criteria for a recommended standard....

OCCUPATIONAL EXPOSURE
TO
HYDROGEN SULFIDE

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
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PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need for standards to protect the health and provide for the safety of workers exposed to an ever-increasing number of potential hazards at their workplace. The National Institute for Occupational Safety and Health has projected a formal system of research, with priorities determined on the basis of specified indices, to provide relevant data from which valid criteria for effective standards can be derived. Recommended standards for occupational exposure, which are the result of this work, are based on the health effects of exposure. The Secretary of Labor will weigh these recommendations along with other considerations such as feasibility and means of implementation in developing regulatory standards.

It is intended to present successive reports as research and epidemiologic studies are completed and as sampling and analytical methods are developed. Criteria and standards will be reviewed periodically to ensure continuing protection of the worker.

I am pleased to acknowledge the contributions to this report on hydrogen sulfide by members of the NIOSH staff and the valuable constructive comments by the Review Consultants on Hydrogen Sulfide, by the ad hoc committees of the American Academy of Industrial Hygiene and the American Occupational Medical Association, and by Robert B. O'Connor, M.D., NIOSH consultant in occupational medicine. The NIOSH recommendations for standards are not necessarily a consensus of all the consultants and professional societies that reviewed this criteria document on hydrogen sulfide. A list of Review Consultants appears on page vi.

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The Division of Criteria Documentation and Standards Development, National Institute for Occupational Safety and Health, had primary responsibility for development of the criteria and recommended standard for hydrogen sulfide. The division review staff for this document consisted of J. Henry Wills, Ph.D., Chairman, Howard C. McMartin, M.D., Douglas L. Smith, Ph.D., and Paul E. Caplan, with Kenneth J. Kronoveter (Division of Surveillance, Health Evaluations, and Field Studies), Charles S. McCammon, Jr. (Division of Physical Sciences and Engineering), and Howard C. Spencer (consultant). Stanford Research Institute (SRI) developed the basic information for consideration by NIOSH staff and consultants under contract No. CDC-99-74-31. Herbert L. Venable served as criteria manager.

The views expressed and conclusions reached in this document, together with the recommendations for a standard, are those of NIOSH, after reviewing the evidence and considering the comments of reviewers; these views and conclusions are not necessarily those of the consultants, other federal agencies, and professional societies, or of the contractor.

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CRITERIA DOCUMENT:
RECOMMENDATIONS FOR AN OCCUPATIONAL EXPOSURE STANDARD FOR HYDROGEN SULFIDE

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I. RECOMMENDATIONS FOR A HYDROGEN SULFIDE STANDARD

The National Institute for Occupational Safety and Health (NIOSH) recommends that worker exposure to hydrogen sulfide in the workplace be controlled by adherence to the following sections. The standard is designed to protect the health and to provide for the safety of employees for up to a 10-hour work shift, 40-hour workweek, over a working lifetime. Compliance with all sections of the standard should prevent adverse effects of hydrogen sulfide on the health and safety of workers. Techniques recommended in the standard are valid, reproducible, and available to industry and government agencies. Sufficient technology exists to permit compliance with the recommended standard. The criteria and standard will be subject to review and revision as necessary.

Hydrogen sulfide is a nearly ubiquitous, acute acting toxic substance. It is a leading cause of sudden death in the workplace. Brief exposures to hydrogen sulfide at high concentrations have caused conjunctivitis and keratitis, and exposures at very high concentrations, have caused unconsciousness, respiratory paralysis, and death. Conclusive evidence of adverse health effects from repeated, long-term exposure to hydrogen sulfide at low concentrations was not found. However, there is some evidence that hydrogen sulfide alone at low concentrations or in combination with other chemical substances (eg, hydrocarbons or carbon disulfide) has caused nervous-system, cardiovascular, and gastrointestinal disorders, and effects on the eyes.

Hydrogen sulfide is especially dangerous when it occurs in low-lying areas or confined workspaces or when it exists in high concentrations under pressure. As a result, work practices, such as continuous monitoring and the use of specified respiratory protective equipment in certain work situations, are of great importance.

"Hydrogen sulfide" refers to either the gaseous or liquid forms of the compound. Synonyms for hydrogen sulfide include hydrosulfuric acid, sulfurated hydrogen, sulfur hydride, rotten-egg gas, and stink damp. "Occupational exposure to hydrogen sulfide" refers to any workplace situation in which hydrogen sulfide is stored, used, produced, or may be evolved as a consequence of the process. All sections of this standard shall apply where there is occupational exposure to hydrogen sulfide.

Section 1 - Environmental (Workplace Air)

(a) Concentration

Exposure to hydrogen sulfide shall be controlled so that no employee is exposed to hydrogen sulfide at a ceiling concentration greater than 15 mg of hydrogen sulfide per cubic meter of air (15 mg/cu m or approximately 10 ppm), as determined with a sampling period of 10 minutes, for up to a 10-hour work shift in a 40-hour workweek. Evacuation of the area shall be required if the concentration of hydrogen sulfide equals or exceeds 70 mg/cu m.

(b) Sampling and Analysis

Procedures for sampling and analysis of workplace air for the ceiling limit shall be as provided in Appendices I and II or by any other methods shown to be at least equivalent in precision, accuracy, and sensitivity to the methods specified.

Monitoring for the evacuation limit shall be as provided in Appendix III, or by any method shown to be at least equivalent in accuracy, reliability, sensitivity, and speed to that specified.

Section 2 - Medical

Medical surveillance shall be made available as outlined below to all workers subject to occupational exposure to hydrogen sulfide.

(a) Preplacement examinations shall include at least:

(1) Comprehensive medical and work histories with special emphasis directed to symptoms related to the eyes and the nervous and respiratory systems.

(2) Physical examination giving particular attention to the eyes and to the nervous and respiratory systems.

(3) A judgment of the worker's ability to use positive and negative pressure respirators.

(b) Periodic examinations shall be made available at least every 3 years to any workers who have been exposed to hydrogen sulfide above the recommended ceiling limit and shall include:

(1) Interim medical and work histories.

(2) Physical examination as described for the preplacement examination.

(c) During examinations, applicants or employees having medical conditions which would be directly or indirectly aggravated by exposure to hydrogen sulfide shall be counseled on the increased risk of impairment of their health from working with this substance and on the value of periodic physical examinations.

(d) Initial medical examinations shall be made available to all workers within 6 months after the promulgation of a standard based on these recommendations.

(e) In the event of adverse effect or illness known or suspected to be caused by exposure to hydrogen sulfide, a physical examination, as described above for preplacement, shall be made available.

(f) If an emergency involving hydrogen sulfide arises, rescuers using respiratory protection shall remove victims to a safe area quickly and initiate appropriate first aid, including artificial respiration if necessary. The victim's lungs should first be cleared of hydrogen sulfide by applying back-pressure artificial respiration briefly before using the more effective mouth-to-mouth artificial respiration. Provision shall be made for prompt transportation to hospital of workers exposed to hydrogen sulfide who have become unconscious, who have respiratory distress, or who feel unwell. Appropriate local hospitals and medical and paramedical personnel shall be informed by the employer of the possibility of hydrogen sulfide poisoning, even if the chance of emergency is considered remote. Workers sent to the hospital because of hydrogen sulfide exposure shall be identified as such to emergency-room personnel. A qualified medical attendant designated by the employer shall examine all employees who may have been exposed above the occupational exposure limits. Written emergency medical procedures shall be posted where hydrogen sulfide is used.

(g) Pertinent medical records shall be maintained for all employees who are involved in the manufacturing, processing, or handling of hydrogen sulfide or are in any other way exposed to it in the workplace. Such records shall be kept for at least 30 years after termination of employment. These records shall be made available to the designated medical representatives of the Secretary of Health, Education, and Welfare, of the Secretary of Labor, of the employer, and of the employee or former employee.

Section 3 - Labeling and Posting

All containers of hydrogen sulfide shall be labeled and all areas where hydrogen sulfide is stored, handled, used, produced, or released shall be posted in accordance with the following subsections.

All warning signs and labels shall be printed in English and in the predominant language of non-English-reading workers. Employers shall ensure that all employees are informed of the hazards of working with hydrogen sulfide and of the hazardous areas within the establishment in which they work, special care being taken to ensure that workers unable to read labels and signs understand the hazards of working with hydrogen sulfide, the areas of the plant that are particularly likely to become hazardous, and the appropriate self-help and first-aid procedures in suspected cases of intoxication by hydrogen sulfide vapor or of direct contact of eyes and skin with liquid hydrogen sulfide.

(a) Cylinders of hydrogen sulfide shall bear the following label in addition to, or in combination with, labels required by other statutes, regulations, or ordinances:

HYDROGEN SULFIDE

DANGER! POISON

LIQUID AND GAS UNDER PRESSURE

DEADENS SENSE OF SMELL
DO NOT DEPEND UPON ODOR

GAS IS NOT VISIBLE

FLAMMABLE--KEEP AWAY FROM HEAT AND OPEN FLAME

Do not breathe gas.
Use only with adequate ventilation.

First Aid: Remove patient to fresh air. Administer artificial respiration if breathing has stopped. Obtain medical care; keep patient warm.

(b) The following warning sign shall be posted in a readily visible location at or near entrances to areas in which hydrogen sulfide is stored, handled, used, produced, or potentially released:

WARNING--HAZARDOUS AREA

HYDROGEN SULFIDE

EXTREME HEALTH HAZARD
FATAL OR HARMFUL IF INHALED

Keep upwind.
Do not breathe gas.
In emergency, enter area ONLY if wearing approved respiratory protection.
Untrained and unauthorized persons keep out.

First Aid: Remove patient to fresh air. Administer artificial respiration if breathing has stopped. Obtain medical care; keep patient warm.

Section 4 - Personal Protective Equipment

Employers shall use engineering controls and safe work practices to keep exposure to hydrogen sulfide below the prescribed limits. When necessary, these shall be supplemented by the use of personal protective equipment, in accordance with 29 CFR 1910, subpart I. Emergency equipment shall be located at clearly identified stations within the work area and shall be adequate to permit all employees to escape safely from the area. Protective equipment suitable for emergency use shall be located at clearly identified stations outside the exposure area.

(a) The only times when compliance with the permissible exposure limit may be achieved by the use of respirators are:

(1) During the time necessary to install and test the required engineering controls.

(2) During nonroutine operations, such as maintenance and repair activities causing brief exposure at concentrations in excess of the ceiling concentration limit.

(3) In emergencies when air concentrations of hydrogen sulfide may exceed the ceiling concentration limit.

(b) When use of a respirator is permitted or required by paragraph (a) of this section, it shall be selected in accordance with the specifications in Table I-1 and shall comply with the standards jointly approved by NIOSH and the Mining Enforcement and Safety Administration, as specified in 30 CFR 11. Employers shall provide respiratory protection for each employee and shall establish and enforce a respiratory protection program meeting the requirements of 29 CFR 1910.134, as amended, and shall ensure that employees use the respiratory protective equipment when necessary.

(c) Employers shall ensure that respirators are properly cleaned and maintained and that employees are trained and drilled in the location and use of respirators assigned to them and in testing donned respirators for leaks.

(d) Respirators shall be easily accessible and employees shall be informed of their location and recognition if respirators for more than one purpose are present.

(e) Any respirator recommended for use in higher concentrations of hydrogen sulfide may be used for any lower concentrations.

(f) Training in respiratory protection shall include actually wearing and using the equipment. Training in respiratory equipment shall be started before a worker goes on the job and shall be repeated at least quarterly and each time a new crew is formed. All members of a crew should receive the same training, even if some have had a previous training session in the same quarter. Workers actually or potentially exposed frequently to hydrogen sulfide shall receive training in respiratory protection before starting work.

(g) Full-facepiece respiratory protection also protects the eyes.

TABLE I-1

RESPIRATOR SELECTION GUIDE FOR HYDROGEN SULFIDE

Concentration	Respirator Type Approved under Provisions of 30 CFR 11
Less than or equal to 70 mg/cu m	(1) Any supplied-air respirator with full facepiece (2) Any self-contained breathing apparatus with full facepiece
Greater than 70 mg/cu m	(1) Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive pressure mode (2) Combination Type C supplied-air respirator with full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode
Emergency (entry into area of unknown concentration for emergency purposes, eg, firefighting)	(1) Self-contained breathing apparatus with full facepiece operated in pressure-demand or other positive pressure mode (2) Combination Type C supplied-air respirator with full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode
Escape (from an area of unknown concentration)	(1) Any self-contained breathing apparatus (2) Any gas mask providing adequate protection against hydrogen sulfide (not to be used in confined spaces)

Section 5 - Informing Employees of Hazards from Hydrogen Sulfide

(a) Employees who will do primary or maintenance work in areas required to be posted in accordance with Section 3 shall be informed of the hazards from hydrogen sulfide exposure, symptoms of overexposure, emergency and first-aid procedures, and precautions to ensure safe use of the gas and to minimize exposure; all shall be taught the meaning of alarms and evacuation procedures. Employers shall post this information in the workplace and shall keep it on file, readily accessible to employees.

(b) Employers shall institute a continuing educational program, conducted by persons qualified by experience or training, for employees whose jobs may involve exposure to hydrogen sulfide, including employees engaged in maintenance and repair. This is to ensure that all such employees have current knowledge of job hazards, procedures for entering confined spaces, relevant maintenance procedures, and cleanup methods, and that they know how to use respiratory protective equipment.

(c) Required information shall be recorded on the "Material Safety Data Sheet" shown in Appendix IV or on a similar form approved by the Occupational Safety and Health Administration, US Department of Labor, and shall be kept on file, readily accessible to employees.

Section 6 - Work Practices

(a) Emergency Procedures

For all work areas where there is a potential for the occurrence of emergencies involving hydrogen sulfide, employers shall take all necessary steps to ensure that employees are instructed in and follow the procedures specified below and any others appropriate for the specific operation or process.

(1) Procedures shall include prearranged plans for immediate evacuation of employees exposed to hydrogen sulfide at potentially life-threatening concentrations, designation of medical receiving facilities, and provision of appropriate emergency telephone numbers, including those for alerting medical facilities of the impending arrival of ill employees and for calling public safety and environmental protection agencies in major emergencies. Reentry procedures for maintenance or cleanup of areas where leaks or discharges of hydrogen sulfide have occurred shall be prepared.

(2) Approved respiratory protection as specified in Section 4 shall be used by personnel essential to emergency operations.

(3) Employees not essential to emergency operations shall be evacuated from hazardous areas during emergencies. Perimeters of these areas shall be delineated, posted, and secured. Wind direction indicators should be used outdoors, and safe areas designated upwind.

(4) Only personnel properly trained in emergency procedures and protected against the attendant hazards shall shut off sources of hydrogen sulfide, clean up spills, and control and repair leaks.

(5) In case of fire, hydrogen sulfide cylinders should be removed to a safe place, or cooled with water if they cannot be removed safely and if no leaks exist.

(6) If workers or designated emergency teams cannot cope with the emergency, assistance shall be requested. Telephone numbers for emergency help shall be prominently posted.

(7) Employees who inhale hydrogen sulfide shall be removed to an uncontaminated atmosphere and given artificial respiration if it is needed. Victims shall be kept quiet and warm; medical attention shall be summoned as quickly as possible.

(b) Control of Airborne Hydrogen Sulfide

Engineering controls shall be used when needed to keep hydrogen sulfide concentrations at or below the recommended limit. The use of enclosed processes is an effective method for controlling hydrogen sulfide. Local exhaust ventilation may also be effective, used alone or in combination with process enclosure. Nonsparking ventilation systems shall be designed to prevent accumulation or recirculation of hydrogen sulfide in the workroom, to keep concentrations within the limits of the recommended standard, and to remove hydrogen sulfide from the breathing zones of workers. Ventilation systems shall be inspected for corrosion, subjected to regular preventive maintenance, and cleaned at least every 6 months to ensure effectiveness, which shall be verified by periodic airflow measurement at least annually or more frequently according to the judgment of an industrial hygienist. Tempered makeup air shall be provided as required to workrooms in which exhaust ventilation is operating.

(c) Storage

Storage areas shall be isolated, well ventilated, and fire-resistant. Hydrogen sulfide cylinders shall be stored away from strong oxidizing materials and corrosive liquids and gases, heat, heated surfaces, open flames, and spark-producing devices. When cylinders are stored in the open, no dirt, snow, or other debris shall be allowed to accumulate on or around them. No hydrogen sulfide cylinders shall be exposed to direct sunlight.

(d) Confined and Enclosed Spaces

(1) Entry into confined spaces, such as tanks, pits, tank cars, barges, process vessels, and tunnels, shall be controlled by written permit or an equivalent system. Permits shall be signed by an authorized representative of the employer certifying that the confined space has been prepared as described in this section, and that precautions have been taken to ensure that prescribed procedures will be followed. Signed permits shall be kept on file for 1 year after the date of use.

(2) Confined spaces which have contained hydrogen sulfide shall be inspected and tested before and during entry for oxygen deficiency, hydrogen sulfide, and flammable or explosive gas mixtures, shall be thoroughly ventilated, cleaned, neutralized, and washed, as necessary, shall be sealed off from adjacent spaces or vessels prior to entry of employees, and shall be mechanically ventilated during entry.

(3) Employees entering confined spaces where they may be exposed to hydrogen sulfide shall wear respiratory protective equipment in accordance with Table I-1, if there is a chance that mechanical ventilation may not be adequate to control a surge of released hydrogen sulfide. In confined spaces, supplied-air respirators shall be operated only in the positive pressure continuous-flow or pressure-demand mode and shall have an auxiliary self-contained air supply sufficient to permit escape.

(4) Employees entering confined spaces shall also wear suitable harnesses with lifelines tended by an employee outside the confined space who shall also be equipped with the appropriate respiratory

protective equipment. The two workers shall be in constant communication by some appropriate means and shall be under the surveillance of a third person equipped to take appropriate action to rescue them if necessary.

(5) Confined spaces shall be ventilated while work is in progress to keep the concentration of hydrogen sulfide below the recommended environmental limit and to prevent oxygen deficiency.

(6) Enclosed spaces, such as rooms or buildings, which ordinarily are safe to enter but which, in the event of failure of a system inside, could contain hydrogen sulfide at hazardous concentrations, shall have a continuous automatic monitor set to sound an alarm that is audible both inside and outside the enclosed space if hydrogen sulfide concentrations exceed the peak concentration limit of 50 ppm. An easily visible and distinctive warning light is recommended as a supplement to or as a substitute for an audible alarm in noisy areas. If such areas are not monitored in this way, any employee entering the area shall wear a suitable respirator and a lifeline with safety harness and shall be observed by a coworker, unless the hydrogen sulfide concentration is measured and determined to be at a safe level and the enclosed space does not contain a source of hydrogen sulfide.

(e) Maintenance

Lines and fittings which may carry hydrogen sulfide shall be made of appropriate materials and must be inspected frequently for corrosion, embrittlement, and leaks. All hydrogen sulfide equipment, including valves, fittings, and connections, shall be checked for tightness and good working order. Such inspections shall be made immediately after new connections are made and after hydrogen sulfide is introduced. Needed repairs and adjustments shall be made promptly.

Section 7 - Sanitation

(a) Sanitation shall meet the requirements of 29 CFR 1910.141.

(b) Smoking shall be prohibited in areas where hydrogen sulfide is used, transferred, stored, manufactured, or potentially released.

(c) Waste material contaminated with hydrogen sulfide and containers of hydrogen sulfide under pressure shall be disposed of in a manner not hazardous to employees. The disposal method must conform to applicable local, state, and federal regulations and must not constitute a hazard to the surrounding population or environment. Pressure containers shall be disposed of by trained personnel.

Section 8 - Monitoring and Recordkeeping Requirements

Within 6 months of the promulgation of a standard based on these recommendations, employers shall determine by an industrial hygiene survey at each location where hydrogen sulfide may be released into workplace air where exposure to hydrogen sulfide at concentrations above the recommended occupational exposure limits may occur. Employers shall keep records of these surveys. If an employer concludes that concentrations are at or below the recommended ceiling limit, the records must contain the basis for this conclusion. Surveys shall be repeated at least once every 3 years and immediately after any process change likely to result in increased concentrations of airborne hydrogen sulfide. If it has been determined that there is occupational exposure to hydrogen sulfide, the employer shall fulfill the following requirements:

(a) Personal Monitoring

(1) A program of personal monitoring shall be instituted to determine the ceiling exposures of each employee occupationally exposed to hydrogen sulfide. Source and area monitoring may be used to supplement personal monitoring. Such monitoring may be done quarterly or as recommended by an industrial hygienist. Recording automatic monitors shall be permitted to show short-term (<1 minute) peaks of up to 70 mg/cu m (50 ppm), as long as no more than one such peak appears in any 30-minute record. The recording automatic monitor shall be arranged to signal as specified in paragraphs (b)(1) and (3) below.

(2) In all personal monitoring, samples representative of the exposure to hydrogen sulfide in the breathing zone of the employee shall be collected. Procedures for sampling, calibration of equipment, and analysis of hydrogen sulfide samples shall be as provided in Section 1(b).

