

Occupational Health Guideline for Hydrogen Sulfide

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: H₂S
- Synonyms: Sulfuretted hydrogen; hydrosulfuric acid; hepatic gas
- Appearance and odor: Colorless gas with a strong odor of rotten eggs. The odor of this gas should not be used as a warning, since its presence may deaden the sense of smell. Hydrogen sulfide can also exist as a liquid at low temperature and high pressure.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for hydrogen sulfide is a ceiling level of 20 parts of hydrogen sulfide per million parts of air (ppm) or a maximum allowable peak of 50 ppm for 10 minutes once, if no other measurable exposure occurs. NIOSH has recommended that the permissible exposure limit be reduced to 15 mg/m³ (10 ppm) averaged over a 10-minute period, and that work areas in which the concentration of hydrogen sulfide exceeds 70 mg/m³ be evacuated. The NIOSH Criteria Document for Hydrogen Sulfide should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- Routes of exposure
Hydrogen sulfide can affect the body if it is inhaled or if it comes in contact with the eyes, skin, nose or throat. It can also affect the body if it is swallowed.

- Effects of overexposure

1. *Short-term Exposure:* Inhalation of high concentrations of hydrogen sulfide vapor may cause loss of consciousness and death. Inhalation of lower concentrations may cause headache, dizziness, and upset stomach. Exposure to hydrogen sulfide can cause temporary loss of the sense of smell, and irritation of the eyes, nose, or throat.

2. *Long-term Exposure:* Not known.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to hydrogen sulfide.

- Recommended medical surveillance

The following medical procedures should be made available to each employee who is exposed to hydrogen sulfide at potentially hazardous levels:

1. *Initial Medical Examination:*

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the eyes and lungs should be stressed.

—Eye disease: Hydrogen sulfide is a severe eye irritant and may cause tissue damage. Those with pre-existing eye problems may be at increased risk from exposure.

—14" x 17" chest roentgenogram: Hydrogen sulfide may cause human lung damage. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Hydrogen sulfide is a respiratory irritant. Persons with impaired pulmonary function may be at increased risk from exposure. Periodic surveillance is indicated.

2. *Periodic Medical Examination:* The aforementioned medical examinations should be repeated on an annual basis, except that an x-ray is considered necessary only when indicated by the results of pulmonary function testing, or by signs and symptoms of respiratory disease.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

- **Summary of toxicology**

Hydrogen sulfide gas is a rapidly acting systemic poison which causes respiratory paralysis with consequent asphyxia at high concentrations. It irritates the eyes and respiratory tract at low concentrations. Inhalation of high concentrations of hydrogen sulfide, 1000 to 2000 ppm, may cause coma after a single breath and may be rapidly fatal; convulsions may also occur. Exposure to concentrations of hydrogen sulfide above 50 ppm for one hour may produce acute conjunctivitis with pain, lacrimation, and photophobia; in severe form this may progress to keratoconjunctivitis and vesiculation of the corneal epithelium. In low concentrations, hydrogen sulfide may cause headache, fatigue, irritability, insomnia, and gastrointestinal disturbances; in somewhat higher concentrations it affects the central nervous system, causing excitement and dizziness. Prolonged exposure to 250 ppm of hydrogen sulfide may cause pulmonary edema. Prolonged exposure to concentrations of hydrogen sulfide as low as 50 ppm may cause rhinitis, pharyngitis, bronchitis, and pneumonitis. Repeated exposure to hydrogen sulfide results in increased susceptibility, so that eye irritation, cough, and systemic effects may result from concentrations previously tolerated without any effect. Rapid olfactory fatigue can occur at high concentrations.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 34.08
2. Boiling point (760 mm Hg): -60 C (-76 F)
3. Specific gravity (water = 1): Liquid = 1.54
4. Vapor density (air = 1 at 15 C (59 F)): 1.189
5. Melting point: -82.4 C (-116 F)
6. Vapor pressure at 25 C (77 F): 20 atm
7. Solubility in water, g/100 g water at 20 C (68 F): 2.9 (slight)
8. Evaporation rate (butyl acetate = 1): Not applicable

- **Reactivity**

1. Conditions contributing to instability: Elevated temperatures may cause containers to burst.
2. Incompatibilities: Contact with strong oxidizers and oxidizing materials may cause fires and explosions. Hydrogen sulfide attacks many metals, which results in the formation of sulfides.
3. Hazardous decomposition products: Toxic gases and vapors (such as sulfur oxides) may be released in a fire involving hydrogen sulfide.
4. Special precautions: Liquid hydrogen sulfide will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Hydrogen sulfide is a flammable gas.
2. Autoignition temperature: 260 C (500 F)
3. Flammable limits in air, % by volume: Lower: 4.3; Upper: 46
4. Extinguishant: Alcohol foam, carbon dioxide

- **Warning properties**

1. **Odor Threshold:** According to the AIHA *Hygienic Guide*, hydrogen sulfide can be recognized by the "sense of smell at low concentrations. Odor not reliable at high concentrations, and olfactory fatigue occurs quickly Threshold is 0.13 ppm. Faint but readily perceptible at 0.77 ppm. Easily noticeable at 4.6 ppm. Strong, unpleasant, but not intolerable at 27 ppm." The *Hygienic Guide* also states that "olfactory fatigue can occur with(in) 2 to 15 minutes at 100 ppm."

