense of smell within 2 to 15 minutes in exposures of approximately 100 ppm. A single breath of hydrogen sulfide at about 1000 ppm may paralyze the respiratory system and result in coma and death. Convulsions may also occur. Prolonged exposure at about 250 ppm hydrogen sulfide may cause the lung tissue to swell and fill up with water (pulmonary edema).

This effect may occur after the exposed worker recovers from the irritant effects of the gas. Exposures of 20 to 50 ppm hydrogen sulfide for one hour may cause inflammation of the cornea and the delicate lining of the eye and eyelid (a condition called keratoconjunctivitis). Exposures for long periods at 50 ppm may cause severe irritation of the nose, throat and lungs. Workers exposed to lower concentrations of hydrogen sulfide may develop headaches, eye disorders and chronic bronchitis.

Physiological Response	
10 ppm	Beginning eye irritation
50-100 ppm	Slight conjunctivitis and respiratory tract irritation after 1 hour exposure
100 ppm	Coughing, eye irritation, loss of sense of smell after 2-15 minutes. Altered respiration, pain in the eyes and drowsiness after 15-30 minutes followed by throat irritation after 1 hour. Several hours exposure results in gradual increase in severity of these symptoms and death may occur within the next 48 hours.
200-300 ppm	Marked conjunctivitis and respiratory tract irritation after 1 hour of exposure
500-700 ppm	Loss of consciousness and possibly death in 30 minutes to 1 hour.
700-1000 ppm	Rapid unconsciousness, cessation of respiration and death.
1000-2000 ppm	Unconsciousness at once, with early cessation of respiration and death in a few minutes. Death may occur even if individual is removed to fresh air at once.

Monitoring

Each employee shall be issued a personal hydrogen sulfide detection monitor with an audible alarm preset for 10 ppm. At no time shall the PAM's be preset to exceed 20 ppm.

Monitoring for airborne concentrations of hydrogen sulfide at Hilscher-Clarke work sites is conducted using a four-gas meter and accomplished using the procedures detailed in the Confined Space Entry Program.

- Area four gas monitors will be set to alarm when airborne hydrogen sulfide concentrations exceed the OSHA STEL limit of 20ppm.
- Hilscher-Clarke employees will not work in areas with airborne concentrations above OSHA Permissible Exposure Limits.
- If circumstances require an exception to the above, NIOSH approved self contained breathing apparatus or air-supplied respirators will be used.
- In confined spaces, hydrogen sulfide hazards will be controlled in accordance with Hilscher-Clarke's Confined Space Entry program. Controls include but are not limited to dilution, ventilation, forced air ventilation and the use of NIOSH approved respiratory protection (SCBA and air supplied only).

- Other safety precautions include:
 - Whenever a PAM or four-gas monitor alarms leave the area immediately to a designated fresh air area and do not reenter until conditions are proven safe or appropriate respiratory protection is donned.
 - Upon commencing operations at a work site, obtain, know and understand the host facility's contingency plan. This will be reviewed at each individual work site within the host facility as the evacuation route and meeting point may vary with each location.

Training

- Hilscher-Clarke employees will be trained in the hazards and safe control of hydrogen sulfide exposure using the training materials included in this program.
- Training is documented according to the recordkeeping section of this program as well as the recordkeeping sections of the Hazard Communication Program and Confined Space Entry programs.
- Hilscher-Clarke employees will be trained for safe confined space entry according to the implemented Confined Space Entry Program.

Recordkeeping

- Training records included in this program are retained with and according to the requirements of the Hilscher-Clarke Hazard Communication Program.
- Confined Space Entry training records are kept according to the Confined Space Entry Program.
- Hydrogen sulfide monitoring results are documented and retained according to the Hilscher-Clarke Confined Space Entry Program.



Hydrogen Sulfide (H₂S)

Instructor Name (please print):	Instructor's Signature:	Date of Training:	
Training Roster			
Employee I.D. #	Name (Please Print)	Signature	Job Title
Summary of Training Session			
(Check all categories presented during training/retraining)			
	The occurrence of Hydrogen Sulfide – Production processes, decay of organic material, natural gas production, refinery processes		
	Properties of Hydrogen Sulfide		
	Routes of exposure and OSHA exposure Limits		
	Host Employers Emergency Contingency Plan – Routes of evacuation, meeting place		
	Respiratory protection		
	Hilscher-Clarke's Confined Space Program		
	Monitoring H ₂ S levels; Placement of PAM's		
	Health effects of exposures to H ₂ S		
	Question and Answers.		
Please list materials passed out, media and video presented, and any pertinent lectures or materials:			

Hydrogen Sulfide H₂S Personal Air Monitors (PAM) Marathon SPI - 73A

Hydrogen sulfide is a colorless, flammable, extremely hazardous gas with a "rotten egg" smell. It occurs naturally in crude petroleum and natural gas, and can be produced by the breakdown of organic matter and human/animal wastes (i.e., sewage). It is heavier than air and can collect in low-lying and enclosed, poorly ventilated areas such as trenches, manholes, sewer lines and underground telephone/electrical vaults

Detection by Smell

- ▶ Can be smelled at low levels, but with continuous low level exposure or at higher concentrations you lose your ability to smell the gas even though it is still present.
- ▶ At high concentrations - your ability to smell the gas can be lost instantly.
- ▶ **DO NOT** depend on your sense of smell for indicating the continuing presence of this gas or for warning of hazardous concentrations.

Responsibilities

- ▶ All personnel entering PPE Designated Areas are required to wear a H₂S PAM and respond accordingly if it alarms. You are also required to ensure that your H₂S Pam is bump tested and recorded monthly and that you "check" your monitor at a minimum pre-shift (i.e., daily). If you have any questions or problems with your H₂S Pam do not use it. Contact your supervisor or our on-site safety person immedi-

ately, explain your concerns and have them re-issue you another H₂S PAM.

- ▶ Likewise, our organization will maintain an adequate supply of spare H₂S PAMs and manage the monthly bump testing and required record-keeping.

Required Response to Alarm

- ▶ If a H₂S PAM alarms, personnel in the immediate areas shall evacuate immediately to a safe distance and notify the area operator. **DO NOT** return to the work area without prior approval from the area operator.
- ▶ For re-entry after an alarm, the area atmospheric conditions must be verified by Operations, Product Control, or Safety personnel wearing proper PPE and approved for re-entry before personnel can return to the area where the alarm occurred.
- ▶ All credible (non-interference H₂S PAM alarm and fixed area H₂S monitor alarm events shall be reported to the Shift Supervisor to generate a refinery Incident Report prior to the end of the shift. Witness statements shall be completed by those personnel involved with the alarm event. The peak exposure value shall be collected from the effected employee's H₂S PAM and be documented in the Refinery Incident Report.
- ▶ After an exposure your H₂S PAM must be bump tested prior to being returned to service.

Concentration (ppm)	Health Effect
0.01—0.3	Odor Threshold
1-20	Offensive odor, possible nausea, tearing of the eyes or headaches with prolonged exposure.
20-50	Nose, throat and lung irritation; digestive upset and loss of appetite; sense of smell starts to become fatigued; acute conjunctivitis may occur (pain, tearing & light sensitivity)
100-200	Severe nose, throat and lung irritation; ability to smell odor completely disappears.
250-500	Pulmonary edema (build up of fluid in the lungs).
500	Severe lung irritation, excitement, headache, dizziness, staggering, sudden collapse, unconsciousness and death within a few hours, loss of memory for the period of exposure. the lungs)
500-1000	Respiratory paralysis, irregular heart beat, collapse and death without rescue.
>1000	Rapid collapse and death.

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