(3) If an employee is found to be exposed to hydrogen sulfide above the recommended ceiling concentration limit, the exposure of that employee shall be monitored at least once a week, control measures shall be initiated, and the employee shall be notified of the exposure and of the control measures being implemented. Weekly monitoring shall continue until two consecutive determinations, at least 1 week apart, indicate that the employee's exposure no longer exceeds the recommended environmental limit; then, quarterly or less frequent monitoring may be resumed as specified above.

(b) Alarm/Evacuation Monitoring for Peak Concentrations

(1) A program of continuous monitoring shall be instituted to signal a spark-proof audible or visual alarm, as appropriate, if and when the concentration of hydrogen sulfide in workplace air equals or exceeds 70 mg/cu m (50 ppm). Requirements for such a system are given in Appendix III.

(2) When an alarm signals that hydrogen sulfide is present at a concentration of 50 ppm or greater, the workers in the contaminated area shall be evacuated immediately to safe areas. Workers using appropriate respiratory protection may reenter the contaminated area for rescue, repair, or contingency activity.

(3) Fixed monitors shall also have a different alarm to signal the presence of hydrogen sulfide at concentrations of 15-70 mg/cu m (10-50 ppm). This alarm is for alert only and shall not require evacuation. The workers shall be trained to recognize and distinguish between the alarms.

(4) Continuous direct-reading hydrogen sulfide monitors shall be used in fixed locations near the ground or near operations where hydrogen sulfide may be released. This may be done only if air currents will not move air from areas where hydrogen sulfide is released away from the detector.

(5) Portable monitors shall be used in areas where fixed monitors are not appropriate or to supplement fixed monitoring, for example, where there are air currents.

(6) NIOSH-approved detector tubes for hydrogen sulfide shall be an acceptable substitute for continuous monitoring where there are no air currents, as in some confined spaces.

(c) Recordkeeping

Employers or their successors shall keep records of environmental monitoring for each employee for at least 30 years after the individual's employment has ended. These records shall include: dates of measurements, job function and locations of the employees at the worksite, sampling and analytical methods used, number, duration, and results of the samples taken, ceiling concentrations estimated from these samples, type of personal protective equipment used, and the exposed employees' names. Employees shall have access to information on their own environmental exposures. Environmental records shall be made available to designated representatives of the Assistant Secretary of Labor for Occupational Safety and Health and of the Director of the National Institute for Occupational Safety and Health. Pertinent medical records shall be retained by the employer for 30 years after termination of employment. Records of environmental exposures applicable to an employee shall be included in that employee's medical records.

II. INTRODUCTION

This report presents the criteria and the recommended standard based thereon which were prepared to meet the need for preventing occupational disease or injury arising from exposure to hydrogen sulfide. The criteria document fulfills the responsibility of the Secretary of Health, Education, and Welfare under Section 20(a)(3) of the Occupational Safety and Health Act of 1970 to "...develop criteria dealing with toxic materials and harmful physical agents and substances which will describe...exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of his work experience."

The National Institute for Occupational Safety and Health (NIOSH), after a review of data and consultation with others, formalized a system for the development of criteria upon which standards can be established to protect the health and to provide for the safety of employees exposed to hazardous chemical and physical agents. Criteria for an environmental standard should enable management and labor to develop better engineering controls and more healthful work practices and should not be used as a final goal.

These criteria for a standard for hydrogen sulfide are part of a continuing series of documents published by NIOSH. The recommended standard applies to workplace exposure to hydrogen sulfide resulting from its processing, manufacture, storage, handling, use, generation, or liberation as applicable under the Occupational Safety and Health Act of 1970. The standard was not developed for the population-at-large, and any extrapolation beyond occupational exposures is not warranted. It is intended to (1) protect against sudden death caused by unexpected high concentrations of hydrogen sulfide, (2) protect against the development of eye irritation or other harmful effects of hydrogen sulfide exposures, (3) protect against the fire hazards posed by hydrogen sulfide, (4) be measurable by techniques that are valid, reproducible, and available to industry and government agencies, and (5) be attainable with existing technology.

Hydrogen sulfide is a leading cause of sudden death in the workplace. Occupational exposure to hydrogen sulfide has been shown to have adverse effects on the eyes and the respiratory system. Brief exposures to hydrogen sulfide at high concentrations (for example, 140 mg/cu m) have commonly caused conjunctivitis and keratitis, and, at very high concentrations (for example, above 280 mg/cu m), unconsciousness, respiratory paralysis, and death. Case histories have shown that cardiovascular, nervous-system, and gastrointestinal disorders also have resulted from exposure to hydrogen sulfide. No conclusive reports were found of adverse health effects from repeated, long-term exposure to hydrogen sulfide alone at low concentrations. Reports of long-term human exposures to carbon disulfide have indicated the concurrent presence of hydrogen sulfide, but possible toxic synergism has not been thoroughly investigated.

Hydrogen sulfide is nearly ubiquitous. It occurs naturally in volcanic gases, in sulfur springs and fumaroles, in decaying of plant and animal protein, and in intestines as a result of bacterial action. Hydrogen sulfide is a serious hazard to the health of workers employed in energy production from hydrocarbon or geothermal sources, in the production of fibers and sheets from viscose syrup, in the production of deuterium oxide (heavy water), in tanneries, sewers, sewage treatment and animal waste disposal, in work below ground, on fishing boats, and in chemical operations. NIOSH recognized the hazards posed by hydrogen sulfide in the gas and oil industry and issued recommendations for work practices (Appendix V).

The development of the recommended standard for occupational exposure to hydrogen sulfide has revealed the need for additional data in several areas. The following research is needed: (1) epidemiologic studies of chronic exposure to hydrogen sulfide, (2) studies correlating measured concentrations of hydrogen sulfide with health effects, (3) further studies on possible teratogenesis and brain damage from hydrogen sulfide exposure, and (4) studies designed to assess the possible synergism of toxic effects when carbon disulfide and hydrogen sulfide occur together.

The recommended standard has been developed to protect workers from different hydrogen sulfide hazards. A ceiling concentration has been proposed to prevent eye effects and other possible adverse effects, including anorexia, nausea, weight loss, insomnia, fatigue, and headache, from prolonged exposure to hydrogen sulfide at low concentrations, and to prevent acute eye effects, unconsciousness, and death, which can rapidly follow exposure to hydrogen sulfide at high concentrations.

III. BIOLOGIC EFFECTS OF EXPOSURE

Extent of Exposure

Hydrogen sulfide, H2S (formula weight 34.08), is a colorless, flammable gas which may be liquified under pressure and which occurs in a variety of natural and industrial settings. Some of its physical and chemical properties are listed in Table XIV-1 [1,2]. It is present in most volcanic gases, in "sulfur springs," and as a bacterial decomposition product of protein [2]. It occurs to some extent in most petroleum and natural gas deposits and in many mines, and it is therefore a potential health hazard in related drilling, mining, smelting, or processing operations. In other industries, hydrogen sulfide is usually an undesirable byproduct of some manufacturing process. It is formed whenever elemental sulfur or certain sulfur compounds are present with organic chemicals at high temperatures [2]. Industries in which hydrogen sulfide is a principal reagent or byproduct are listed in Table XIV-2 [3-6].

Hydrogen sulfide may be prepared directly from hydrogen gas and sulfur vapor, but this process is economical only if hydrogen is a waste product at the location [2]. Most hydrogen sulfide is obtained as a byproduct of other operations. Often its recovery is motivated more by the need to purify the source material than by the value of the recovered gas. Hydrogen sulfide in substantial quantities is recoverable from natural-gas and petroleum refining operations and is converted to sulfuric acid or high-quality sulfur or disposed of by burning in flares. Hydrogen sulfide is also used in the preparation of various sulfides and organic sulfur compounds and is a common reagent in chemical laboratories [2].

NIOSH estimates that approximately 125,000 employees are potentially exposed to hydrogen sulfide in the United States; a partial list of their occupations is shown in Table XIV-2 [3-6]. Large or frequent exposures to hydrogen sulfide are peculiar to some occupations. Exposure to hydrogen sulfide in other occupations may be rare or at low concentrations.

Historical Reports

An 18th century treatise on occupational health, De Morbis Artificum Diatriba [7], was inspired by the observation of the physical condition of sewer cleaners. The author, an Italian physician named Ramazzini who is revered as the father of occupational medicine, described cases of eye irritation similar to those more recently being attributed to chronic exposures to hydrogen sulfide.

> I am inclined to think some volatile acid is given off by this carnerine of filth when workers disturb it...such effluvia ought, one would think, to impair the lungs. Nevertheless it is only against the eyes that these foul exhalations wage ruthless war, and they attack them so cruelly with their piercing stings that they rob them of life, that is to say of light [7].

In connection with an investigation of hydrogen sulfide poisoning, Mitchell and Davenport [8] reviewed the literature on the subject. The first description of the chemical properties of hydrogen sulfide, by Rouelle, dates back to 1773, although the composition of the gas was unknown at the time [8]. Scheele, in 1777, was the first to make a systematic study of the gas [8]. He observed the solubility of hydrogen sulfide in water and its oxidation to sulfur by air, nitric acid, or chlorine and noted its reactions with solutions of several metallic salts.

It was not until 1796 that Berthollet analyzed the gas and recognized it as hydrogen sulfide [8]. In 1785, a commission was appointed in Paris to investigate numerous accidental deaths which were apparently caused by gases emitted from the sewers [8]. Although hydrogen sulfide had not been identified at that time, two distinct types of poisoning, now recognized as being characteristic of exposure to low and high concentrations of hydrogen sulfide, were described. The first type, referred to as the "mitte," was an inflammation of the eyes and mucous membranes, and the second, referred to as the "plomb," was a form of asphyxia. Chemical analyses by Dupuytren, Thenard, and Barruel in the early 19th century confirmed the presence of hydrogen sulfides in the sewers, and these investigators attributed many of the sewer-related deaths to this gas [8].

Chaussier, in 1803, described an experiment on hydrogen sulfide toxicity in animals and indicated that skin absorption was a possible route of poisoning, as well as inhalation and injection into stomach or rectum [8]. In further experimentation, Nysten injected saturated hydrogen sulfide solutions into the veins of animals and found that three injections of 10 cc of a saturated hydrogen sulfide solution into a dog caused excitation followed by depression of respiratory and motor activity with complete recovery by the next day [8].

Christinson, in 1827, observed two types of hydrogen sulfide poisoning which he designated as acute and subacute [8]. In his 1829 analysis of air in Paris sewers, Gaultier de Claubry found up to 2.99%, with a mean of 2.29%, of hydrogen sulfide present [8]. In 1861, Holden and Letheby described the medical histories and post-mortem examination results of workers poisoned in London sewers [8]. Hoppe-Seyler, in 1863, observed that a dark green substance termed "sulphmethemoglobin" resulted from the passage of hydrogen sulfide through blood, presumably from the action of hydrogen sulfide on the oxyhemoglobin. His work led to a number of chemical studies of hydrogen sulfide on the blood [8].

Experiments on animals were reported by Eulenberg in 1865 and by Biefel and Polek in 1880 [8]. Eulenberg found that cats, rabbits, and doves were killed within a short time by hydrogen sulfide at a concentration of 0.1% and that young animals were more sensitive to this substance than adult ones. Biefel and Polek observed that a rabbit died within 75 minutes when exposed to hydrogen sulfide at a concentration of 0.05%; they also observed crying, convulsions, trembling, respiratory disturbances, and increased salivation [8]. Total amounts of hydrogen sulfide used were not specified.

In the first case of hydrogen sulfide poisoning reported in the United States, Bell and Raphael described in 1851 an accident caused by the liberation of gas formed in an outhouse [8].

Most early industrial physicians in the United States were unfamiliar with hydrogen sulfide poisoning because hydrogen sulfide poisoning had become an important industrial hazard only in the last 60 years [9]. It was not until the 1920's that any practical information on hydrogen sulfide exposures became available in the United States. Since then, because of increased use and, therefore, an increased number of accidents caused by hydrogen sulfide, investigations have been undertaken by such groups as the Yale University Department of Applied Physiology, the Health Laboratory of the US Bureau of Mines, the American Petroleum Institute, the National Safety Council, and the Manufacturing Chemists Association [3].

Hand [10] reported in 1939 that more than 50,000 men and women were employed in about 20 viscose factories in 13 states. In one US viscose factory, where several hundred tons of hydrogen sulfide were produced over a period of 15 years, 174 poisonings, but no deaths, were recorded [3,11]. According to Legge [12], 78 workers in the spinning department and the acid cellars of an artificial silk factory in the Netherlands were surveyed in 1922. Complaints of burning and smarting of the eyes were recorded for 25 of the 78 workers, headache for 32, loss of appetite for 31, and loss of weight for 20. More than a quarter of the workers experienced dizziness. Hydrogen sulfide concentrations in the air of that factory were reported to vary from 20.4 to 35.4 mg/cu m [12].

Hydrogen sulfide had been cited as a potential hazard in 50 occupations in 1945 [13]. Its effects were recognized in the petroleum industry more than 40 years ago [13]. The discovery of large deposits of high-sulfur oil in the United States resulted in a substantial increase in occupational exposures to hydrogen sulfide, and hydrogen sulfide exposure in the petroleum industry was one of the major industrial hazards in this country in 1930 [9]. Men have been found dead on derrick floors, apparently overwhelmed by the rush of gas when they first drilled into a pocket [9]. Before the danger became known, exposures to large quantities of hydrogen sulfide gas occurred without respiratory protection, and as many as 31 workers became unconscious while "closing in" a single oil well [14]. In some oil-producing fields, gases were found to contain up to 10-12% of hydrogen sulfide by volume [9].

Several investigations have suggested that the toxicity of hydrogen sulfide is enhanced by humid air, such as that present in many mines [13].

In a 1942 mining incident [13], four men attempting to prevent water from entering a shaft were overcome by hydrogen sulfide. The hydrogen sulfide detector showed a concentration of 25 ppm hydrogen sulfide above the water 5 minutes after the fan that had been run to disperse the gas was stopped.

Historical reports of chronic hydrogen sulfide poisoning are relatively uncommon. Legge [12] described the case of a workman who had been exposed to hydrogen sulfide for 2 years in the early 1900's at a sulfur-black establishment. In April 1905, he experienced ataxia, pains, paresthesias, muscular atrophy, and a narrowing of the visual field. By December 1906, he was totally blind, with pain and persistent paresthesia; he died of bronchopneumonia in May 1910. Microscopic examination of sections of the spinal cord revealed no inflammation, but extensive degeneration. That this change can be attributed to the workman's exposure to hydrogen sulfide is uncertain.

Effects on Humans

Most of the reports discussed in this section describe effects of acute exposure to hydrogen sulfide. Persistent effects on humans after long-term exposure to hydrogen sulfide have not been conclusively demonstrated, but results of numerous studies [3,15-18] suggest that there are subacute effects.

In the high-sulfur oil fields of Wyoming and western Texas, 26 persons died from exposure to hydrogen sulfide at unspecified concentrations between October 1, 1974, and April 28, 1976 [19]. A young man was hospitalized with pneumonia that was attributed to exposure to hydrogen sulfide at unspecified concentration. He survived, but details of his recovery were not reported [19].

A driver cleaning his chemical-waste tank-truck in 1971 was overcome by hydrogen sulfide and died [20]. Hydrogen sulfide was later measured inside the tank hatch at a concentration of 12,000 ppm. Small birds in the vicinity were also killed.

Breysse [21] reported that a worker was found dead after he had gone to plug a leaking exhaust line from a poultry feather cooker used to make fertilizer. Measurements were later made during the cooking cycle, and hydrogen sulfide was found to escape from the leaking pipe at concentrations of 2,000-4,000 ppm.

Prouza [22] reported in 1970 that 10 Czechoslovakian workers were poisoned, 1 fatally, when hydrogen sulfide seeped into an empty viscose spinning tank from another tank through a common overflow pipe. The hydrogen sulfide concentration inside the tank was measured at 2,800 ppm 4.5 hours after the accident. A maintenance worker who entered the tank to loosen and remove a heating element complained of the odor and of not feeling well, then collapsed. Two coworkers entered the tank without protective equipment and tried to lift the stricken man up to the foreman, who stood outside the tank, but the foreman felt weak as he bent over the tank and the two would-be rescuers within the tank were also becoming stuporous. The foreman let the first worker fall back into the tank and managed to help the other two out of it. A fifth worker went for protective equipment and returned to find that the total of poisoned would-be rescuers had risen to nine, six of them unconscious. The first victim and four of the rescuers were removed from the tank by workers wearing protective equipment and were taken to the factory first-aid station and then to the hospital. The first man was pronounced dead.

The post-mortem examination showed a greenish discoloration of the gray matter of the brain. The four hospitalized rescuers complained of nausea, weakness, and pain in the chest. They were discharged after 7 days with normal eye, neurologic, and psychiatric examination results but slightly abnormal electrocardiograms (ECG's). Similar examinations showed no abnormalities in the remaining five, who declined hospitalization. One of these workers, who had had a history of heart trouble but normal ECG's for the preceding 13 years, had a nonfatal heart attack a month after the accident. Prouza [22] concluded that the first worker probably died in a few seconds and that his fellow workers had showed "solidarity and a loss of judgment" in rushing to the rescue without protective equipment and routine precautions.

In a similar incident in Michigan, hydrogen sulfide at a concentration of 1,000 ppm caused the death in a well of a worker and four would-be rescuers, including the fire chief, who entered wearing a supplied-air respirator but removed the face mask to attempt to shout instructions to men on the surface [23]. Hydrogen sulfide poisoning may be mistaken for drowning, as it was in this case [23], or heart attack [24], or electrocution [25], with grave hazard to rescuers.

McCormack [26] reported hydrogen sulfide poisoning of two sewer workers exposed at an unknown concentration. One descended into a small, confined space to unclog a drain and collapsed. A second worker attempted to rescue him and was also overcome. Paramedics were called and initiated resuscitation at the scene after the workers were removed from the sewer, but the first worker was dead on arrival at the hospital. The second was hospitalized, cyanotic and unconscious, with rigid extremities, thrashing his legs in a bicycling fashion. He was breathing vigorously, and his pupils were dilated and reactive. He was incontinent of feces. Methane poisoning was suspected initially, but hydrogen sulfide was inculpated by blackened coins found in the patient's pocket. He was given amyl nitrite by inhalation and sodium nitrite intravenously to prevent poisoning of the cytochrome system and was given medication for agitation and pulmonary edema. The patient was discharged 5 days later without residual effects. This occurred in 1975; a similar incident was also reported by Breysse in 1970 [27].

St. Hill [28] reported the deaths, attributed to hydrogen sulfide, of two boys, 15 and 16 years of age, who worked in a tannery. A limepit had been filled with clean water and left unused for 2 years, in which time lime and acid solutions had drained off hides nearby and trickled into the pit. The pit, 7 feet deep and 6 feet square, was drained, and a man and the older boy stirred up the sludge at the bottom with water from a hose, then put on thigh boots and climbed in to move the sludge toward the open drain with their feet. After they had stirred and thinned the sludge for some time, the man collapsed and the boy clutched the ladder and fell backwards with it into the sludge. The foreman managed to prop the man against the wall and then collapsed himself. Two other workers, one of them the 15-year-old, also entered the pit and lost consciousness. Eventually, all were removed, but the two boys were dead. On autopsy, sludge saturated with hydrogen sulfide was found in the air passages and stomachs of the two boys, and their bodies smelled strongly of hydrogen sulfide. Followup data were not reported for the survivors. No air concentrations were reported for hydrogen sulfide in the pit, but St. Hill [28] inferred that the gas was evolved in large quantities when the sludge was stirred. No one at ground level had noticed any unusual odors.

Freireich [29] reported the death of a 17-year-old boy exposed to an undetermined concentration of hydrogen sulfide while attempting to rescue his father in a cesspool-cleaning operation. The father had entered the cesspool to complete a cleanup undertaken the previous day by professional cesspool cleaners who had pumped the 10-foot-deep cesspool half empty and poured in several gallons of concentrated sulfuric acid. The father noticed smarting or burning of his eyes and left the cesspool, then returned and left twice more. On his fourth descent, he felt weak, called to his son, and lost consciousness. When he regained consciousness, he saw the boy lying on the floor of the cesspool. He tried to move the boy but was again overcome before both were rescued by neighbors. The father recovered quickly, but the son died despite artificial respiration.

At autopsy, the son's corpse had a greenish-blue cyanosis of the head and face, hands, and legs. A faint yellow-brown stain appeared on lead acetate paper applied to the pectoral muscles, and the paper turned dark brown when held near the cut end of a bronchus. Pulmonary edema and congestion and several large subpleural hemorrhages were present. Sandy material mixed with sewage obstructed bronchi of the third and fourth order. The spleen and kidney showed congestion. Spectroscopic examination of the blood failed to reveal the presence of sulfhemoglobin or methemoglobin. Whether the cause of death was hydrogen sulfide poisoning or mechanical asphyxia from aspirated material was not determined. Freireich [29] suggested that the increased respiration from the son's attempts to rescue his father may have caused the son to inhale a greater quantity of hydrogen sulfide than the father.