2. **Eye Irritation Level:** Grant states that "effects of hydrogen sulfide on the eyes are notable only at sublethal concentrations, most commonly at concentrations so low that they have no discernible systemic effect Typically, workmen exposed to low concentrations of hydrogen sulfide gas . . . have no sensation of irritation or discomfort for at least several hours, or sometimes for several days while working in the presence of low concentrations. Ocular symptoms generally start after several hours of exposure and may not appear until the patient has finished his work for the day. There is then gradual onset of a scratchy, irritated sensation in the eyes, with tearing and burning Experimentally it is demonstrable that at a concentration of 100 ppm in air an immediate irritation of the eyes and respiratory tract is produced, but conditions responsible for the vast majority of cases of hydrogen sulfide keratoconjunctivitis are those in which the concentration is too low to cause immediate irritation and has toxic effect only after several hours or days of exposure. However, in industries where the concentration is regularly kept below 10 ppm in air, it is rare to have any irritation of the eyes."

The *Hygienic Guide* states that "50 to 100 ppm causes slight conjunctivitis and respiratory tract irritation after 1 hour."

3. **Evaluation of Warning Properties:** Since olfactory fatigue occurs at high concentrations, and since the irritant effects are delayed, hydrogen sulfide is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **Eight-Hour Exposure Evaluation**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Ceiling Evaluation**

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of hydrogen sulfide. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15)

minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Peak Above Ceiling Evaluation**

Measurements to determine employee peak exposure should be taken during periods of maximum expected airborne concentration of hydrogen sulfide. Each measurement should consist of a 10-minute sample or a series of consecutive samples totalling 10 minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

• **Method**

Sampling and analyses may be performed by collection of hydrogen sulfide in an impinger containing an alkaline suspension of cadmium hydroxide, followed by chemical treatment, and spectrophotometric analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure hydrogen sulfide may be used. An analytical method for hydrogen sulfide is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 6, 1980, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00369-6).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing

necessary to prevent the skin from becoming frozen from contact with liquid hydrogen sulfide or from contact with vessels containing liquid hydrogen sulfide.

- Any clothing which becomes wet with liquid hydrogen sulfide should be removed immediately and not reworn until the hydrogen sulfide has evaporated.
- Employees should be provided with and required to use splash-proof safety goggles where liquid hydrogen sulfide may contact the eyes.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to hydrogen sulfide may occur and control methods which may be effective in each case:

Operation	Controls
Liberation from pockets during underground mining operations near sulfide ores	Local exhaust ventilation; respiratory protective devices
Liberation during refining of high-sulfur petroleum	Concentration and recovery of H ₂ SO ₄
Liberation from accumulations of decaying organic matter in sewers and waste waters of tanneries, glue factories, fat-rendering plants, and fertilizer plants	Provide continuous water discharge to sewer and cover and vent waste drains
Liberation as a by-product of dehairing and tanning process	Provide separate sewage lines and cover and vent waste drains; add neutralizing agents (CaCl ₂) as appropriate; local exhaust ventilation
Liberation during manufacture of viscose rayon	Local exhaust ventilation
Liberation during production of sulfur dyes, carbon disulfide, sulfur, oleum, and thioprene	Local exhaust ventilation or process enclosure
Liberation during vulcanization of rubber; during manufacture of coke from coal having high gypsum content	Local exhaust ventilation or process enclosure
Liberation during excavation projects	Respiratory protective equipment

Liberation in closed containers containing organic matter

Respiratory protective equipment; life-support line

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Eye Exposure

If liquid hydrogen sulfide gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• Skin Exposure

If liquid hydrogen sulfide gets on the skin, immediately flush the contaminated skin with water. If liquid hydrogen sulfide penetrates through the clothing, remove the clothing immediately and flush the skin with water. If irritation is present after washing, get medical attention.

• Breathing

If a person breathes in large amounts of hydrogen sulfide, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL AND LEAK PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If hydrogen sulfide is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak to disperse gas.
3. If in the gaseous form, stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.
4. If in the liquid form, allow to vaporize.

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RESPIRATORY PROTECTION FOR HYDROGEN SULFIDE

Condition	Minimum Respiratory Protection* Required Above 10 ppm
Gas Concentration	
300 ppm or less	Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
Greater than 300 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against acid gases or hydrogen sulfide. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