Just as unconsciousness produced by hydrogen sulfide may cause death by drowning in as little as 6 inches of water [28-31], it may also cause death from falls. Spolyar [32] reported that a worker cleaning a 12-foot-deep gluten vat in a starch-manufacturing plant lost consciousness 25 minutes after entering the tank. The supervisor, on seeing the worker slump, entered the vat and placed the unconscious man on his shoulder. He started back up the ladder, but lost consciousness himself near the top and fell back to the bottom of the vat with the worker. Another worker went to summon a rescue squad with oxygen masks, but in the meantime a third worker also entered the vat and collapsed. The supervisor was dead on arrival at the hospital, and a fractured skull was confirmed at autopsy. The other two workers were hospitalized and remained unconscious for 2 days. They showed marked respiratory difficulty, but recovered completely in 7 days. The vat was aerated after the rescue operation, and analysis showed no more than 10 ppm of hydrogen sulfide the following morning. A 200-gram sample of sludge from the bottom of the vat was placed in a 5-liter jar, and within 4 hours hydrogen sulfide was detected in air from the jar at a concentration of 300 ppm; after 9 hours, the concentration was over 400 ppm. The vat had been idle for 10 days when the incident occurred, though normally it was emptied every 2-3 days. Spolyar [32] concluded that the men in the vat had been overcome by hydrogen sulfide liberated by the cleaning process. Several similar incidents of fatal falls caused by unconsciousness from hydrogen sulfide have been described [14,33].

Convulsions have been reported [15,31,33] with exposure to hydrogen sulfide, but the range of intensity of the convulsions seldom has been mentioned. Poda [3] mentioned twitching, but violent convulsions may occur. Milby [4] reported an acute exposure to hydrogen sulfide at an undetermined but high concentration when a cylinder containing the gas (liquified under a pressure of 250 psi) was punctured by a rifle shot. The liquid-and-gas cloud moved some 50 yards upwind and caused two men to collapse. One developed convulsions after 5 minutes of artificial respiration, and eight men were required to move him to the ambulance. Despite the severe convulsions, he survived.

Kaipainen [34] reported that a farm laborer was found unconscious in a cowshed where he had been shoveling manure. The duration and level of exposure were not known, but the exposure was reported to have lasted perhaps 2 hours and fit a pattern suggesting exposure to hydrogen sulfide. The worker was taken to the hospital, where he had epileptiform convulsions. The following day, he was restless and incoherent; patellar, Achilles tendon, and radial reflexes were absent, and the ECG showed negative T waves on leads II and III. Leg spasticity and the abnormal ECG persisted through the 3rd day but returned to normal by the 5th day. On the 3rd day, urinalysis showed 0.5% albumin and a sediment containing red and white blood cells and hyalin cylinders, indicating kidney damage. Two weeks later, blood cells and hyalin cylinders, but no albumin, were still present in the patient's urine. In the same 2-week period, nonprotein nitrogen in the urine decreased from 90 mg/100 ml of urine to 46 mg/100 ml of urine. The patient was discharged from the hospital after 3 weeks. At followup examination a month later, he reported that he had felt well except for slight dizziness.

Accidental mixing of acid with sulfide solutions in a tannery [24,35], or in sewer lines [36,37], resulted in the release of enough hydrogen sulfide (concentrations unknown) to kill eight workers and sicken dozens of others, some of whom required hospitalization.

Kemper [38] reported a case of acute hydrogen sulfide poisoning that was unusual in several ways. The victim, a 31-year-old refinery worker, survived exposure to hydrogen sulfide at about 1,000 ppm, a concentration that generally is rapidly fatal. The concentration was measured soon after the accident. The worker was found unconscious and deeply cyanosed near a spill of diethanolamine contaminated with hydrogen sulfide. He was not breathing and was given artificial respiration by the back-pressure arm-lift method. He was admitted to the hospital within 25 minutes of the time he was last seen walking in the vicinity of the accident. Oxygen was administered en route. When he arrived at the hospital, red foam was coming from his mouth, his respirations were depressed, and his heart rate was 180/minute and regular. No blood pressure could be determined from either arm. Violent convulsive seizures occurred repeatedly, and the worker developed opisthotonos. Endotracheal intubation was performed to permit alternating suction and oxygen administration. The patient's condition improved within 5 minutes; his color became less dusky, his systolic blood pressure was 85 mmHg (diastolic unobtainable), and his pulse rate was 150 beats/minute and regular.

He was transferred from the emergency department to the respiratory unit of the hospital, and was rendered hypothermic to reduce his body's demand for oxygen. Convulsions were controlled with drugs, the excess bronchial secretion stopped, and the patient's vital signs improved, although he was still comatose. He was given 500 ml of mannitol intravenously to promote urine flow, and he later showed gross hematuria. When respiratory distress occurred, the patient was ventilated by mechanical respirator. An hour after admission, the patient's color was normal, and 48 hours later he was awake and responsive. His kidney function was returning to normal, but he showed signs of lung consolidation and patchy bronchopneumonia. An ECG taken the following day showed "a left ventricular parietal block with posterolateral myocardial ischemic changes"; his heart rate was 132 beats/minute and regular. A chest radiograph was normal 12 days after the accident, and the patient was discharged from the hospital 3 days later. Serial ECG's taken during the latter part of his hospital stay and after his discharge showed a gradual return to normal over several weeks. There were sequelae; the worker suffered mild depression and lassitude for several months. He was absent from work for 134 days and a year later still had complete amnesia of the day of the accident. Kemper [38] believed that cerebral hypoxia probably accounted for the amnesia and the long period of depression and lassitude. The method of treatment departed from the usual supportive therapy by being much more active; the nearly complete recovery of the worker indicates that even severe poisoning by hydrogen sulfide may be overcome by sufficiently prompt, vigorous, and intensive treatment.

An air pollution incident in Poza Rica, Mexico, lasted only 20 minutes but resulted in the hospitalization of 320 persons and in the deaths of 22 [16]. About half the domestic animals, birds, and pets living in the area also died. The poisoning was attributed to hydrogen sulfide released from a malfunctioning sulfur recovery unit of the local natural gas industry. No measurements of the gas concentrations were reported, but the investigators estimated the peak concentration to have been 1,000-2,000 ppm of hydrogen sulfide in the air [16]. Clinical findings for the exposed persons included loss of the sense of smell, burning eyes, cough, dyspnea, pulmonary edema, nausea, vomiting, unconsciousness, severe headaches, vertigo, partial paralysis, neuritis of the acoustic nerve, lingual difficulty, and aggravation of a preexistent case of epilepsy. Of the people who died, nine were dead on arrival at the hospital, four died within 2 hours, four within 6 hours, one 24 hours after arrival, and one each on the 2nd, 5th, 6th and 9th days after hospitalization. Lasting sequelae were reported for only four of the human survivors (two with acoustic-nerve neuritis, one with dysarthria, and one with aggravated epilepsy and new nervous manifestations). Most of the animals that died (canaries, chickens, ducks, geese, cattle, pigs, and dogs) did so in the acute phase of the air-pollution crisis, except for one pig that died 3 days later.

The release of hazardous quantities of hydrogen sulfide during the stirring of human sewage [39] and animal manure [34] has also been reported. Aufdermaur and Tonz [39] reported three cases of poisoning, one fatal, of children exposed to hydrogen sulfide evolved at unspecified concentrations in rustic latrines connected directly to cesspools equipped with stirrers. One child died, one recovered, and one had lasting sequelae in the form of aphasia, agraphia, and mental retardation.

Johnstone and Miller [31] reported the survival, but with massive brain damage, of a worker exposed to hydrogen sulfide at an unspecified concentration. A few days after exposure, the worker's ECG recording gave indications of a right bundle branch block.

Sukhanova [40] reported observations of gastrointestinal changes in refinery workers and in animals exposed to hydrogen sulfide at unpsecified concentrations in air. Reduced gastric pepsin secretion (measured as uropepsin activity) was found in workers exposed to "cracking gas" (hydrocarbons, hydrogen, and hydrogen sulfide). These workers also had higher blood amylase activity levels and decreased trypsin activity. These results were generally confirmed in experiments with rats exposed for 5 months to cracking gas, but the concentrations of hydrogen sulfide were not specified, nor was the hydrogen sulfide exposure separate from exposures to hydrocarbons or other constituents of cracking gas.

In a few human subjects, the forearm was exposed to a solution containing 8.3% ammonium hydrogen sulfide or to pure hydrogen sulfide gas for 10-20 minutes; this produced a localized warm sensation, erythema, and pigmentation similar to a sunburn. Increased hydrogen sulfide absorption was reported in animals when the skin was damaged mechanically or by a chemical agent [41].

A case of chronic intoxication by carbonization gas (from the low-temperature distillation of lignite) appeared to resemble hydrogen sulfide intoxication in many ways [42]. The patient, who had worked in the gas plant for an unspecified time characterized as long by the author, complained of increasing torpor, coughing, and burning and a feeling of pressure in his eyes. Later, he developed stomach pains, headaches of increasing severity, and vertigo. There was bilateral conjunctivitis. The hydrogen sulfide content of carbonization gas averaged 2%. Methane and carbon monoxide, about 10% each, and heavy hydrocarbons, almost 1%, were also present.

Howes [43] investigated tannery workers' complaints of painfully sore eyes, severe photophobia, and tears which "burned the cheeks." Sulfides were being used in an adjoining building, and rapid darkening of a piece of lead acetate paper exposed in the affected men's work area indicated the presence of hydrogen sulfide. Howes concluded that the eye inflammation was an early warning signal of hydrogen sulfide poisoning and that open-air ventilation of the work area had prevented more serious poisoning.

Brown [44] reported that a foreman in a rubber company developed "blue vision" after "heavy" but unspecified exposures to hydrogen sulfide. His vision was normal by the following day. Brown drew a parallel with the effect seen with amine accelerators, in which the superficial layer of corneal cells acted as a filter. The author [44] also described the sudden collapse of a worker during the splitting and handling of ebonite (hard rubber foam) boards in which hydrogen sulfide may be trapped. The hydrogen sulfide concentration was not measured, but the work area was poorly ventilated because large quantities of materials were stacked nearby, and smelled "overpoweringly" of hydrogen sulfide 2.5 hours after the accident. To determine the approximate exposure concentration, four boards were cut with the saw; a hydrogen sulfide concentration of 100 ppm was measured at face level. The worker who collapsed had handled 850 boards. He had not complained of the odor, but had said he had felt tired before his collapse. He recovered promptly, without complaints except of a severe frontal headache, and returned to work the following day.

Beasley [45] described three cases of delayed eye irritation in two maintenance fitters and a visiting engineer in a gas plant. Clogged pipes were being cleaned with steam, resulting in exposures to steam, ammonia, carbon dioxide, and hydrogen sulfide at unspecified concentrations. Beasley attributed the delayed eye effects to hydrogen sulfide. The exposed workers described a gritty sensation in the eyes, blurred or hazy vision (headlights merged into a dumbbell-shaped glare; a silk screen seemed to be interposed in the line of vision), rainbow rings seen around street lamps, spasm of the eyelids, and retro-orbital pain. Beasley [45] cited other papers describing similar eye effects produced by hydrogen sulfide in support of his conclusion that that gas was the principal irritant in the cases he reported.

Commenting on the same cases reported by Beasley [45], Carson [46] noted that, of five men who might have been exposed, it was the three oldest who had vision disturbances. None of the workers complained of heat, humidity, or odor at the time they were exposed, which lends support to Beasley's [45] conclusion that hydrogen sulfide, not steam or ammonia, was responsible for the eye irritation.

Michal [18] reported eye lesions caused by hydrogen sulfide in a sugar-beet washing operation. Hydrogen sulfide concentrations were not given. Water containing sulfites was drawn from a river and stored in a holding tank where microorganisms converted the sulfites to hydrogen sulfide. Workers (number unspecified) using this water to wash the beets first saw colored rings around lights and then developed ocular lesions, severe pain and burning in the eyes, lacrimation, spasms of the eyelids, and conspicuous redness of the eyes. After 2-4 days of rest, the condition improved, so that the workers were able to return to work after 3-5 days.

Masure [47] reported studies of spinning-room conjunctivitis. Wide differences existed in individual susceptibility to the chemicals, including hydrogen sulfide and carbon disulfide, found in spinning rooms. Most workers appeared to become accustomed to the chemicals, but a few became sensitized. Related animal experiments led Masure to conclude that the conjunctivitis was caused by hydrogen sulfide, though concomitant exposure to carbon disulfide or sulfuric acid lowered the corneal threshold to hydrogen sulfide. The natural lack of blood supply to the central part of the cornea was thought to be a factor in the preferential development of lesions in that area.

Epidemiologic Studies

Nesswetha [48] studied etiologic factors in 6,500 cases of keratitis superficialis punctata (spinner's eye), attributed to occupational exposure to hydrogen sulfide in 1969. At a hydrogen sulfide concentration of 15 mg/cu m (about 10 ppm), eye irritation occurred after 6-7 hours of exposure. At a hydrogen sulfide concentration of 20 mg/cu m (about 14 ppm), symptoms developed after 4-5 hours. Spinner's eye appeared at hydrogen sulfide concentrations below the maximum allowable concentration (15 mg/cu m) when carbon disulfide was present. Other stressors, including noise, thioformaldehyde, and other irritating chemicals likewise caused increased susceptibility to eye irritation by hydrogen sulfide. Night-shift workers had a 41% higher incidence of spinner's eye than day-shift workers. The investigator [48] concluded that the mechanism of production of spinner's eye was neural and that the condition resulted from the joint effects of several factors, of which hydrogen sulfide was the most important. The neural etiology is plausible because the conjunctivitis was reported to be usually accompanied by hyperemia of the ciliary body ("ciliarer Injektion") [48]. The concomitant presence of carbon disulfide in the air of spinning rooms should be considered in evaluating the correlation of effects on the eyes with the reported amount and duration of exposure to hydrogen sulfide.

According to Ahlborg [15], 70% of workers exposed to hydrogen sulfide in their daily work, often at 20 ppm or more, complained of fatigue, somnolence, lack of initiative, decreased libido, loss of appetite, headache, irritability, poor memory, anxiety, dizziness, itching, eye irritation, respiratory tract irritation, gastrointestinal disorders, insomnia, and backache. Acute exposures to hydrogen sulfide at higher, generally unspecified, concentrations were associated with signs of cerebral and extrapyramidal damage, facial paralysis, prolonged reaction time, absent or abnormal reflexes at both cranial and spinal nerve levels, poor memory for recent events, depression, either timidity or fierceness, and with an epileptic-like seizure. Sequelae of acute hydrogen sulfide exposure occurred even when the affected individual had not lost consciousness. In one person, gastritis persisted for 1 year after exposure at an unspecified concentration. Another worker developed problems of maintaining equilibrium 6 months after acute exposure to hydrogen sulfide at an unspecified concentration. The disturbance of equilibrium still persisted after 3 years [15].

Poda [3] observed 174 workers exposed to hydrogen sulfide at two heavy-water manufacturing plants. The hydrogen sulfide concentrations were not reported, but the normal maximum working concentration limit voluntarily adopted at the heavy-water plants was 10 ppm of hydrogen sulfide for an 8-hour day, which was said to permit work with safety and to avoid the problems which had occurred before the adoption of this limit.

Examination of the records on 42 exposed workers who had become unconscious after exposure to hydrogen sulfide revealed that the majority described the odor of hydrogen sulfide as sickeningly sweet, rather than as that of rotten eggs. A survey of the signs and symptoms reported by 123 of the workers showed, in decreasing order of frequency: weakness, nausea, dizziness, headache, nervousness, burning or watery eyes, clinical shock, gastrointestinal upset, vomiting, elevated blood pressure, dyspnea, sweating, cyanosis, flushed face, abdominal cramps, flatulence, arm and leg pain, rigidity, irrational and combative behavior on returning to consciousness, twitching, and frothy sputum. The most significant sign is clinical shock. The combative individual had been drinking alcoholic beverages the previous evening; however, other papers have mentioned combative behavior, irritability [15], or excitability [49] without mentioning consumption of alcohol. The worker with frothy sputum had been drinking heavily the night before and had an upper respiratory infection [3]. In at least 27 workers, symptoms, including nervousness, headache, nausea, insomnia, weakness, cough, eye irritation, throat irritation, and soreness of the neck and shoulders, persisted for more than 4 hours. One mechanic, incontinent of urine and feces, was found unconscious and cyanotic with no apparent pulse or respiration. He was revived by artificial respiration. Upon hospitalization thereafter, he was discovered to have pulmonary edema, a productive cough, and a shock level of blood pressure. His blood pressure failed to rise until the 3rd day, despite administration of caffeine, phenylephrine hydrochloride, digitalis, and carbogen (3-5% carbon dioxide in oxygen). When discharged from the hospital, the worker had only a dry cough. No sequelae were observed during the next 3 years. Poda [3] reported no increase or decrease in sensitivity to hydrogen sulfide with exposure, but did say that workers who had consumed alcohol in the 24 hours before exposure were affected at lower concentrations.

Bulatova et al [50] studied 2,465 high-sulfur petroleum refinery workers in two different cities who were exposed to hydrogen sulfide at unspecified concentrations, with 601 machine-tool workers and 706 railroad-station workers as controls. The incidence of cholecystitis (gall bladder disease), cholangitis (bile duct disease), and cholelithiasis (gallstones) and the number of workdays lost because of these were greater in the oil refinery than in the other groups. The morbidity of oil refinery workers with over 5 years service was greater than that of those with less time in service. With contrast cholecystography, it was determined that 56 of 74 cases of biliary dyskinesia in oil-refining workers were of a hypermotor type and 12 were of a hypertonic type, whereas hypomotor dyskinesia was more common in other patients with cholecystitis. An electrogastrogram showed unevenness, indicating an irritated stomach, in 20 of 68 subjects. Gastric secretion was normal in 49 persons; 56 showed reduced pepsin activity.

In May and June 1964, the city of Terre Haute, Indiana, had a succession of air pollution incidents in which citizens' complaints were recorded and the hydrogen sulfide concentration in the air was measured [17]. The highest concentrations of hydrogen sulfide reported in this study [17] were between 2 and 8 ppm at the fence line near a chemical-disposal lagoon. Some recorded data were lost. Hydrogen sulfide levels ranged between 0.022 and 0.125 ppm for 7 consecutive hours, and 26 odor complaints were registered. Citizens reported nausea, vomiting, diarrhea, abdominal cramps, shortness of breath, choking, coughing, sore throat, chest pain or heaviness, headache, burning eyes, fainting, awakening at night, loss of sleep, acute asthma attacks, anorexia, and weight loss. In general, they did not consult physicians or seek assistance at a hospital. There were, however, four deaths attributed to chest diseases (emphysema, asthma, bronchitis) in April and May 1964; no deaths from these causes were recorded in the preceding higher risk months of February and March. Conclusions of the study were that complaints were related to the concentrations of hydrogen sulfide in the air and that potential danger existed for susceptible individuals (notably infants, the aged, and the infirm). Worker populations are generally healthier than city populations and might prove less susceptible to the effects of hydrogen sulfide. Still, this study did suggest that hydrogen sulfide can irritate the eyes and respiratory system at concentrations below 1 ppm, and that it has adverse effects on sleep and appetite and poses a danger at low concentrations to individuals with heart or lung diseases.

Animal Toxicity

The effects of hydrogen sulfide on humans and animals are similar. The studies in this section have firmer data on environmental concentrations than do the human case studies and describe results that could not ethically be obtained with human subjects.

Michal [18] exposed rats to hydrogen sulfide for 3 hours at 36 ppm or briefly at 860 ppm. Upon microscopic examination of the rats' corneas, he found nuclear pyknosis, edema, and separation of cells. Michal noted that these eye irritations were similar to those in workers in the viscose rayon industry, which he attributed, therefore, to the action of hydrogen sulfide.

Lund and Wieland [51] demonstrated the effects of exposure of three Rhesus monkeys in a chamber to hydrogen sulfide which reached a concentration of 500 ppm within 3 minutes. That concentration was maintained while the air was being recirculated to remove carbon dioxide and water vapor. The brain, liver, heart, kidneys, and adrenals were examined microscopically on autopsy. No control animals were mentioned. Typically, the animals lost consciousness abruptly in 15 minutes, without warning signals except repeated deep breaths as if gasping or yawning just before collapse, and fell from a standing position with stiff extremities, as if struck a violent blow. The first monkey had respiratory arrest and cardiac failure after 35 minutes of continuous exposure. No changes were observed on examination of the brain, heart, kidneys, or adrenals. The second animal was exposed to hydrogen sulfide at 500 ppm for 25 minutes on 1 day and for 17 minutes after a 3-day interval. The exposure was halted the first time because the monkey stopped breathing and required artificial respiration by compression of the thoracic wall. The second exposure was terminated when the monkey lost consciousness. The monkey was killed 5 days later and showed necrosis of the occipital cortex of the brain, necrosis, hyperemia, and gliosis of the basal ganglia, a decrease in the number of Purkinje cells in the cerebellar cortex, moderate hyperemia of the liver, and normal heart, kidneys, and adrenals. The third monkey was exposed to hydrogen sulfide for 22 minutes at 500 ppm and was still breathing spontaneously upon termination of exposure. It regained consciousness 140 minutes later, but remained somnolent for days, had no appetite, and its few movements were uncoordinated. The monkey was killed 10 days later, its condition having become only slightly more normal by that time. Microscopic examination revealed extensive necrosis of the parietal and occipital cortex of the brain, a reduced number of Purkinje cells in the cerebellar folia, isolated accumulation of glial cells in otherwise normal basal ganglia, and normal heart, liver, kidneys, and adrenals. The results indicated that the brain, particularly the motor cells of the cerebellum, was the principal target of inhaled hydrogen sulfide. This finding is supported by the work of Evans [11], who noted that "the most conspicuous actions of sulphides are on the nerve centres, which are first stimulated, then paralysed." Evans suggested that artificial respiration may be an effective treatment for poisoning by hydrogen sulfide because the paralysis of the nerve centers, the "reduction of oxyhemoglobin," and the combination of sulfides with iron in cytochrome A3 are reversible processes.

Cralley [52] reported inhibition of tracheal ciliary activity of adult rabbit tissue in vitro by hydrogen sulfide at concentrations between 300 and 800 ppm in warm air pumped over the excised tissue at a rate and volume simulating respiration in a living rabbit. Exposure to hydrogen sulfide in air at 800 ppm resulted in cessation of ciliary activity in less than 2 minutes; at 700 ppm, in 2 minutes; at 600 ppm, in 2.5 minutes; at

500 ppm, in 3 minutes; at 400 ppm, in 4.5 minutes; and at 300 ppm, in 6.5 minutes. Exposure to hydrogen sulfide at 600 ppm for 5 minutes or at 400 ppm for 10 minutes caused cessation of ciliary activity without recovery in air but, after exposure at 800 ppm for 3, 5, or 10 minutes, recovery occurred in Ringer's solution. The ciliary response in rabbits was, according to Cralley [52], similar to that of human tracheal mucosa.

Kosmider et al [53] exposed rabbits, about 1 year old, to hydrogen sulfide at a concentration of 0.1 mg/liter (72 ppm). Ten animals were exposed once for 1.5 hours, and 17 were exposed for 30 minutes/day for 5 days. Ten rabbits were controls. ECG's were recorded under Evipan (hexobarbital) anesthesia. Baseline ECG's for all rabbits were obtained 10 days before exposure. Rabbits exposed for 1.5 hours lost consciousness and showed disorders of repolarization of the ventricles but no arrhythmias. Those exposed for several days had arrhythmias, including atrial fibrillation in two rabbits, ventricular extrasystoles, and one or more ectopic pacemakers, in addition to disorders of repolarization similar to those seen in the first group. Arrhythmias persisted for several days after exposure ended but could be controlled by intravenous injections of sodium citrate. The activity of the enzymes ATP phosphohydrolase and NADPH2 oxidoreductase in heart muscle and in the lining of blood vessels was reduced in exposed animals. The authors cited this in support of the contention that hydrogen sulfide inhibits intracellular respiration.

Kosmider and others [54] also investigated "subacute" hydrogen sulfide poisoning, using 70 adult rabbits of mixed breed and either sex. Twenty rabbits were used as controls; 10 were given "Vitaral" (a dietary supplement of vitamins and minerals) with their food but were not exposed to hydrogen sulfide; 20 were exposed to hydrogen sulfide in air at a concentration of 0.1 mg/liter (72 ppm) for 1 hour/day for 14 days and received the dietary supplement with their food; and 20 were similarly exposed to hydrogen sulfide but were fed the regular food with no Vitaral supplement. Arterial blood samples were taken for chemical studies. The rabbits were killed after 14 days of exposure, and samples of blood, liver, kidney, cerebrum, and heart were taken for chemical tests or microscopic examination. Also, human blood serum was tested chemically in vitro, the tests being repeated 10 times. One part of the human serum served as control and four other parts were saturated for 20 minutes with hydrogen sulfide. Dilute solutions of magnesium chloride, cupric sulfate, or both, were added to three of the hydrogen-sulfide-saturated serum samples. Exposure to hydrogen sulfide resulted in a drop in the albumin level and a rise in serum globulins, especially beta globulin; although these changes were not statistically significant, more normal values were found after administration of Vitaral. The calcium ion concentration in the rabbit serum was unchanged after the animal was exposed to hydrogen sulfide, but there were lower serum concentrations of iron, copper, carbon dioxide, alkaline buffers, and magnesium, and a lower pH, the last two observations being statistically significant. Thymol turbidity and glutamic-oxaloacetic transaminase activity were singificantly increased in exposed rabbits, as were serum and heart alkaline phosphatase activity and ceruplasmin activity in serum, heart, and brain. All these changes were reversed by administration of Vitaral with the diet. Vitaral had little effect on the unexposed rabbits.

Microscopic examination of the rabbit tissues [54] for the enzymes succinyl dehydrogenase, acid phosphatase, alkaline phosphatase, and adenosine triphosphatase revealed a reduction in succinyl dehydrogenase activity in liver and kidney, reduction in alkaline phosphatase activity in the liver, and an increase in acid phosphatase activity in the liver after exposure to hydrogen sulfide. Vitaral increased the succinyl dehydrogenase activity and alkaline phosphatase activity in the liver.

The studies of human serum in vitro [54] showed a decrease or cessation of alkaline phosphatase and ceruloplasmin activity with exposure to hydrogen sulfide. These enzymes were reactivated by administration of "microelements of Vitaral." Magnesium chloride alone activated alkaline phosphatase after hydrogen sulfide inhibition; copper ions had a like effect on hydrogen-sulfide-inhibited ceruloplasmin. The authors concluded that hydrogen sulfide produces protein, mineral, and, consequently, acid-base disturbances. They also concluded that hydrogen sulfide poisoning disturbs brain, liver, and kidney metabolism and produces liver damage. One mechanism of action of hydrogen sulfide, they suggested, is based on its ability to bind alkali metals and thus decrease the activities of enzymes that require activation by these metals. "The protective mechanism of Vitaral is due to its ability to reactivate the disordered metal enzymatic activities [54]." The results of this study are consistent with the effects on cellular respiratory enzymes that have been attributed to hydrogen sulfide and with the observations of unconsciousness and other signs of adverse effects on the brain that have been produced by hydrogen sulfide.

Following injections by Sorokin and Olshanskaya [55] of 1-7.5 ml of water containing hydrogen sulfide at a concentration of 265 mg/liter into the ear veins of an unspecified number of rabbits, the heart rate slowed by lengthened diastole, and there were aberrations in the P and T waves of the ECG. The T wave increased at the start of injections, then decreased and, in some cases, disappeared. Usually, the T wave reappeared 30-40 seconds after an injection. The P wave disappeared at lower hydrogen sulfide concentrations and took longer to reappear. Rabbits that were given injections every 4-5 days for a month or longer showed adaptation, with less slowing of the heart and a quicker return to a normal rhythm in the ECG record. The authors noted that sensitivity (based on ECG) to hydrogen sulfide returned to original levels or higher, 10-15 days after cessation of repeated injections. It is not clear whether the authors attributed the adaptation to the heart itself or to some other organ or tissue, such as the blood or liver.

Duan [56] reported that 20 young male white rats weighing 60-90 g were exposed to hydrogen sulfide and tested for motor chronaxie. Ten other rats were used as controls and were tested similarly. All 30 were later autopsied. Twenty rats were exposed to hydrogen sulfide: 10 at a concentration of 0.02 mg/cu m (0.014 ppm) and 10 at 10 mg/cu m (7 ppm) for 12 hours each day for 3 months, except weekends. The chronaxie of extensors was longer than that of flexors in the control rats, as is normal. In the rats exposed to hydrogen sulfide, this relationship was reversed, beginning in the 8th week at the lower concentration and in the 3rd week at the higher concentration. By the 8th week, the group exposed at 10 mg/cu m (7 ppm) showed the normal relationship again but there was greater than normal variability in both flexor and extensor chronaxies which continued into the postexposure recovery period. Microscopic examination showed swelling of dendrites on neurons in the cerebral cortices of the more heavily exposed rats, coupled with mild irritation of tracheal and bronchial mucosa. No microscopic evidence of damage was apparent either in the rats used as controls or in those exposed to the concentration of hydrogen sulfide reported to be 0.02 mg/cu m.

Hays [57] subjected mice, goats, and dairy cows to experimental exposures of hydrogen sulfide. Mice and goats were placed inside exposure chambers; cows were exposed in hoods that enclosed their heads and communicated with an established concentration of hydrogen sulfide in air. Each goat or cow served as its own control; groups of mice equal in number to the exposed groups served as controls. Body weight and food and water intake were recorded for all species, as were rectal temperatures for mice and goats. Carbonic anhydrase activity and pentobarbital sleeping time in mice, plasma cortisol concentration in goats, heart rate in goats and cows, and milk production in cows were measured. The goats were individually exposed; the data were then pooled in nominal experimental or control groups of 3-5 animals. Six Swiss-Webster mice were exposed to hydrogen sulfide at a concentration of 10 ppm and had a decrease in body temperature which was statistically significant within this experimental group but, because their mean body temperature was not significantly different from that of the control group, probably had no biologic importance. Eight mice exposed to hydrogen sulfide at a concentration of 20 ppm for 48 hours showed no significant difference from the control group in pentobarbital sleeping time. Hydrogen sulfide at 20 ppm depressed the food and water intakes and body weight of mice. The LC50 for mice was 100 ppm for a 7.5-hour exposure, 50 ppm for 15 hours, and 30 ppm for 18.5 hours. Goats, like mice, showed decreases in food and water intake in the first few days of exposure to hydrogen sulfide, but the effects seemed only temporary. Hayes suggested different suppression mechanisms for exposure at 10 ppm versus 50 or 100 ppm. At these higher hydrogen sulfide concentrations, goats showed elevated plasma cortisol levels (about 50% mean increase). No statistically significant changes occurred in the cows, though milk production decreased both during and after exposure to hydrogen sulfide.

It is possible that toxic quantities of hydrogen sulfide can be absorbed through the skin, but the evidence is not conclusive. Walton and Witherspoon [58] reported the survival of two guinea pigs exposed for 1 hour to pure hydrogen sulfide gas on a 0.78-sq-in area of shaved abdominal skin and the deaths of two guinea pigs exposed, one for 38 minutes and one for 45 minutes, to pure hydrogen sulfide gas on half their bodies. A dog exposed for 1 hour to hydrogen sulfide gas on its shaved abdomen survived without adverse signs [58]. Petrun [59] observed changes in blood chemistry of rabbits whose backs were shaved and exposed to hydrogen sulfide at concentrations of 717 ppm and higher. Laug and Draize [41] found that, when rabbits' bodies were exposed to hydrogen sulfide for as little as 7 minutes, the air exhaled by the rabbits gave positive lead acetate tests for hydrogen sulfide. They also noted that two of the rabbits so exposed died in about 2 hours. The exposed skin showed a slate-gray discoloration with dark chocolate areas.

Wakatsuki [60] exposed four rabbits weighing about 2 kg each to hydrogen sulfide at a concentration of 100 ppm for 30 minutes/day for 4 months. Four rabbits were used as controls. The hydrogen sulfide was produced in a Kipp generator and passed through iodine to remove traces of arsine. Records were kept of the rabbits' body weight, erythrocyte and reticulocyte counts, leukocyte count, serum calcium concentration, serum proteins, and specific gravity of the blood. All results were normal, except for a leukopenia and lymphocytosis. These findings suggest that hydrogen sulfide may have an adverse effect on the reticuloendothelial system. Other effects might have developed if the exposures had been of longer duration.

Kuwai [61] conducted a similar study, using a somewhat more sophisticated gas-mixing apparatus, in which five rabbits were exposed to hydrogen sulfide at a concentration of 20-25 ppm for 4 hours/day for 150 days. He measured body weight, reticulocyte count, blood specific gravity, serum proteins, and serum cholesterol. Five rabbits were used as controls. Kuwai's rabbits, like Wakatsuki's, had results within normal limits in most of the variables measured. One rabbit exposed to hydrogen sulfide failed to gain weight, unlike the controls and the others exposed. The exposed rabbits also had higher amounts of serum gamma globulin than did the controls. It is difficult to conclude anything from studies using only four or five animals in the experimental and control groups. Kuwai's study does, however, tend to support the suggestion of reticuloendothelial system changes in Wakatsuki's results, and does match observations by other investigators of weight loss and loss of appetite in humans exposed to hydrogen sulfide.

Barilyak et al [62] studied the effects of a combination of carbon disulfide and hydrogen sulfide on reproduction in rats. Rats were exposed to carbon disulfide and hydrogen sulfide at a combined concentration of 10 mg/cu m (the actual concentrations of carbon disulfide and hydrogen sulfide were not given); 26 rats were used as controls. In the first experimental group, 11 females and an unspecified number of males were exposed to the mixture continuously for 70-90 days and then mated; the pregnant females were then subjected to further exposure at the same experimental conditions until the 20th day of gestation. In the second group, 13 females were exposed for 70-90 days, mated with unexposed males, and kept under exposed conditions. In group 3, an unspecified number of males exposed for 70 days were mated with 11 unexposed females, with gestation under control conditions. The 12 females of group 4 were exposed during days 1-20 of gestation. In group 5, 11 females were exposed for 70-90 days, kept under control conditions for 70 days, and then mated to unexposed males. A control group of 26 females were mated to unexposed males. All pregnancies were terminated on day 20 of gestation. Fetuses were examined for terata, and portions of liver and kidneys were taken from both mothers and fetuses for microscopic examination. Numbers of corpora lutea, implantation sites, and live fetuses were determined for each group. These figures were used to calculate the numbers of embryonic deaths before and after implantation and the total number of intrauterine deaths.

The mean numbers of live fetuses were 5.4, 3.8, 6.4, 6.7, 6.5, and 9.0 for each female rat in groups 1-5 and controls, respectively. The corresponding percentages of deaths of concepti given by the authors were 50, 62, 39, 22, 35, and 9.3%; however, calculation from the authors' data gives a value of 35% rather than 22% for group 4. Carbon disulfide and hydrogen sulfide showed definite embryotoxicity; calculations from their data show that differences between exposed and control rats were significant for all groups. The most pronounced effects were in group 2, although group 1 was also markedly affected. Even when exposed animals were not mated until 70 days after the end of exposure, preimplantation and postimplantation mortality rates were significantly higher than in controls ($P<0.005$ and $P<0.001$). In group 1, there were 2 cases of hydronephrosis in the 32 fetuses, and 1 fetus in 24 had a supernumerary 14th rib. Also, 5.4% of the embryos in group 1 showed "developmental anomalies," whereas there were none in the controls. In group 2, two fetuses had hydrocephaly and hydronephrosis. Microscopic examination showed changes in small blood vessels in the livers of the embryos of groups 1 and 2. Eight rats of group 1 and four of group 2 had retarded ossification. Rats of other groups did not show such substantial abnormalities. Barilyak et al [62] described their data as showing a "weak teratogenic effect" of exposure to carbon disulfide and hydrogen sulfide. However, data and many methodologic details of this study are inadequately reported. It is unclear whether the rats were exposed to 10 mg/cu m of carbon disulfide and 10 mg/cu m of hydrogen sulfide or to a total concentration of 10 mg/cu m. It is difficult to interpret the results quantitatively since individual litter data were not given. Proper statistical tests were not performed on the teratologic data; therefore, conclusions about the teratogenic effects of exposure to carbon disulfide and hydrogen sulfide cannot be made with confidence.

Sandage [63,64] conducted a series of experiments designed to simulate exposure during space flight to toxic chemicals found in feces. In the first study [63], 50 rats, 100 mice, and 10 monkeys were exposed continuously for 90 days to a mixture of indole (10 ppm), skatole (3 ppm), hydrogen sulfide (20 ppm), and methyl mercaptan (50 ppm). Similar groups were exposed to fresh air and were used as controls. Hematology, blood chemistry (monkeys only), urinalysis, kidney function (monkeys and rats only), and swimming-stress tests were done on a sampling schedule. No clear pattern of results emerged, but all exposed species had sulfhemoglobin and an increased number of reticulocytes in the blood samples, and all exposed groups failed to gain as much weight as controls. Of the exposed monkeys, 80% died, but the cause of death was unknown.

The second study [64] was designed to sort out which compounds had caused which effects. There were four groups of animals composed of 10 monkeys, 50 rats, and 100 mice. Each group was exposed continuously for 90 days to one of the following: (1) a mixture similar to that used in the first experiment, methyl mercaptan (50 ppm), hydrogen sulfide (20 ppm), indole (10.5 ppm), and skatole (3.5 ppm); (2) hydrogen sulfide (20 ppm); (3) methyl mercaptan (50 ppm); and (4) indole (10.5 ppm). A fifth group was housed in the same room as the exposure chambers and served as controls. All animals were males. Again, studies were done on hematology, blood chemistry (monkeys only), urinalysis, and swimming stress. Liver function tests replaced kidney function tests and were done on monkeys only. The author stated that, "... in no single instance did all three species of the same group show the same physiological response to the toxic agent.... Only rats appeared to have pathology referable to H2S exposure, and this is in the lung [64]." Increased mortality over controls was seen in rats and mice, and all species showed a higher incidence of changes in the lungs than did controls, but these findings were not statistically significant. It is unfortunate that the author did not report all the data said to have been collected. It is also unfortunate that the control animals were not sham-exposed in a chamber with the same air temperature, pressure, and humidity as the experimental groups' chambers, but the study does suggest that hydrogen sulfide, alone or in combination with exertion stress, may lead to pathologic changes of the lungs.

Correlation of Exposure and Effect

Clear and compelling evidence of chronic or cumulative effects of hydrogen sulfide exposure has not been found in the literature, though a few papers [50,54] suggested that there were such effects. A number of studies suggest that hydrogen sulfide produces subacute effects, particularly with indications of brain damage [3,15-18]. Among the signs and symptoms indicative of brain damage are rigidity [3] abnormal reflexes [15], dizziness [3,15,18], sleep disturbance [3,15,17], and loss of appetite [15,18]. Reports exist of a short-term effect (conjunctivitis) of hours-long, low-level exposure [43,48], and of residual effects (abnormal ECG, brain damage) of brief, massive exposure to hydrogen sulfide [15]. Zander [42] used the term "chronic," but the exposures that led to the "chronic" intoxication were to a mixture of gases and volatile substances. Legge [12] reported a case of spinal cord degeneration associated with a 2-year exposure to hydrogen sulfide, but the evidence for a cause-and-effect relationship is meager.

There have been many reports of adverse health effects produced by acute exposure to hydrogen sulfide at high concentrations (several hundred ppm or higher). There are few reports [17,65] showing untoward effects from instances of prolonged exposure (several hours or longer) to hydrogen sulfide at low concentrations (below 50 ppm). There are few long-term studies (using animals) which reported exposure to hydrogen sulfide at low concentrations [57,64]. Hydrogen sulfide concentrations and related effects on humans and animals are summarized in Tables III-1 and III-2.

Measurements of the olfactory threshold for hydrogen sulfide have both dose-response and duration-response relationships. The lower limit for detection of hydrogen sulfide by odor is 0.02-.003 ppm [17]. At concentrations up to 30 ppm, the gas has an odor like that of rotten eggs. At a concentration of about 30 ppm, the odor of hydrogen sulfide may appear to be sweet or sickeningly sweet. Above 100 ppm, hydrogen sulfide rapidly abolishes the sense of smell, so that high concentrations may not be detected by odor at all. Similarly, olfactory fatigue may result from prolonged exposure to hydrogen sulfide at concentrations below 100 ppm. The sense of smell should not be relied on, therefore, to warn workers of the presence of hydrogen sulfide, particularly in dangerous quantities.

Hydrogen sulfide at low concentrations may cause headaches [17], but these headaches, unlike those caused by carbon monoxide poisoning, are not early warning signals of high hydrogen sulfide concentrations. Headaches were frequently associated with exposure to hydrogen sulfide [3,15-18,44].

Duan [56] described swelling of dendrites in the brains of two rats exposed to hydrogen sulfide in air at a concentration of 7 ppm. The change was small enough to be an artifact.

Cough, disturbed sleep, nausea, vomiting, and diarrhea have been reported after exposures to hydrogen sulfide at a wide range (0.022-2,000 ppm) of concentrations [3,16,17].

At high concentrations (several hundred ppm or more for 15 minutes or longer), hydrogen sulfide may cause respiratory difficulty, pulmonary edema with hemorrhage, respiratory depression, neural damage (central or peripheral), and abnormalities of the cardiovascular system [14,16,20,38]. Hydrogen sulfide at or above a concentration of 1,000 ppm usually produces unconsciousness immediately and causes death from respiratory arrest in minutes [21,23,38]. Hydrogen sulfide may also interfere with cellular respiration by poisoning the cytochrome system [26]. Sequelae of hydrogen sulfide exposure, including epilepsy [16], acoustic-nerve neuritis [16], abnormal ECG [31,38], and memory impairment or amnesia [15,25,38], may be the result of anoxia. Rarely, vegetative survival without a return to consciousness may follow survival of a major exposure to hydrogen sulfide [31].

At low concentrations (20 ppm or less), hydrogen sulfide may cause eye irritation after several hours of exposure, but this effect does not occur in all who are exposed [48,65]. Hydrogen sulfide causes painful conjunctivitis, sometimes with corneal erosion and spasm of the eyelids [18,43-46,48,66]. These effects may occur in less than 8 hours at concentrations of hydrogen sulfide at or below 15 ppm in air [48,65,67], and they develop more rapidly if carbon disulfide is also present in the air [48].

The reported eye effects in humans (conjunctivitis, keratitis, and corneal blistering, pitting, and opacity) from hydrogen sulfide exposure are generally acute effects, which have been confirmed in some instances by animal experiments. No reports of lasting eye damage were found, although recovery often requires absence from work for several days [15,18,48], and secondary infection may lead to permanent blindness [68].

Although several papers have featured the adverse effects of hydrogen sulfide on the eyes [18,43-46,65-67], a summary of 26 signs and symptoms resulting from an acute exposure of 89 persons to hydrogen sulfide at unspecified concentrations which caused two deaths [37] placed conjunctivitis last in order of decreasing frequency. Also unusual in this frequency distribution [37] was the reported low frequency of pulmonary edema.

Carcinogenicity, Mutagenicity, Teratogenicity, and Effects on Reproduction

No reports associating hydrogen sulfide in air with carcinogenesis, mutagenesis, or teratogenesis were found in the literature.

Barilyak and his coworkers [62] reported what they concluded was a "weak teratogenic effect" in rats following low-level exposures to a combination of hydrogen sulfide and carbon disulfide. This study presents no strong evidence that supports teratogenic effects from exposure to hydrogen sulfide alone, so that without more specific corroborating evidence, the results of this investigation must be considered tentative.

TABLE III-1

EFFECTS OF HYDROGEN SULFIDE INHALATION ON HUMANS

No. of Subjects	Concentration (mg/cu m)	Duration of Exposure	Effects	Reference
1	17,000	-	Death	20
1	2,800-5,600	<20 min	"	21
10	1,400	<1 min	Death 1/10, unconsciousness, abnormal ECG	22
342	1,400-2,800	<20 min	Hospitalization of 320, death of 22 including 13 in hospital, residual nervous system damage in 4	16
5	1,400	Instant	Unconsciousness, death	23
1	1,400	<25 min	Unconsciousness, low blood pressure, pulmonary edema, convulsions, hematuria	38
4	400 - 760	-	Unconsciousness	69
1	320	20 min	Unconsciousness, arm cramps, low blood pressure	15
78	20 - 35	-	Burning eyes in 25, headache in 32, loss of appetite in 31, weight loss in 20, dizziness in more than 19	12
6,500	15 - 20	4-7 hr	Conjunctivitis	48
City of Terre-Haute	0.003-11	Intermittent air pollution episodes over a 2-mon period	Numerous complaints of nausea (13), headache, shortness of breath (4), sleep disturbance (5), throat and eye irritation (5)	17

TABLE III-2

EFFECTS OF EXPOSURE TO HYDROGEN SULFIDE ON ANIMALS

Route of Exposure	Species	Exposure Concentration*	Exposure Duration	Effects	Reference
Inhalation	Monkey	700	25 min; 17 min 3 d later	Extensive changes in gray matter, moderate liver hyperemia	51
"	"	700	35 min	Irritation of conjunctivae, sudden loss of consciousness, respiratory and cardiac arrest	51
"	"	700	22 min	Ataxia, anorexia, parenchymal necrosis in brain	51
"	"	28	90 d	Weight loss, increased blood amylase and alkaline phosphatase activities	64
"	Rat	28	"	Weight loss, abnormal changes in lungs, increased number of reticulocytes, increased mean corpuscular volume, death	64
"	"	10	12 hr/d 3 mon	Mild irritation of tracheal, bronchial mucosa; weight gain less than in controls; motor chronaxie abnormalities; abnormal cerebral cortex dendrites	56

TABLE III-2 (CONTINUED)

EFFECTS OF EXPOSURE TO HYDROGEN SULFIDE ON ANIMALS

Route of Exposure	Species	Exposure Concentration*	Exposure Duration	Effects	Reference
Inhalation	Rat	0.018	12 hr/d 3 mon	Motor chronaxie abnormalities	56
"	Mouse	140	7.5 hr	LC50; anorexia	57
"	"	70	15 hr	"	57
"	"	28	90 d	Weight loss, abnormal changes in lungs, increased number of reticulocytes, increased mean corpuscular volume	64
"	"	15	5 d	Anorexia	57
"	Rabbit	140	0.5 hr/d 4 mon	Leukopenia, lymphocytosis	60
"	"	100	1 hr/d 14 d	Disturbed metabolism in liver, brain, and kidneys; blood serum mineral, protein, and enzyme activity changes, depletion of buffers, lowered blood pH	53
"	"	100	0.5 hr/d 5 d	Cardiac irregularities, decreased myocardial enzyme activities	53
"	"	100	1.5 hr	Unconsciousness, cardiac irregularities, decreased myocardial enzyme activities	53

TABLE III-2 (CONTINUED)

EFFECTS OF EXPOSURE TO HYDROGEN SULFIDE ON ANIMALS

Route of Exposure	Species	Exposure Concentration*	Exposure Duration	Effects	Reference
Inhalation	Rabbit	28-35	4 hr/d 150 d	No weight gain, increased serum gamma globulin	61
Dermal	"	2 mg/1 1 mg/1	-	Decrease in carbo-anhydrase activity, anhydrase index, blood-hemoglobin content, erythrocyte respiration, and cholinesterase activity	59
"	Dog	100%	1 hr	No effects	58
Dermal, 0.78 sq in	Guinea pig	100%	"	Slight swelling and black discoloration of exposed skin	58
Dermal, half of body	"	100%	45 min	Leg-muscle relaxation, dyspnea, death	58

*Concentration in mg/cu m for inhalation exposures

IV. ENVIRONMENTAL DATA

Environmental Concentrations

Little information has been reported on the hydrogen sulfide concentrations to which workers have been repeatedly exposed in the workplace. One report [70] gave concentrations found in viscose rayon churn rooms, spinning tanks, and drying and storage cellars. Typically, workers in these places were exposed during the workday to hydrogen sulfide at concentrations of 20 mg/cu m (15 ppm) or less, with occasional peaks of about 140 mg/cu m (100 ppm). However, most reports of hydrogen sulfide exposure have dealt with short exposures at high concentrations, and the related workplace environmental data were collected after the emergency had subsided. In one incident [69], hydrogen sulfide concentrations of 400-760 mg/cu m (295-540 ppm) were measured in an outdoor pit 5 days after four workmen became unconscious there. In other cases [21,32,44], hydrogen sulfide concentrations present at the time workers were exposed have been estimated by determinations made during reenactment or simulation. A leaking pipe conducting waste gases from a cooker in which fertilizer was being made from poultry feathers discharged hydrogen sulfide at concentrations of 2,800-5,600 mg/cu m (2,000-4,000 ppm) during the cooking cycle, which was presumably the same concentration range that was fatal to a workman trying to plug the leak [21]. A sludge sample removed from a starch vat, in which one worker died trying to rescue another who had collapsed, evolved hydrogen sulfide in a jar, which accumulated to concentrations of 420 mg/cu m (300 ppm) after 4 hours and to 560 mg/cu m (400 ppm) after 9 hours [32]. A workman became unconscious while sawing ebonite boards [44]. Other workers noticed that his work area reeked of hydrogen sulfide; hydrogen sulfide was measured at a concentration of 140 mg/cu m (100 ppm) at face level after four boards were passed through the saw several hours later [44].

Hydrogen sulfide is slightly heavier than air [71] and may accumulate to dangerous concentrations in wells, sewers, and confined spaces. Five men died in a well or cistern containing hydrogen sulfide at a concentration of 1,400 mg/cu m (1,000 ppm) [23]. One man died in an "empty" viscose spinning tank, and nine others lost consciousness from the effects of hydrogen sulfide measured at 3,900 mg/cu m (2,800) ppm [22]. A driver cleaning his industrial waste tank truck died from exposure to hydrogen sulfide at a concentration of 17,000 mg/cu m (12,000 ppm) [20].

Control of Exposure

Adequate spark-proof ventilation is one of the basic principles of engineering control of hydrogen sulfide exposure and is effective in preventing eye irritation from hydrogen sulfide [43]. For example, waste gases containing hydrogen sulfide should be removed by portable ventilators or other devices before tunnels and sewers are entered [21,22]. Adequate provision must be made for situations in which the hydrogen sulfide content of waste gas may fluctuate between safe and unsafe levels. Ventilation and continuous monitoring are advisable when dissolved, adsorbed, or occluded hydrogen sulfide may be liberated by stirring of sludge [32] or other masses of submerged fecal, animal, or plant materials. In chemistry laboratories, hydrogen sulfide must be handled in fume hoods with efficient exhaust fans, and care must be taken to avoid mixing sulfides and acid accidentally in drains. The principles set forth in Industrial Ventilation--A Manual of Recommended Practice [72], published by the American Conference of Governmental Industrial Hygienists (ACGIH), and Fundamentals Governing the Design and Operation of Local Exhaust Systems, Z9.2-1971 [73], published by the American National Standards Institute, should be applied to control workplace atmospheric concentrations of hydrogen sulfide. An industrial hygienist should decide questions of whether the system should be air-supplied or exhaust. Ventilation systems must be inspected and maintained to ensure effective operation. A program of scheduled inspections of ventilation systems should be established, including face velocity measurements of the collecting system, inspection of the entire ventilation system, and measurements of workroom airborne concentrations. The effects of any changes that may affect the ventilation system or the operations being ventilated must be assessed promptly to ensure that engineering controls provide adequate protection of employees engaged in the affected operation or operations.

Guidelines for drilling operations are given in the US Geological Survey's safety requirements for drilling operations in a hydrogen sulfide environment (GSS-OCS-1) [74], the American Petroleum Institute recommended drilling practices (RP 49) [75], the State of Michigan Guidelines for Sour Oil and Gas Wells and Associated Facilities [76], and the State of Texas Railroad Commission Rule 36 [77]. Included in these guidelines are blowout prevention, use of chemical inhibitors, use of air pressure or ballast mud, air monitoring and alarm system, gas detection on mud return, and air-supplied respiratory protection at the worksite and, in the case of offshore drilling, in the crew's quarters, at the heliport, and on the helicopter for the pilot. Abandoned wells should first be closed with conditioned mud and then sealed with concrete. Hazardous areas, particularly confined spaces, should be monitored and ventilated continuously before and during entry.

Environmental Sampling and Analytical Methods

(a) Sampling

Hydrogen sulfide may be sampled intermittently or continuously. The samples should be representative of the workers' breathing-zone air. Intermittent samples have been taken in plastic bags, evacuated bottles, Tutweiler gas-absorption burets [78], and length-of-stain tubes [79]. Hydrogen sulfide has been continuously sampled by exposing lead acetate-treated paper tape [80,81] or ceramic tiles [82] to air, by pumping air through lead-acetate filters or silver mesh [83-85], by bubbling air through one or more impingers containing absorbing or colorimetric solutions [79,86], and by using long-duration detector tubes or electronic detectors [87,88]. Qualitative hydrogen sulfide detection has been based on the blackening of coins, keys, lead-based paint, and paper moistened with lead acetate solution.

With the invention in 1922 of the Greenburg-Smith impinger, continuous and automated sampling for dusts and soluble gases became possible [86,89]. Hydrogen sulfide has been trapped in impingers in alkaline solutions of zinc or cadmium ions [79]. Usually more than one collector in series has been used to absorb all the hydrogen sulfide [86]. Precipitated sulfides may adhere to fritted bubblers [86]. Before the development of plastic impingers, impingers were made of glass and were comparatively expensive. Also, the sampling of the employee's breathing zone had to be done by someone following the worker around carrying the impinger, because the absorbing solution would be spilled if the worker wore or carried the impinger.

In the last 5 years, several direct-reading instruments have made real-time monitoring of hydrogen sulfide feasible [87]. Some of these instruments have two steps for sampling and analysis; the gas is absorbed and then reacted to obtain a reading. Other methods, including those with detector tubes or with metal-oxide-coated chips that react with the gas and give an electrical deflection directly and those based on electromagnetic absorption or emission, combine sampling and analysis into a single step.

(b) Analysis

Analytical methods for the ceiling limit should be capable of differentiating between hydrogen sulfide concentrations in the 0-28 mg/cu m (0-20 ppm) range. Detection of the evacuation limit requires a range of 0-100 mg/cu m (0-70 ppm); the method of analysis for the evacuation limit also must be rapid (in real time, within 20 seconds) to be of value in protecting workers and must be continuous unless the workplace air environment is static and free of hydrogen sulfide and hydrogen-sulfide sources or is adequately controlled by ventilation.

An automatic direct-readout hydrogen sulfide detection and alarm system was described in 1944 by Clough [90]; it used chemically treated paper tape, a photocell, and an amplifier. There are seven general types of hydrogen sulfide analysis with direct-readout capability [87]:

(1) Magnetic, notably mass spectrometry. This does not work well because hydrogen sulfide may react with a variety of chemicals at

the temperatures employed for mass spectrometry.

(2) Electromagnetic, including absorption or emission spectrometry in the infrared, visible, or ultraviolet ranges. These techniques may be automated; they are direct, one-step analyses, unless dilution is required, but they have not been successful in practice for hydrogen sulfide determinations [91-93].

(3) Chemicophysical, including colorimetry, chemiluminescence, and flame photometry. Although sensitive, these techniques are slow, two-step analyses. The best established of these techniques is the methylene-blue technique recommended by NIOSH for determining ceiling concentrations of hydrogen sulfidee.

(4) Electrochemical, with and without a selectively permeable membrane, including measurements based on conductivity, coulometry, potentiometry, and ionization. Conductivity measures require a constant temperature. These are adaptations of wet-chemical techniques to portable applications.

(5) Gas-liquid chromatography, a sensitive special technique requiring considerable technical and logistical support but feasible for situations like petroleum production. Gas-liquid chromatography [94-99] provides semicontinuous monitoring of hydrogen sulfide in discrete samples. It is sensitive to hydrogen sulfide at low or high concentrations, although it is most sensitive at concentrations greater than 70 mg/cu m (50 ppm) [92]. Problems in using this method for estimating hydrogen sulfide include variation in response with temperature fluctuations, interference from water, and condensation of samples in the lines entering the apparatus [92]. Gas-liquid chromatography has been used

in the field by oil and gas production companies. Gas-liquid chromatography combined with either flame photometry [100-102] or ionization detection [103] covers a much wider range of concentrations (six orders of magnitude) but requires carrier gases. Gas chromatography with flame ionization is insensitive for detection of hydrogen sulfide [93].

(6) Metal-oxide-coated chip semiconductors, a "dry" analytical method in which the surface of the detector reacts with hydrogen sulfide to produce a signal by potentiometry or voltametry. The surface can be modified to detect certain substances and "ignore" others.

(7) Length-of-stain indicator tubes, having granules coated with, or a gel impregnated with, a color-generating chemical, such as lead acetate, cadmium cyanide, or silver cyanide [79]. These devices were introduced in 1935 [89], but they were described in 1956 as unsuitable for air pollution studies [104]. The objection was probably made because the lower limit of detection was too high for ambient air monitoring. Indicator tubes can be used for both intermittent and continuous sampling. Indicator tubes have been developed for 8-hour sampling periods. Although such systems have been automated, sampling with indicator tubes is, in practice, mostly manual. Although the variability of these tubes from different manufacturers once was great, it has been limited now to ±25% by NIOSH's certification program, and many are certified within ±10%.

In 1935, Littlefield et al [104] recommended the use of length-of-stain tubes for detection and quantitative estimation of hydrogen sulfide at concentrations between 25 and 500 ppm in the field, stating:

> The usual methods of detection...either are too cumbersome for frequent and rapid analyses or, like the wet lead acetate paper test, afford only qualitative results. A quantitative determination usually involves the use of solutions, bubblers, flowmeters, standard solutions, burettes, and indicators manipulated by trained technical men. All apparatus and methods in common laboratory use are, in general, unsuitable for the field [104].

Detector tubes [80,105-107] have the advantages of being inexpensive, responsive over a wide range of concentration (eg, 1-800 ppm), and useful for probing confined spaces. However, other sulfides, sulfur dioxide, and nitrogen dioxide interfere with hydrogen sulfide determinations made with detector tubes, generally giving false positive readings. Nevertheless, detector tubes are valuable and are widely used in industry to provide a quick indication of whether the environment is safe, questionable, or definitely hazardous.

The American Public Health Association Subcommittee on Chemical Methods in Air Analysis [108], in 1943, recommended collecting hydrogen sulfide with cadmium chloride in two simple petticoat bubblers in series and then doing a titration with iodine using starch as an indicator, or using an excess of iodine and back-titrating with sodium thiosulfate solution. The iodometric bubbler was the method recommended by the Harvard School of Public Health in 1943 [109], although it was noted that detector tubes were the most rapid method.

Paper tape [80,81,110-114] or film [115,116] treated with lead acetate or a similar chemical, and lead acetate-treated tile [82] are inexpensive and sensitive below 1 ppm, but methods using them generally are semiquantitative and subject to interference from ultraviolet light, particulate matter, nitrogen dioxide, air turbulence, and changes in airflow. Additional disadvantages of lead acetate-treated tiles are that their quality varies with the manufacturer and the acetate is easily washed off by rain [92]. The tiles can be protected from rain [117], but then they cannot be seen readily. They have been used chiefly in monitoring environmental air pollution rather than occupational exposures to hydrogen sulfide.

In 1965, the American Industrial Hygiene Association Analytical Guide [118] listed three methods for determining hydrogen sulfide and their sensitivities: iodine oxidation using the Tutweiler buret, sensitive to 14-30 mg/cu m (10-20 ppm); cadmium sulfate and iodine in one midget impinger, sensitive to 1 ppm; and formation of cadmium sulfide colloid at a temperature below the boiling point of water using two midget impingers in series, sensitive to 7-170 mg/cu m (5-120 ppm). Mercaptans interfered with all three techniques.

There are colorimetric techniques [80,119] which are selective for hydrogen sulfide, as opposed to other sulfides or mercaptans. The result is generally expressed as an average value for a 30-minute sample [92], so that these techniques are suitable for TWA concentration determinations but not for alarm systems.

In 1937, Gonzales et al [120] proposed a method for determining the concentration of hydrogen sulfide in the air that involved aspirating a known quantity of air through an acidic solution of soluble lead salt and then weighing the precipitate. This method was slow and cumbersome. In 1940, Shaw [78] discussed the limitations of the Tutweiler gas-absorption buret and proposed instead a titration with iodine of hydrogen sulfide trapped as precipitated cadmium sulfide.

Hydrogen sulfide reacts readily with a great variety of chemicals, giving rise to manifold chemical methods of analysis which evolved before the development of modern instrumental methods of analysis. Some of these chemical methods are still popular, including methylene blue colorimetry. In 1949, Sands et al [121] reported for the US Bureau of Mines that the "colorimetric methylene blue test appeared to be the most promising" analytical method for hydrogen sulfide. This report included spectrophotometric calibration curves.

Methylene blue techniques have been widely accepted [122-126] for continuous, quantitative monitoring; they are sensitive to hydrogen sulfide at concentrations as low as about 0.001-0.003 ppm. However, light, mercaptans, sulfides, nitrogen dioxide, and sulfur dioxide interfere [92], and the system is not portable.

Silver filters have been used in combination with light and chemical techniques for analyzing hydrogen sulfide [84,85], but they have no advantages. Their response is slow, sometimes giving an average value for a 1-week sample, and no automated system has been established [93]. Sulfides, disulfides, ultraviolet light, particulate matter, and variations in moisture in the air all interfere with this type of measurement [92].

High and Horstman [83] also used silver in a method reported in 1952. Reflectance measurements from silver tarnished by hydrogen sulfide generally yielded results similar to those obtained by the methylene blue technique or with lead acetate filter tape. They did note, however, that spots on lead acetate tape were as likely to become either darker or lighter with time as they were to stay the same shade. This meant that the result of a determination of hydrogen sulfide by this method depended on the length of time that had elapsed since the spot was formed, but the authors did not consider this a crucial defect in the use of lead acetate tape.

Mass spectrometry was used to monitor furnace stack gas and digester blow gas in kraft pulpmills for hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide [127]. No hydrogen sulfide was detected in these gases by mass spectrometry, probably because hydrogen sulfide reacted with sulfur dioxide or oxygen. Hydrogen sulfide was detected in these gases by potentiometric titration with silver nitrate [127]. Mass spectrometry is unsuitable for use by personnel who have not had specialized training or for field use because the necessary apparatus is large and complex.

Fluorescence techniques have been used to measure concentrations as small as 0.0005 ppm of hydrogen sulfide [128,129], but these techniques are subject to interference by light. Also, disulfides and mercaptans quench fluorescence, and the lag time in a fluorescent system may be as long as 10 minutes [129]. No satisfactory system may yet be commercially available [129].

Instrument prototypes exist for determination of hydrogen sulfide by bioluminescence although they are not yet commercially available [93]. The lower limit of sensitivity was measured at about 0.07 ppm.

Ultraviolet spectrometry was used for determining hydrogen sulfide and sulfur dioxide, but this method is more useful for establishing the ratio between the concentrations of these gases than for estimating absolute concentrations [93]. Sulfur dioxide, ozone, and sulfides were reported to interfere with the measurement of hydrogen sulfide by ultraviolet spectrometry [93]. Sensitivity and rapidity of response were not discussed.

Infrared spectroscopy has not been a successful technique for analysis of hydrogen sulfide [91,92] because it does not discriminate between different sulfides; any sulfide or disulfide interferes. Further, it is not sensitive to hydrogen sulfide at concentrations below 10 ppm. The spectrum of hydrogen sulfide is weak [93]. Perhaps infrared techniques using lasers can be applied in the future [92].

Potentiometric [130-133] and amperometric [134] methods have been reported sensitive to hydrogen sulfide at 10 ppm [131] and at concentrations below 0.01 ppm [132]. Sulfur dioxide interferes, particularly when it is present at concentrations above 120 ppm [131]. Dynamic catalytic titration [135] has some similarities with these electrometric techniques, but it is too complex for field use and has not been evaluated in the United States. A copper-iodine-bromine technique is also sensitive but complex. The method requires the solving of simultanous equations in calculating the result [136] and has the other disadvantage of being subject to interference from water.

Plasma chromatography may become a useful analytical tool in the future, but it is not commercially available [93]. At present, this method is more useful for detection of mercaptans and organic disulfides than of hydrogen sulfide [93].

In general, at the present time, the more a method can be characterized as "wet chemical," the greater its analytical specificity and precision will be, the more suitable it will be for characterizing mixed gas streams at sources, the more limitations of temperature and portability will be encountered, and the higher will be the amount and technical sophistication of the maintenance required. Alternatively, the more a system can be characterized as "coated-chip" or "semiconductor," the greater its cross-sensitivities will be (although detectors can be made with different cross-sensitivities for different applications), the more portable the system will be, the longer its reponse time may be, and the less frequent and sophisticated will be the required maintenance. Some semiconductor and related systems require a constant temperature, as do some wet-chemical systems.

(c) Recommendations

For confirming compliance with the ceiling concentration limit, NIOSH recommends air sampling with a midget impinger and analysis by the methylene-blue method for hydrogen sulfide as described in Appendices I and II. NIOSH-certified hydrogen sulfide detector tubes may be used, when appropriate, as alternatives to the methylene-blue method of sampling and analysis for hydrogen sulfide. NIOSH recommends continuous real-time monitoring for hydrogen sulfide with automatic alarms at the specified evacuation limit as described in Appendix III. NIOSH-approved detector tubes may also be used for spot-checking for hydrogen sulfide and before entry into static air environments where hydrogen sulfide sources are not expected. Alternate methods may be used if equally effective.

Hydrogen sulfide can produce serious toxic effects in minutes or even in seconds. Therefore, to confirm that hydrogen sulfide concentrations are below the evacuation limit and to prevent worker exposure to hydrogen sulfide at hazardous concentrations, a continuous real-time monitoring of workplace air will usually be required in addition to periodic personal breathing zone sampling and analysis to determine compliance with the ceiling concentration standard. (Exceptions not requiring continuous monitoring might include testing isolated manholes for gases before entry and, where continuous ventilation is used, before and during entry.)

Portable hydrogen sulfide monitors are designed to be durable enough for field use but are of no value when damaged. Workers should be trained to use and care for the instrument properly before being given a portable hydrogen sulfide monitor; they should know its limitations. Batteries should be checked each shift, and the instrument should be calibrated at least weekly. Quality control charts should be kept on the instruments and batteries. Fixed monitors should also be calibrated at least once a month, and should have an auxiliary power supply. When alarms are reset, care should be taken to return to the previous effective set points because operators will sometimes turn off an alarm by raising the triggering level.

In selecting instruments, employers should weigh worker protection more heavily than analytical precision. If substances that give false positive readings by a detector system are themselves also toxic, they should be considered "additional sensitivities" rather than "interferences" of the system.

Biologic Monitoring

No biologic monitoring appears to be of value in preventing harmful effects of hydrogen sulfide exposure. Most of the effects that have been associated with hydrogen sulfide exposure are not cumulative but arise from sudden, comparatively brief exposures at high concentrations or from a few repeated exposures to individually bearable concentrations.

V. WORK PRACTICES

Work practices and safety precautions for handling hydrogen sulfide are the subjects of several reports [75,76,137-141]. Hydrogen sulfide is an extremely hazardous gas which can be immediately life threatening at high concentrations (300 mg/cu m or 200 ppm).

Occupational exposures to hydrogen sulfide can occur in a variety of industries, including the manufacture of viscose rayon, pulp and paper, rubber, plastics, and steel, refining, leather tanning, sulfur and sulfuric acid production, and mining. Hydrogen sulfide is easily recognizable by smell at concentrations less than 1 ppm. However, the sense of smell is unreliable because of the deceptively sweet smell of hydrogen sulfide at concentrations between 30 and 100 ppm and because of the olfactory fatigue that occurs at higher concentrations.

Hydrogen sulfide is a gas with lower and upper explosive limits of 4.3% and 45.5%, respectively, and an autoignition temperature of 260 C. The National Fire Protection Association (NFPA) has classified hydrogen sulfide in the highest flammability class [142]. Ten percent of the lower explosive limit allows what is considered an acceptable margin of safety for flammable substances (29 CFR 1917.11(a)(2) and 29 CFR 1915.11(a)(2)); therefore, precautions against fire and explosion hazards must be taken to ensure that airborne hydrogen sulfide does not accumulate at concentrations of 0.43% (4,300 ppm) or more. All potential sources of ignition or combustion, including oxidizing material, spark-producing devices, and direct sunlight, must be kept away from hydrogen sulfide cylinders.

Hydrogen sulfide is stored in steel pressure cylinders, which must be protected against physical damage. The storage area must be cool, well ventilated, and isolated. In case of fire, water should be used to cool fire-heated cylinders and to protect firefighters.

Disposal of hydrogen sulfide presents special problems. Usually, hydrogen sulfide is burned or mixed with caustic solutions, but people with special training who are familiar with the handling of hydrogen sulfide hazards must be consulted in each case. Cylinders must be disposed of by trained personnel. Disposal of hydrogen sulfide must comply with all local, state, and federal regulations [138,142].

The formation of hydrogen sulfide may be avoided or reduced by control of bacterial decomposition and organic digestion in various ways, including the use of refrigeration on fishing boats, maintaining adequate flow rates in sewers, preventing the accumulation of bagasse or other organic matter, and frequent cleaning of starch vats and tanning pits.

Where the delivery of chemical solutions in bulk presents a potential hazard if the chemicals are mixed, as with acid and sulfide solutions at a tannery, the pipes for the different solutions must be physically separated, labeled, and have dissimilar connections.

If an employer has determined that occupational exposure to hydrogen sulfide might occur in the workplaces under his control, the standard air sampling and analysis to determine compliance with the ceiling concentration limit must be supplemented by a monitoring system, and the workers must be advised of the hazards of exposure to hydrogen sulfide and trained in the use of respiratory protective devices and in the administration of artificial respiration. Hazardous areas must be posted and controlled by permit or by an equally effective control system, and contingency plans must be prepared and disseminated.

Fixed hydrogen sulfide detector systems must have a two-stage, spark-proof alarm: the lower triggering level must be set no higher than 10 ppm of hydrogen sulfide to warn workers that hydrogen sulfide is present above the ceiling limit, and the higher triggering level set no higher than 50 ppm of hydrogen sulfide to signal workers to evacuate the area and to obtain respiratory protection for rescue or repair efforts or for carrying out contingency plans [143(p 85)]. Fixed hydrogen sulfide monitors should also automatically trigger supplementary ventilation of the workplace [143(p 84)].

Portable hydrogen sulfide monitors should be used to supplement or replace fixed monitors when air currents may move released hydrogen sulfide away from a fixed detector or when the area of hydrogen sulfide release cannot be predicted. A portable hydrogen sulfide detector should have an alarm set to trigger at a hydrogen sulfide concentration of 50 ppm or lower. A two-stage alarm may be desirable on portable monitors.

Detector tubes may be used for probing confined spaces before they are entered and for spot-checking other areas that have static air conditions, but operations involving excavation, digging, drilling, agitation of standing water or sludge, opening closed compartments including reaction vessels, unclogging drains, cleaning cesspools or water wells, or mixing acid with sewage should be continuously monitored for hydrogen sulfide with a system provided with an alarm. Continuous monitoring can protect the workers only when it is combined with an alerting and alarm system, adequate ventilation, respiratory protection, and other appropriate measures.

Hydrogen sulfide is not released accidentally in lethal quantities very often, but, when there is an unexpected release of a large amount of hydrogen sulfide, it may cause the death of workers. Although respiratory protective equipment may never be needed, it must be available, and workers must know how to use it in case an emergency occurs which involves the release of hydrogen sulfide.

Intensive training in respiratory protection, in which the worker's physical and psychologic ability to use respirators is confirmed by actual use of the equipment, must be started before the employee begins his assigned work. This training should be repeated at least quarterly and each time a new crew is formed. All members of a crew ought to receive the same training, even if they have had a previous training session in the same quarter. Repeated practice by those who are already proficient will help to make the drill automatic and ensure swift and accurate reaction in an emergency. Also, the more experienced workers can serve as examples of proficiency and help to instruct the less experienced workers in the use of respiratory protection. During their 1st year on the job, workers who are often potentially or actually exposed to hydrogen sulfide in their work (eg, oil-production or sewer workers) may profit from monthly training and practice wearing and using respirators.

Training in the use of canister respirators should stress: choosing the right canister, using the canister mask only for open-air escape and not for confined spaces or work areas below grade, removing the tape seal from the canister before donning the mask, and keeping the canister inlet from falling into gas streams or liquids. Workers learning to use air-line respiratory protection should be taught to avoid fouling or kinking the air line and become familiar with proper techniques and time limits of use for the auxiliary escape air tank. Workers being trained with self-contained breathing apparatus should be made familiar with the correct method of donning the equipment with the valve down, with proper operation of the valves for demand or continuous flow, and with alarm systems indicating low air pressure.

While engineering controls should be used to keep airborne hydrogen sulfide below the concentrations at which it is hazardous to the health of workers, certain situations, such as vessel entry, nonroutine maintenance or repair operations, or emergencies, may require respiratory protection. The respirators should be immediately accessible to employees in emergency situations.

Before workers enter a confined space and during entry, they must be required to test the atmosphere for hydrogen sulfide, combustible gas, and low oxygen concentration and must obtain either self-contained or air-line respiratory protection with an escape cylinder and lifeline. An observer must be posted outside to monitor the activities and lifelines of the entering workers and to be in communication with them. Continuous ventilation should be provided in a confined space to maintain a safe breathing and working atmosphere, or the workers must wear appropriate respirators with sufficient air to permit escape, rescue, or other contingency activities. Suspect areas and confined spaces that are mechanically ventilated should also be washed, cleaned, or neutralized and retested for hydrogen sulfide, oxygen deficiency, and explosive gases before and during entry. If there is a chance that mechanical ventilation may not adequately control a surge of released hydrogen sulfide, workers should be equipped either with a combination type-C supplied-air respirator operated in the continuous-flow or pressure-demand mode (positive pressure) and an auxiliary self-contained breathing air supply or with a self-contained breathing apparatus operated in the pressure-demand mode (positive pressure). Whichever is used should have a full facepiece.

Each individual entering a confined space must wear a suitable harness with lifelines tended by another worker who is also equipped with a self-contained breathing apparatus that operates in the pressure-demand mode (positive pressure) and has a full facepiece [144]. Communications (visual, voice, signal line, telephone, radio, or other suitable means) must be maintained between the standby person and the employee inside the enclosed or confined space [144]. The standby person shall be physically or mechanically equipped to withdraw the monitored worker safely without the latter's participation in his own recovery. A third person should have general surveillance of the first two and should be suitably equipped to effect their rescue if necessary.

Because hydrogen sulfide can cause fatigue of the sense of smell or actual anosmia, a worker can enter an area where high concentrations of hydrogen sulfide are present without knowing it. There should be constant monitoring with an automatic audible (or audiovisual) warning device in places where a sudden release of hydrogen sulfide might not be expected and would otherwise not be recognized [144]. Fixed continuous monitors may be used to activate ventilation or shut down processes at preset hydrogen sulfide concentrations.

Laboratory work that involves release of hydrogen sulfide should be done with an exhaust hood. Workers must not work with their heads inside the hood, even for short periods.

Physical security systems (eg, fences) should be used to exclude unauthorized workers or visitors from places where hydrogen sulfide is being evolved, but these systems must not impede appropriate emergency responses and do not obviate the need for appropriate emergency precautions. Passageways and manholes should be large enough to permit a worker wearing a self-contained breathing apparatus to enter and remove a victim.

Because hydrogen sulfide may readily cause pipes and valves to corrode or become brittle, lines and fittings likely to contain hydrogen sulfide should be inspected frequently and receive special attention, monitoring, and maintenance to prevent leaks. Besides the primary work force, the support, maintenance, and repair personnel should be trained in the dangers of hydrogen sulfide, the meaning of alarms, and evacuation procedures.

VI. DEVELOPMENT OF STANDARD

Basis for Previous Standards

The development of hydrogen sulfide standards in Europe and the United States followed regulations governing exposure to carbon disulfide in the viscose rayon industry [145]. Based on surveys of occupational disease in viscose plants, the Occupational Disease Prevention Division of the Pennsylvania Department of Labor and Industry [145], in 1938, established a "permissible limit" in the breathing zone of 10 ppm for carbon disulfide alone and a total limit of 10 ppm for carbon disulfide and hydrogen sulfide combined, eg, 5 ppm carbon disulfide and 5 ppm hydrogen sulfide.

In 1939, Elkins [146], under the auspices of the Massachusetts Division of Occupational Hygiene, compiled a table of maximum allowable concentrations (MAC's) for 41 substances. This list was derived from comments of occupational health and industrial hygiene authorities on available data and on previously existing standards. Although concentrations for hydrogen sulfide suggested by respondents ranged from 50 to over 100 ppm, Elkins recommended a limit of 20 ppm based on his finding that conjunctivitis or eye irritation was common in rayon spinning-room workers unless the concentration of hydrogen sulfide was kept below 20 ppm. He remarked that effects on the eyes would not be eliminated at a hydrogen sulfide concentration above 10 ppm, but he did not explain why he proposed an MAC of 20 ppm rather than one of 10 ppm or less.

In 1940, Bowditch et al [147] cited the Massachusetts code for maximum safe concentrations as a guide for controlling occupational exposures to toxic substances, but they cautioned that observing the given values was not a guarantee that effects would be prevented. A value of 20 ppm for hydrogen sulfide was recommended, but no basis was given.

A list of MAC's for industrial atmospheric contaminants published by Cook [148] in 1945 included those of the American Standards Association, of the US Public Health Service, and of California, Connecticut, Utah, Oregon, Massachusetts, and New York. The values for the last two states were not official but were intended as guidelines. Each of these states and agencies recommended a 20-ppm MAC for hydrogen sulfide. In substantiating the proposed limit of 20 ppm for hydrogen sulfide, Cook [148] cited a study by Barthelemy [149] on conditions in a viscose rayon plant. Barthelemy reported that, when carbon disulfide levels were below 0.1 mg/liter (less than 32 ppm) and hydrogen sulfide levels were below 0.03 mg/liter (less than 20 ppm), "no trouble whatever was experienced." Cook [150] also claimed that the 20-ppm value for hydrogen sulfide was generally accepted as causing neither poisoning nor eye irritation, but he cited no basis for this statement.

Bloomfield [151], in 1947, reviewed the reports of an ACGIH committee which was attempting to develop a list of MAC's for adoption by all the states. He reported that, of 26 states and cities responding to the inquiry on hydrogen sulfide, all agreed on an MAC of 20 ppm.

In 1946, the ACGIH [152] adopted a list of MAC's for air contaminants prepared by its Subcommittee on Threshold Limits. For hydrogen sulfide, an MAC of 20 ppm (30 mg/cu m) was adopted. In 1946, the ACGIH terminology was changed from MAC to Threshold Limit Value (TLV), but the hydrogen sulfide standard remained at 20 ppm [153]. In 1953, the ACGIH listing [154] specified that the TLV's represented "the maximum average atmospheric concentration...to which workers may be exposed for an 8-hour working day." In a 1964 revision [155], the TLV for hydrogen sulfide was changed to 10 ppm (15 mg/cu m), but no basis was given for this change. The 1971 ACGIH Documentation [156] listed a TLV of 10 ppm for hydrogen sulfide. As the basis for this value, several reports were cited, including one by Masure [47] of eye effects from exposures at 20 ppm or below. It was also noted that two heavy-water plants had voluntarily observed a 10-ppm MAC for hydrogen sulfide [3]. In 1976, the ACGIH added a tentative short-term exposure limit (STEL) of 27 mg/cu m (15 ppm) [157].

The American Industrial Hygiene Association (AIHA), in a 1962 report [158], recommended an MAC for hydrogen sulfide of 20 ppm, based on an 8-hour workday. This value was substantiated by human experience and animal studies which were referred to in a US Public Health Service report [159]. This report cited a study by Kranenburg and Kessener [160], who stated that eye irritation was a major complaint of viscose plant workers exposed to hydrogen sulfide at concentrations of 18-28 ppm. The AIHA report [158] noted that local effects, especially irritation of the eyes, had been reported at concentrations as low as 15 ppm.

In 1941, the American Standards Association [71], now the American National Standards Institute (ANSI), recommended an MAC of 20 ppm for hydrogen sulfide for exposures not exceeding 8 hours/day. ANSI [1] revised the standard in 1966, specifying that 20 ppm was the acceptable ceiling concentration, with an acceptable maximum peak of 50 ppm for periods of 10 minutes or less. Because hydrogen sulfide was considered an "acute acting substance," no TWA limit was designated, but 10 ppm was cited as the "acceptable concentration to avoid discomfort." In 1972, ANSI [161] set 10 ppm as the 8-hour TWA concentration limit for hydrogen sulfide.

Occupational exposure limits for hydrogen sulfide set by foreign countries vary between 7 and 20 ppm. In 1969, the German Democratic Republic had a limit of 10 ppm, and the Federal Republic of Germany, 20 ppm; each was listed as a "maximum allowable concentration" [162]. In 1974, the Federal Republic of Germany adopted a standard of 10 ppm, based on an 8-hour TWA concentration. The USSR, in 1967, and Czechoslovakia, in 1969, recommended limits of 7 ppm [162]. The acceptable ceiling concentration in the USSR in 1972 was 10 ppm [163]. In Hungary [164], Bulgaria, Romania, and Yugoslavia [162], the MAC for hydrogen sulfide in the work environment is 10 mg/cu m (about 7 ppm). In Japan, the standard, which was set in 1963, was 15 mg/cu m (about 10 ppm) [162]. Finland, the United Arab Republic, and the Syrian Arab Republic used 30 mg/cu m (20 ppm) as the limit [162]. In 1975, Sweden had a standard TWA concentration limit of 10 ppm, while Argentina, Great Britain, Norway, and Peru had standards equivalent to that of the United States [163].

The present federal standard for occupational exposure to hydrogen sulfide (29 CFR 1910.1000) is 20 ppm as a ceiling concentration determined for an 8-hour day, based on ANSI standard Z37.2-1966. The acceptable peak concentration above the ceiling is 50 ppm for no longer than 10 minutes.

Basis for the Recommended Standard

(a) Permissible Exposure Limits

Hydrogen sulfide has been reported to have adverse effects on many organ systems. The deaths of 26 persons resulted from accidental exposures to hydrogen sulfide during a recent 19-month period in the oil fields of Texas and Wyoming [19]. Hydrogen sulfide at high concentrations has caused death from paralysis of the respiratory centers in the brain [16,37,165]. Other areas of the brain also have been adversely affected [3,15,38,39,51]. Brain damage may be a secondary result of anoxia, but other symptoms and signs suggesting brain damage, including headache, dizziness, rigidity, sensory impairment, sleep disturbance, loss of appetite, and weight loss, have followed exposure to hydrogen sulfide at concentrations insufficient to produce unconsciousness in the affected individuals [3,15,17,18].

Irritation of the respiratory passages and lungs have occurred, and sometimes hemorrhagic pulmonary edema has resulted [3,15-17,25,36,37]. Signs of kidney damage have been observed [16,38]. Alteration of blood composition has been reported in animals [60], and enzyme activities have changed in workers exposed to hydrogen sulfide [50]. Adverse effects on the heart [34,38,53,55] and on the peripheral circulation [15,38] have been reported in workers.

Hydrogen sulfide exposure over a wide range of concentrations has produced nausea and a variety of changes in digestive secretory and motor activities in workers [3,15,17,25,50,69]. There are reports suggesting damage to the reticuloendothelial system [15,60].

Eye irritation with erosion of the cornea has been reported in workers. This damage was reversed when the workers were removed from exposure to hydrogen sulfide [15,43,44,48], but it can be a cause of permanent blindness, particularly when secondary infection occurs [68].

The rapidity with which hydrogen sulfide at high concentrations produces unconsciousness or death has been shown by numerous incidents in which coworkers attempted to aid persons overcome by hydrogen sulfide and were themselves overcome suddenly and without warning [23,25-29,32,35,37,165].

In one incident, four men entered a well to rescue a worker who had been instantly overcome [23]. Each was overcome in turn, and all five died. Hydrogen sulfide was detected in the well at a concentration of 1,000 ppm.

Breysse [21] reported that a workman collapsed and died when exposed to hydrogen sulfide while trying to plug a leaking pipe. Hydrogen sulfide at concentrations of 2,000-4,000 ppm was later measured at the site of the leak under similar conditions.

Kemper [38] wrote that a refinery workman was found unconscious after exposure to spilled diethanolamine contaminated with hydrogen sulfide at a concentration which "probably approached 1,000 ppm" in air. On admission to the hospital, he was unconscious and had convulsions, muscle spasms, cyanosis, blood in the urine, and low blood pressure with a heart rate of 180 beats/minute. He was discharged after 2 weeks but experienced depression and lassitude for several months. Amnesia of the day of the accident still persisted a year later.

Four workers collapsed while working in an open pit, 12 feet deep, in marshy land [69]. The men revived after being given oxygen by pulmotor, although one who was hospitalized regained consciousness after 8 hours. Air tests 5 days later detected hydrogen sulfide at concentrations of 295-540 ppm at the bottom of the pit.

Ahlborg [15] reported that a 30-year-old stoker at a shale-oil plant suffered a circulatory collapse after exposure to hydrogen sulfide at a concentration of 230 ppm for "at least 20 minutes." The worker was hospitalized and was discharged 6 days later with normal blood pressure; he showed no recurrence of pertinent signs during the next 2 years.

Eye effects from exposure to hydrogen sulfide at concentrations of 20 ppm or lower have been reported [47,48,57,67]. Flury and Zernik [65] reported, without elaboration, "a long enduring inflammation of the eye conjunctiva" after exposure to hydrogen sulfide at a concentration of 10-15 ppm for 6 hours. On the other hand, Poda [3] stated that the voluntary adoption by two heavy-water plants of a TWA of 10 ppm was successful from an industrial hygiene standpoint. Previous standards have been based on eye effects.

Hydrogen sulfide at concentrations that vary unpredictably between safe and hazardous levels arises from a great variety of sources. Paradoxically, hydrogen sulfide at the more dangerous concentrations is less likely to be detected by odor, because olfactory fatigue sets in more rapidly at higher concentrations. Exposure to hydrogen sulfide at low concentrations for extended periods of time (hours) has been associated with corneal damage, headache, sleep disturbance, nausea, weight loss, and other signs and symptoms which suggest possible brain damage. To prevent these subacute effects, any possible chronic ones, and acute eye irritation from hydrogen sulfide, a ceiling occupational exposure limit of 15 mg/cu m (10 ppm) for 10 minutes is recommended. Because brief exposure to hydrogen sulfide at high concentrations rapidly causes unconsciousness, cessation of breathing, and death, workers must immediately evacuate the area if the hydrogen sulfide concentration reaches 70 mg/cu m (50 ppm). If exposures to other chemicals also occur, provisions of any applicable standards for the other chemicals shall also apply.

(b) Sampling and Analysis

To determine compliance with the ceiling limits, NIOSH recommends the sampling and analytical methods presented in Appendices I and II, although other methods of comparable reliability and accuracy are acceptable. It is necessary to continuously monitor the hydrogen sulfide concentration in employees' breathing zone air to avoid accumulation of hydrogen sulfide to high concentrations with resulting catastrophic effects on workers' health. Continuous hydrogen sulfide monitors should have spark-proof automatic alarms. Monitoring the employees' breathing zone and suspect areas for peak concentrations should follow the criteria in Appendix III. Environmental sampling and recordkeeping are required for work areas where there is exposure to hydrogen sulfide above the ceiling concentration limit.

(c) Medical Surveillance

In view of individual variation in human response to noxious substances and to hydrogen sulfide specifically, NIOSH recommends that comprehensive preplacement examinations be given to employees who may be occupationally exposed to hydrogen sulfide. These examinations must specifically assess the worker's ability to use respiratory protection. Examinations should be made available at 3-year intervals to all workers exposed to hydrogen sulfide at concentrations above the ceiling concentration limit. In certain cases, an individual may have signs or symptoms warranting more frequent and more specialized examinations. Individuals exposed to hydrogen sulfide at concentrations above 70 mg/cu m (50 ppm) should be examined promptly by a physician.

(d) Personal Protective Equipment

The employer must provide appropriate respiratory protective equipment for each worker, because hydrogen sulfide at high concentrations can produce unconsciousness and death in minutes or seconds. Full-facepiece respiratory protection simultaneously affords eye protection and must be used when the hydrogen sulfide concentration exceeds 15 mg/cu m (10 ppm).

(e) Informing Employees of Hazards

Each worker should be informed that disorders of the eyes and of the respiratory, cardiovascular, nervous, and gastrointestinal systems may result from exposure to hydrogen sulfide.

Each worker should also be warned about the flammability of hydrogen sulfide, its capacity to deaden the sense of smell, and of its tendency to accumulate in low areas and in confined and enclosed spaces.

(f) Work Practices

The extreme flammability of hydrogen sulfide necessitates special caution in its storage, handling, and use. Because of the hazard of hydrogen sulfide building up to a concentration above the environmental ceiling limit in low areas and confined spaces, precautions are recommended for work in such places. Engineering control procedures are recommended to contain hydrogen sulfide and to ensure safe working conditions. Important work practice considerations include handling, storage, ventilation, equipment maintenance, emergency procedures, and training in monitoring, respiratory protection, self-help and basic first aid, including artificial respiration. Certain individuals should be designated to administer first aid, but a majority of the workers should receive training in artificial respiration because casualties caused by hydrogen sulfide frequently involve several workers at the same time.

Training in application of artificial respiration or mechanical ventilation should be given to a majority of workers who may be occupationally exposed to hydrogen sulfide. Both mouth-to-mouth and approved back-pressure techniques of artificial respiration should be taught, because injury might preclude the use of one technique or the other. The mouth-to-mouth technique of artificial respiration is recommended as the most effective, but it may result in the rescuer becoming unconscious [4] if he fails to get the victim to an uncontaminated area and is himself overcome by gas from the same source that felled the victim, if he uses an incorrect technique and inhales air directly from the victim's lungs, or if he hyperventilates [143(p 91)]. A back-pressure method, such as the Holger-Nielssen technique, may be applied initially to clear the victim's lungs of toxic gases before mouth-to-mouth artifical respiration is used.

There must be prearranged plans for obtaining emergency medical care and for transporting injured workers to the hospital. A telephone or radio notification list must be prominently posted and must include the names and phone numbers of company safety and supervisory personnel, local medical facilities and ambulance services, and local, state, and federal public-safety and environmental-protection agencies to be contacted in case of major emergencies. Civilians living near major known or suspected hydrogen sulfide sources should be located and identified; if they must be evacuated, it should be in a direction away from the hydrogen sulfide source, upwind or at right angles to the wind, not downwind. Nonessential personnel must be kept away from the area. Workers and supervisory personnel must be made familiar with the contingency plan through appropriate training. Records of training sessions should be maintained while the individual is employed by the company.

In rendering first aid, one should (1) use respiratory protection and remove the victim to a safe area; (2) apply effective artificial respiration if the victim is not breathing (mechanical or mouth-to-mouth, unless facial injury or something else interferes); (3) check for heartbeat (usually the victim's heart will still beat for several minutes even if the individual has stopped breathing) and apply approved cardiopulmonary resuscitation if needed; and (4) remove the victim quickly to the hospital if he does not respond to emergency treatment. Medical attention must be given as rapidly as possible to anyone rendered unconscious or apneic by exposure to hydrogen sulfide

Appropriate posters and labels must be displayed, and the "Material Safety Data Sheet" shown in Appendix IV or a similar form approved by the Occupational Safety and Health Administration, Department of Labor, shall be filled out and placed on file so that it is accessible to employees. Effective employee education and supervision are necessary to ensure the safety and health of workers potentially exposed to hydrogen sulfide.

(g) Monitoring and Recordkeeping Requirements

Continuous monitors should be used near known sources of hydrogen sulfide at a high concentration, such as sour crude oil wells and storage areas. Continuous monitoring should also be used in enclosed or confined spaces, particularly in sewers and in tanneries, rendering plants, papermills, or other industries where a source of hydrogen sulfide exists.

Trained industrial hygiene personnel should make the decision whether continuous monitoring should be used in those situations that may not obviously need continuous monitoring.

Employers or their successors must keep records of environmental monitoring for at least 30 years after the individual's employment has ended. If an employer has concluded that workplace air concentrations were below the recommended ceiling limit, the records must show the basis for this conclusion. Records should be maintained for quality control of the monitors, batteries, and calibration gases in use.

VII. RESEARCH NEEDS

Most published reports of human exposure to hydrogen sulfide describe acute episodes resulting in catastrophic health effects. While these case studies warn of the hazards of exposure under extreme conditions, they do not provide data on the effects of daily low-level exposure to hydrogen sulfide. Because information on the toxic effects of long-term exposure to hydrogen sulfide or of repeated exposure to hydrogen sulfide at low concentrations is currently lacking, controlled epidemiologic studies which report individual exposure data need emphasis in future research.

Because neuronal degeneration in the basal ganglia and cerebellum of monkeys and rats exposed to hydrogen sulfide has been observed [51,56], and workers have reported olfactory, acoustic, and vestibular sensory defects [16], dizziness [15], and motor-coordination problems [15] following exposure to hydrogen sulfide, a neurologic and behavioral study (similar to the Westinghouse [166] study on carbon disulfide) ought to be done on workers exposed to hydrogen sulfide.

Studies of the effects on animals of long-term exposure to hydrogen sulfide at low concentrations can provide information on its toxicity which will be useful not only in determining whether truly chronic effects do occur but also in supplementing human epidemiologic data. With exposure schedules similar to those in industry, ie, 8-10 hours/day, 5 days/week, results relevant to worker exposure may be obtained. It is essential that hydrogen sulfide concentrations be accurately measured to establish exposure concentrations corresponding to different reported adverse health effects. Animal experiments should be designed and examined closely to try to develop a biologic indicator of hydrogen sulfide effects, if possible.

Embryotoxicity from hydrogen sulfide has been demonstrated in fish [167], but no reports of similar investigations in other species were found. Therefore, controlled experiments with animals other than fish and with an exposure schedule simulating that of occupational exposure to hydrogen sulfide should be conducted to study possible teratogenicity and mutagenicity. These studies may be combined with the long-term studies outlined in the previous paragraph.

Carbon disulfide may lower the threshold of corneal sensitivity to hydrogen sulfide [48], but synergism has not been conclusively demonstrated. Basic studies to establish the presence and character, or absence, of synergism between hydrogen sulfide and carbon disulfide, sulfur dioxide, carbon monoxide, carbon dioxide, or hydrocarbons would help to clarify reports of effects from mixed exposures.

Considering seven criteria for selection of an analytical technique (compatibility with the sampling method, required sensitivity, specificity and freedom from interferences, speed of response, ease of operation by naive workers, suitability for field use, and reasonableness of cost), direct readout techniques using hydrogen sulfide-sensitive electrodes, semiconductors, electrochemical cells, or similar electronic mechanisms [87,88] may be superior to the methylene-blue technique on all points. The performance and potential use of such electronic techniques should be more extensively evaluated.

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IX. APPENDIX I

AIR SAMPLING METHOD FOR HYDROGEN SULFIDE

The sampling method for hydrogen sulfide is a validated NIOSH method [168].

Collect breathing-zone samples representative of the individual employee's exposure. Collect enough samples to permit calculation of a representative ceiling concentration for every operation or location in which there is exposure to hydrogen sulfide. At the time of the sample collection, record a description of sampling location and conditions, equipment used, time and rate of sampling, and any other pertinent information.

Equipment

The sampling unit for the impinger collection method consists of the following components:

(a) A graduated 25-ml midget impinger with a standard glass-tapered gas delivery tube containing 10 ml of cadmium hydroxide absorbing solution. Petticoat bubblers may be used, but not fritted bubblers. The impinger should be wrapped in metal-foil to protect the sample from exposure to light.

(b) A personal sampling pump whose flow can be determined within 5% at 0.20 liter/minute through the impinger. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

(c) An integrating gas volume meter such as a dry gas or wet-test meter or a rotameter, capable of measuring 2 liters of air at 0.2 liter/minute with an accuracy of ±5%. Collection efficiency is 100% at this rate.

Calibration

The accurate calibration of a sampling pump is essential to the correct interpretation of the volume sampled. The frequency of calibration depends on the use, care, and handling to which the pump is subjected. Pumps should also be recalibrated if they have been misused or if they have just been repaired or received from a manufacturer. If the pump receives hard use, more frequent calibration may be necessary. Maintenance and calibration records should be maintained.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration depends on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, a soapbubble meter is recommended, although other standard calibrating instruments can be used. The actual setups will be similar for all instruments.

Instructions for calibration with the soapbubble meter follow. If another calibration device is selected, equivalent procedures should be used.

(a) Check the voltage of the pump battery with a voltmeter to ensure adequate voltage for calibration. Charge the battery if necessary.

(b) Plan to sample for 10 minutes at 0.2 liter/minute.

(c) Assemble the sampling train as shown in Figure XIV-1.

(d) Turn on the pump and moisten the inside of the soapbubble meter by immersing the buret in the soap solution. Draw bubbles up the inside until they are able to travel the entire buret length without bursting.

(e) Adjust the pump flowmeter to provide the desired flow rate.

(f) Check the water manometer to ensure that the pressure drop across the sampling train does not exceed 2.5 inches of water at 0.2 liter/minute.

(g) Start a soapbubble up the buret and measure with a stopwatch the time it takes the bubble to move from one calibration mark to another.

(h) Repeat the procedure in (g) at least three times, average the results, and calculate the flow rate by dividing the volume between the preselected marks by the time required for the soapbubble to traverse the distance. If, for the pump being calibrated, the volume of air sampled is calculated as the product of the number of strokes times a stroke factor (given in units of volume/stroke), the stroke factor is the quotient of the volume between two preselected marks divided by the number of strokes.

(i) Data for the calibration should include the volume measured, elapsed time or number of strokes of the pump, pressure drop, air temperature, atmospheric pressure, serial number of the pump, date, and the name of the person performing the calibration.

Sampling Procedure

(a) Prepare absorbing solution as described in Appendix II. Pipet 5 ml of cadmium sulfate-arabinogalactan solution directly into the midget impinger and mix with 5 ml of the sodium hydroxide solution. The addition of 5 ml of 95% ethanol to the absorbing solution just prior to aspiration controls foaming for 2 hours.

(b) Connect the impinger (via the absorption tube) to the sampling pump with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and the impinger should be used. Air being sampled should not be passed through any other tubing or other equipment before it enters the impinger.

(c) Set the flowrate as accurately as possible using the manufacturer's directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. Sample air at 0.2 liter/minute for 10 minutes.

(d) Do not remove the impinger stem after sampling since it contains cadmium sulfide deposits. Cadmium sulfide may decomposed if exposed to light, so the impinger should be wrapped in metal foil to protect the light.

(e) Seal the outlets of the stem with Parafilm or other nonrubber covers, and seal the ground glass joints by taping to secure the top tightly.

(f) Treat at least one impinger in the same manner as the other samples (fill, seal, and transport), but do not draw air through this impinger. This impinger serves as a blank.

(g) Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day. Strong reducing agents (eg, sulfur dioxide) inhibit color development in the analysis step; they should be excluded if possible during sampling. Nitrogen dioxide and ozone may also interfere and should be excluded. Cadmium sulfide may be decomposed if exposed to light; the collected sample should be protected from light as described above.

Shipping Instruction

Hand deliver the samples if possible. Otherwise, ship samples in appropriate impinger shipping cases.

Alternative Method

NIOSH-certified hydrogen sulfide detector tubes [169] may be used to supplement or replace this sampling method for determining compliance with the ceiling concentration limit. The manufacturer's directions should be followed in using such tables.

X. APPENDIX II

ANALYTICAL METHOD FOR HYDROGEN SULFIDE

This analytical method for hydrogen sulfide is a validated NIOSH method [170].

Principle of the Method

Hydrogen sulfide is collected by drawing a measured volume of air through an alkaline suspension of cadmium hydroxide. The sulfide is precipitated as cadmium sulfide to prevent air oxidation of the sulfide which occurs rapidly in an aqueous alkaline solution. Arabinogalactan is added to the cadmium hydroxide slurry to minimize photodecomposition of the precipitated cadmium sulfide. The collected sulfide is subsequently determined by spectrophotometric measurement of the methylene blue produced by the reaction of the sulfide with a strongly acid solution of N,N-dimethyl-p-phenylenediamine and ferric chloride.

Range and Sensitivity

This method was validated over the range of 8.5-63 mg/cu m (6-45 ppm), at atmospheric temperature and pressure of 25 C and 760 mmHg, using a 2-liter sample. Under the conditions of sample size (2 liters), the probable range of the method is 5-100 mg/cu m (3-72 ppm). For sample concentrations outside this range, the sampling volume should be modified.

Interferences

The methylene blue reaction is highly specific for sulfide at the low concentrations usually encountered in air. Strong reducing agents, eg, sulfur dioxide, inhibit color development. Even sulfide solutions containing several milligrams of sulfite/ml show this effect and must be diluted to eliminate color inhibition. If sulfur dioxide is absorbed to give a sulfite concentration in excess of 10 μg/ml, color formation is retarded. The use of 0.5 ml of ferric chloride solution during analysis eliminates the sulfur dioxide interference up to 40 μg/ml.

Nitrogen dioxide gives a pale yellow color with the sulfide reagents at 0.5 μg/ml or more. No interference is encountered when 0.3 ppm nitrogen dioxide is aspirated through a midget impinger containing a slurry of cadmium hydroxide-cadmium sulfide arabinogalactan. If hydrogen sulfide and nitrogen dioxide are simultaneously aspirated through the cadmium-arabinogalactan slurry, lower hydrogen sulfide results are obtained, probably because of gas-phase oxidation of the hydrogen sulfide prior to precipitation as cadmium sulfide.

Ozone at 57 ppb reduced the recovery of sulfide previously precipitated as cadmium sulfide by 15%. Substitution of other cation precipitants, eg, zinc or mercury, for the cadmium on the absorbent will shift or eliminate the absorbance maximum of the solution upon addition of the acid-amine reagent.

Cadmium sulfide decomposes significantly when exposed to light unless protected by the addition of 1% arabinogalactan to the absorbing solution prior to sampling.

The choice of the impinger used to trap hydrogen sulfide with the cadmium hydroxide slurry is very important when measuring concentration in the range of 5-100 mg/cu m (3,072 ppm). Impingers or bubblers with fritted-end gas delivery tubes are a source of error if the sulfide in solution is oxidized to free sulfur by oxygen from the atmosphere. The sulfur collects on the fritted-glass membrane and may significantly change the flow rate of the air sampled through the system. One way to avoid this problem is to use a midget impinger with standard glass-tapered tips.

Precision and Accuracy

The coefficient of variation (standard deviation/mean x 100) for the total analytical and sampling method in the range of 8.5-63 mg/cu m (6-45 ppm) is 0.121. The standard deviation at 20 ppm is 8%.

The average agreement between the true values and found values was 10% for the total analytical and sampling method at 20 ppm.

Advantages and Disadvantages of the Method

Collection efficiency is variable below 0.0007 ppm, but this is inconsequential. It is affected by the type of scrubber, the size of the gas bubbles, and the contact time with the absorbing solution and the concentration of hydrogen sulfide. The collection efficiency is 100% at the recommended flow rate.

Hydrogen sulfide is readily volatilized from aqueous solution when the pH is below 7.0. Alkaline aqueous sulfide solutions are very unstable, because the sulfide ion is rapidly oxidized by exposure to the air.

Cadmium sulfide is not appreciably oxidized even when aspirated with pure oxygen in the dark. However, exposure of an impinger containing cadmium sulfide to laboratory or to more intense light sources produces an immediate and variable photodecomposition. Losses of 50-90% of added sulfide have been routinely reported by a number of laboratories. Even though the addition of arabinogalactan to the absorbing solution controls the photodecomposition, it is necessary to protect the impinger from light at all times. This is achieved by the use of low actinic glass impingers, paint on the exterior of the impingers, or a metal-foil wrapping.

Apparatus

Colorimeter with red filter or spectrophotometer at 670 nm. Matched cells, 1-cm path length.

Volumetric flasks: 20, 50, 100, 250, 1,000 ml.

Graduated cylinders or volumetric flasks: 20, 50, 100, 1,000 ml.

Pipets: 5 ml.

Pipeting bulb.

Clean rubber policeman.

Reagents

All reagents must be ACS analytical reagent quality. Distilled water should conform to the ASTM Standards for Referee Reagent Water. All reagents should be refrigerated when not in use.

(a) Amine-sulfuric acid stock solution: Add 50 ml of concentrated sulfuric acid to 30 ml of water and cool. Dissolve in the acid 12 g of

N,N-dimethyl-p-phenylene-diamine dihydrochloride (p-aminodimethylaniline, redistilled if necessary) or 10.5 g of N,N-dimethyl-p-phenylenediamine oxalate. Do not dilute. The stock solution may be stored indefinitely under refrigeration.

(b) Amine test solution: Dilute 25 ml of the stock solution to 1 liter with 1:1 sulfuric acid.

(c) Ferric chloride solution: Dissolve 100 g of ferric chloride, FeCl.36H20, in water and dilute to 100 ml.

(d) Ethanol, 95%.

(e) Arabinogalactan: Stractan 10, available from Stein-Hall and Company Inc, New York, or arabinogalactan sold under other brand names may be used.

(f) Cadmium sulfate-arabinogalactan solution: Dissolve 8.6 g of cadmium sulfate, 3CdSO4.8H20, in approximately 600 ml of water. Add 20 g arabinogalactan and dilute to 1 liter.

(g) Sodium hydroxide solution: Dissolve 0.6 g of sodium hydroxide in approximately 600 ml of water and dilute to 1 liter.

(h) Standard sulfide solution: Place 35.28 g of sodium sulfide, Na2S.9H20, into a 1-liter volumetric flask and add enough oxygen-free distilled water to bring the volume to 1 liter. Store under nitrogen and refrigerate. Standardize with standard iodine and thiosulfate solution in an iodine flask under a nitrogen atmosphere to minimize air oxidation. The approximate concentration of the sulfide solution will be 4,700 μg sulfide/ml of solution. The exact concentration must be determined by iodine-thiosulfate standardization immediately prior to dilution.

(i) Working sulfide solution: Dilute 25 ml of stock solution to 250 ml with oxygen-free water. This solution contains the sulfide equivalent of approximately 500 μg of hydrogen sulfide/ml. Make fresh working sulfide solution daily. The actual concentration of this solution can be determined from the titration results on the stock sodium sulfide standard.

Analysis of Samples

All glassware should be throughly cleaned. Wash the glassware with a detergent and tap water solution followed by tap water and distilled water rinses; then soak in 1:1 or concentrated nitric acid for 30 minutes. Follow with tap water, distilled water, and double-distilled water rinses.

(a) Remove the impinger top and drain it thoroughly into the impinger flask. Set top aside. Transfer the solution and deposit in the impinger flask to a 250-ml volumetric flask. Using 50 ml of distilled water, rinse the bottom twice with a clean rubber policeman on a glass stirring rod. Add the rinse solutions to the contents of the volumetric flask. With the rubber policeman, wash the outside of the impinger stem with 20 ml of distilled water and the washings to the flask. Drain 20 ml of distilled water through the impinger into the flask. The total wash-water volume should be 90 ml.

(b) Add 15 ml of amine test solution through the impinger inlet tube into the volumetric flask. This is necessary to dissolve the cadmium sulfide deposited inside the inlet tube. Mix gently to avoid loss of hydrogen sulfide.

(c) Add 0.5 ml of ferric chloride solution to the mixture within the volumetric flask and mix. Bring to volume with distilled water. Allow to stand 20 minutes.

(d) Measure the absorbance of the color at 670 nm in a spectrophotometer or colorimeter set at 100% transmission against the zero reference.

Calibration and Standards

(a) Aqueous sulfide

(1) Place 5 ml of cadmium sulfate-arabinogalactose solution and 5 ml of sodium hydroxide solution into each of a series of 250-ml volumetric flasks.

(2) Add standard sulfide solution equivalent to 0, 20, 40, 80, 120, and 160 μg of hydrogen sulfide to the different flasks.

(3) Add 90 ml of distilled water.

(4) Add 15 ml of amine test solution to each flask and mix gently.

(5) Add 0.5 ml of ferric chloride solution to each flask. Mix, make up to volume, and allow to stand for 20 minutes.

(6) Determine the absorbance in a spectrophotometer or colorimeter at 670 nm against the sulfide-free reference solution.

(7) Prepare a standard curve of absorbance versus μg of hydrogen sulfide.

(b) Gaseous sulfide

Cylinders of hydrogen sulfide in dry nitrogen in the range desired are available commercially and may be used to prepare calibration curves for use at the 10-60 mg/cu m (7-43 ppm) levels. Nitrogen containing hydrogen sulfide in the range of 322.6-430.2 ppm can be diluted to the desired concentrations. Analyses of these known concentrations give calibration curves which simulate all of the operational conditions performed during the sampling and analytical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of hydrogen sulfide. Prepare or obtain a cylinder of nitrogen containing hydrogen sulfide in the range of 450-600 mg/cu m (322-430 ppm). To obtain standard concentrations of hydrogen sulfide, assemble the apparatus consisting of appropriate pressure regulators, needle valves, and flowmeters for the nitrogen and for a dry air diluent stream. Stainless steel, glass, or rubber tubing must be used for the hydrogen sulfide mixture. Flow of hydrogen sulfide in nitrogen is controlled by a needle valve operated in conjunction with a flowmeter previously at 0.2 liter/minute. Diluent dry air from a cylinder is controlled by a similar needle valve-flowmeter combination in the range of 1-20 liters/minute. The hydrogen sulfide in nitrogen and the diluent air are combined in a mixing chamber at atmospheric pressure. They flow through a baffle tube in which mixing takes place into a 1-liter sampling flask provided with one or more nipples from which samples can be taken. Sampling is done by connecting a midget impinger to the nipple and drawing a known volume of the mixture through the impinger for a measured length of time, using a critical orifice to control flow at a constant known rate.

The dynamic range of the colorimetric procedure fixes the total volume of the sample at 2 liters; to obtain linearity between the absorbance of the solution and the concentration of hydrogen sulfide in ppm, select a constant sampling time. This fixing of the sampling time is desirable also from a practical standpoint. In this case, select a sampling time of 10 minutes. To obtain a 2-liter sample of air requires a flow rate of 0.2 liter/minute. The concentration of standard hydrogen sulfide is computed as follows:

$$C = \frac{cf}{F + f}$$

where:

C = concentration of H2S in mg/cu m
c = concentration of H2S in nitrogen, before dilution
F = flow of diluent air, as measured by calibrated flowmeter
f = flow of hydrogen sulfide in nitrogen, as measured by calibrated flowmeter

Commercially prepared hydrogen sulfide in nitrogen can be obtained with a known concentration, as analyzed by the laboratory preparing the gas. If it is desired to check this concentration, a measured volume of the gas can be bubbled through the absorbing solutions, and the collected sulfide titrated against iodine-thiosulfate. The volume of gas can be measured using a wet-test meter.

If hydrogen sulfide is present at much lower concentrations (0.001-0.1 ppm), commercially available permeation tubes containing liquified hydrogen sulfide may be used to prepare calibration tubes.

Calculations

(a) Determine the sample volume, in liters, from the gas meter or flowmeter readings and the time of sampling. Adjust volume to 760 mmHg and 25 C.

$$Vn = V \times \frac{P}{760} \times \frac{298}{(T+273)}$$

where:

Vn = Volume of air (liters) at standard conditions
V = Volume of air samples (liters)
P = Barometric pressure (mmHg)
T = Temperature of sample air (C)

(b) Use the Beers-Law standard curve of absorbance versus μg of hydrogen sulfide to determine μg of hydrogen sulfide in the sampling impinger corresponding to its absorbance reading at 670 nm.

(c) To determine the concentration of hydrogen sulfide in ppm:

$$\text{ppm H2S} = 0.717 \text{ x } \mu\text{g H2S/Vn}$$

where:

μg H2S = micrograms of hydrogen sulfide determined in paragraph (b)

Alternative Method

NIOSH-certified hydrogen sulfide detector tubes [169] may be used to supplement or replace this method of analysis for determining compliance with the ceiling workplace environmental concentration limit. The manufacturer's directions should be followed in using such tubes.

XI. APPENDIX III

HYDROGEN SULFIDE MONITORS

Whenever the possibility exists that high concentrations of hydrogen sulfide may be released or created as a result of leaks, accidents, and agitation of sludge, it is essential that hydrogen sulfide monitoring devices be installed, worn, or otherwise used, and that these devices give immediate warning of concentrations likely to become hazardous to life. It is difficult to define the limiting circumstances when such devices may be required; if reasonable doubt exists, the decision should be made by an industrial hygienist. Monitoring devices may be based upon several operating principles. A variety of devices are currently available commercially. In the design or purchase of a hydrogen sulfide monitoring device the following criteria shall be considered.

Summary of Specifications

(a) Monitoring devices must sound an alarm or otherwise warn employees whenever a hydrogen sulfide concentration of 70 mg/cu m (50 ppm) is reached or exceeded. Additionally, fixed (nonportable) monitoring devices should have a different alarm to notify employees whenever there is a hydrogen sulfide concentration greater than 15 mg/cu m (10 ppm) but less than 70 mg/cu m (50 ppm). Lower limits may be voluntarily adopted.

(b) The monitoring device must have a response time of 20 seconds or less when hydrogen sulfide is at a concentration of 50 or more ppm. The warmup time for the monitoring device should be 5 minutes or less.

(c) Sampling rate and volume are not critical, and any sampling conditions which will meet the response criteria are adequate.

(d) An operating range of up to 100 ppm of hydrogen sulfide is desirable, but other ranges may be selected to suit individual needs.

(e) The monitoring device for hydrogen sulfide should be accurate within 20% and reliable within 10%.

(f) If a monitoring device shows a systematic bias, it may still be used if the difference is small (less than 5%), if the bias predictably overestimates the hydrogen sulfide concentration, or if the device's alarm set point(s) can be recalibrated.

(g) The monitoring device's zero drift should be less than 5% of full scale in 24 hours.

(h) The set point(s) for the device's alarm(s) must be reset to the previous level(s) as soon as possible if the set point(s) has (have) been raised to silence an alarm following appropriate reaction.

(i) Fixed (nonportable) monitoring devices should activate appropriate ventilation systems at the lower set point as well as trigger an alarm. It may be desirable also to connect fixed monitoring devices to equipment to automatically shut down processes if the hydrogen sulfide concentration reaches preset levels. Automatic remote signaling (eg, by radio) is also possible. The device should have an auxiliary power supply in fixed locations.

(j) Many fixed monitoring devices and some portable ones have continuous strip-chart recording capability. This feature may be combined with an integrator circuit if the continuous monitoring device is to be used also for indicating the ceiling environmental concentrations, but this may only complement, not replace, real-time monitoring for the peak occupational exposure limit.

(k) The device and alarm should be intrinsically safe for use in hazardous locations.

(l) Portable hydrogen sulfide monitoring devices should be durable enough for field use and be light weight, less than 20 pounds (9.08 kg), preferably less than 10 pounds (4.54 kg). They should have a battery-status indicator that can be readily seen. Batteries should be checked frequently to ascertain that they develop the required voltage.

(m) The calibration of each instrument should be checked as needed, and necessary adjustments made.

(n) Alarms that are visible as well as audible are desirable.

Discussion

Hydrogen sulfide monitors in fixed locations are appropriate in enclosed spaces and where likely sources of the gas can be identified. The detector(s) should be positioned near likely sources or equally spaced near the floor, because hydrogen sulfide is slightly heavier than air.

If outdoors, if the source cannot be predicted, or if air currents may move hydrogen sulfide away from a fixed detector, then the fixed-location system shall be supplemented or replaced with portable monitoring devices.

Where considerable distances between work stations or multiple possible sources of hydrogen sulfide exist, additional monitors may be required to ensure worker safety. Alternately, a multipoint sampling system may be established with a single instrument, subject to the considerations in specifications (a), (b), and (c).

All direct-reading hydrogen sulfide monitors require electric power; some require that the detector or other parts of the device be kept at a constant temperature. These conditions are more readily met indoors than outdoors, but outdoor monitoring is still possible. If line current is used, indoors or out, there should be an auxiliary power supply, because an accident or explosion which results in the release of large quantities of hydrogen sulfide might also knock out electric power. Monitors using batteries should have battery-status indicators, and their status should be checked at least every shift to ensure that the device will continue to operate as needed. In cold climates, both batteries and electrochemical detectors may not function properly unless protected from the cold. Portable monitors may be worn under a coat for use outdoors, if the manufacturer's specifications permit, with tubing for air intake (from the lapel, usually) and exhaust. The likelihood that the tubing will absorb some of the gas is a lesser hazard than the failure of the device because of cold.

Monitoring devices should be calibrated at least once a week by exposing the detector to hydrogen sulfide gas at a known concentration. If the calibration is linear, a zero-span calibration of 0-100 ppm or higher may be desirable [171]. If the calibration is nonlinear, a zero-span calibration of 0-50 ppm or a multipoint calibration is desirable [171]. The concentration of the span gas should be checked at 6-month intervals by another method, eg, methylene-blue colorimetry or gas chromatography. A quality-control chart should be kept as a check on the stability of the span gas. Some instruments require that the detector be conditioned and calibrated daily by exposure to an ampule of the gas; this requirement has the advantage of keeping the monitoring device calibrated and the disadvantage that the detector may not respond adequately if this step is omitted.

Many hydrogen sulfide monitors have cross-sensitivities: some compounds other than hydrogen sulfide may elicit false-positive responses. In some cases, this may be advantageous: a detector that responds to hydrocarbons in addition to hydrogen sulfide may be useful for detecting leaks in petroleum production or refining facilities; some hydrogen sulfide monitors may be calibrated with carbon monoxide and conversion tables, and if the device is sensitive to another substance which is also toxic, eg, mercaptans, it can give warning of both hazards. The cross-sensitivities of detectors are often capable of election: a hydrogen sulfide detector which is not sensitive to hydrocarbons may be selected for areas with a high background concentration of hydrocarbons.

Workers must be trained to recognize and differentiate alarms and respond appropriately. An alarm that signals the presence of hydrogen sulfide at a concentration of 50 ppm indicates a serious, perhaps worsening, situation and requires evacuation; an alarm or signal at 10 ppm does not.

XII. APPENDIX IV

MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to a specific product or material shall be provided in the appropriate block of the Material Safety Data Sheet (MSDS).

The product designation is inserted in the block in the upper left corner of the first page to facilitate filing and retrieval. Print in upper case letters as large as possible. It should be printed to read upright with the sheet turned sideways. The product designation is that name or code designation which appears on the label, or by which the product is sold or known by employees. The relative numerical hazard ratings and key statements are those determined by the rules in Chapter V, Part B, of the NIOSH publication, An Identification System for Occupationally Hazardous Materials. The company identification may be printed in the upper right corner if desired.

(a) Section I. Product Identification

The manufacturer's name, address, and regular and emergency telephone numbers (including area code) are inserted in the appropriate blocks of Section I. The company listed should be a source of detailed backup information on the hazards of the material(s) covered by the MSDS. The listing of suppliers or wholesale distributors is discouraged. The trade name should be the product designation or common name associated with the material. The synonyms are those commonly used for the product, especially formal chemical nomenclature. Every known chemical designation or competitor's trade name need not be listed.

(b) Section II. Hazardous Ingredients

The "materials" listed in Section II shall be those substances which are part of the hazardous product covered by the MSDS and individually meet any of the criteria defining a hazardous material. Thus, one component of a multicomponent product might be listed because of its toxicity, another component because of its flammability, while a third component could be included both for its toxicity and its reactivity. Note that a MSDS for a single component product must have the name of the material repeated in this section to avoid giving the impression that there are no hazardous ingredients.

Chemical substances should be listed according to their complete name derived from a recognized system of nomenclature. Where possible, avoid using common names and general class names such as "aromatic amine," "safety solvent," or "aliphatic hydrocarbon" when the specific name is known.

The "%" may be the approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range or maximum amount, ie, "10-40% vol" or "10% max wt" to avoid disclosure of trade secrets.

Toxic hazard data shall be stated in terms of concentration, mode of exposure or test, and animal used, eg, "100 ppm LC50-rat," "25 mg/kg LD50-skin-rabbit," "75 ppm LC man," or "permissible exposure from 29 CFR 1910.1000," or, if not available, from other sources of publications such as the American Conference of Governmental Industrial Hygienists or the American National Standards Institute Inc. Flashpoint, shock sensitivity, or similar descriptive data may be used to indicate flammability, reactivity, or similar hazardous properties of the material.

(c) Section III. Physical Data

The data in Section III should be for the total mixture and should include the boiling point and melting point in degrees Fahrenheit (Celsius in parentheses); vapor pressure, in conventional millimeters of mercury (mmHg); vapor density of gas or vapor (air = 1); solubility in water, in parts/hundred parts of water by weight; specific gravity (water = 1); percent volatiles (indicated if by weight or volume) at 70 degrees Fahrenheit (21.1 degrees Celsius); evaporation rate for liquids or sublimable solids, relative to butyl acetate; and appearance and odor. These data are useful for the control of toxic substances. Boiling point, vapor density, percent volatiles, vapor pressure, and evaporation are useful for designing proper ventilation equipment. This information is also useful for design and deployment of adequate fire and spill containment equipment. The appearance and odor may facilitate identification of substances stored in improperly marked containers, or when spilled.

(d) Section IV. Fire and Explosion Data

Section IV should contain complete fire and explosion data for the product, including flashpoint and autoignition temperature in degrees Fahrenheit (Celsius in parentheses); flammable limits, in percent by volume in air; suitable extinguishing media or materials; special firefighting procedures; and unusual fire and explosion hazard information. If the product presents no fire hazard, insert "NO FIRE HAZARD" on the line labeled "Extinguishing Media."

(e) Section V. Health Hazard Information

The "Health Hazard Data" should be a combined estimate of the hazard of the total product. This can be expressed as a TWA concentration, as a permissible exposure, or by some other indication of an acceptable standard. Other data are acceptable, such as lowest LD50 if multiple components are involved.

Under "Routes of Exposure," comments in each category should reflect the potential hazard from absorption by the route in question. Comments should indicate the severity of the effect and the basis for the statement if possible. The basis might be animal studies, analogy with similar products, or human experiences. Comments such as "yes" or "possible" are not helpful. Typical comments might be:

> Skin Contact--single short contact, no adverse effects likely; prolonged or repeated contact, possibly mild irritation.
>
> Eye Contact--some pain and mild transient irritation; no corneal scarring.

"Emergency and First Aid Procedures" should be written in lay language and should primarily represent first-aid treatment that could be provided by paramedical personnel or individuals trained in first aid.

Information in the "Notes to Physician" section should include any special medical information which would be of assistance to an attending physician including required or recommended preplacement and periodic medical examinations, diagnostic procedures, and medical management of overexposed employees.

(f) Section VI. Reactivity Data

The comments in Section VI relate to safe storage and handling of hazardous, unstable substances. It is particularly important to highlight instability or incompatibility to common substances or circumstances, such as water, direct sunlight, steel or copper piping, acids, alkalies, etc. "Hazardous Decomposition Products" shall include those products released under fire conditions. It must also include dangerous products produced by aging, such as peroxides in the case of some ethers. Where applicable, shelf life should also be indicated.

(g) Section VII. Spill or Leak Procedures

Detailed procedures for cleanup and disposal should be listed with emphasis on precautions to be taken to protect employees assigned to cleanup detail. Specific neutralizing chemicals or procedures should be described in detail. Disposal methods should be explicit including proper labeling of containers holding residues and ultimate disposal methods such as "sanitary landfill," or "incineration." Warnings such as "comply with local, state, and federal antipollution ordinances" are proper but not sufficient. Specific procedures shall be identified.

(h) Section VIII. Special Protection Information

Section VIII requires specific information. Statements such as "Yes," "No," or "If necessary" are not informative. Ventilation requirements should be specific as to type and preferred methods. Respirators shall be specified as to type and NIOSH or US Bureau of Mines approval class, ie, "Supplied air," "Organic vapor canister," etc. Protective equipment must be specified as to type and materials of construction.

(i) Section IX. Special Precautions

"Precautionary Statements" shall consist of the label statements selected for use on the container or placard. Additional information on any aspect of safety or health not covered in other sections should be inserted in Section IX. The lower block can contain references to published guides or in-house procedures for handling and storage. Department of Transportation markings and classifications and other freight, handling, or storage requirements and environmental controls can be noted.

(j) Signature and Filing

Finally, the name and address of the responsible person who completed the MSDS and the date of completion are entered. This will facilitate correction of errors and identify a source of additional information.

The MSDS shall be filed in a location readily accessible to employees exposed to the hazardous substance. The MSDS can be used as a training aid and basis for discussion during safety meetings and training of new employees. It should assist management by directing attention to the need for specific control engineering, work practices, and protective measures to ensure safe handling and use of the material. It will aid the safety and health staff in planning a safe and healthful work environment and in suggesting appropriate emergency procedures and sources of help in the event of harmful exposure of employees.

MATERIAL SAFETY DATA SHEET

I PRODUCT IDENTIFICATION

MANUFACTURER'S NAME	REGULAR TELEPHONE NO. EMERGENCY TELEPHONE NO.
ADDRESS	
TRADE NAME	
SYNONYMS	

II HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	%	HAZARD DATA

III PHYSICAL DATA

BOILING POINT, 760 MM HG		MELTING POINT
SPECIFIC GRAVITY (H_2O=1)		VAPOR PRESSURE
VAPOR DENSITY (AIR=1)		SOLUBILITY IN H_2O, % BY WT
% VOLATILES BY VOL		EVAPORATION RATE (BUTYL ACETATE=1)
APPEARANCE AND ODOR		

IV FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD)			AUTOIGNITION TEMPERATURE		
FLAMMABLE LIMITS IN AIR, % BY VOL.	LOWER		UPPER		
EXTINGUISHING MEDIA					
SPECIAL FIRE FIGHTING PROCEDURES					
UNUSUAL FIRE AND EXPLOSION HAZARD					

V HEALTH HAZARD INFORMATION

HEALTH HAZARD DATA

ROUTES OF EXPOSURE

INHALATION

SKIN CONTACT

SKIN ABSORPTION

EYE CONTACT

INGESTION

EFFECTS OF OVEREXPOSURE

ACUTE OVEREXPOSURE

CHRONIC OVEREXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

EYES

SKIN

INHALATION.

INGESTION

NOTES TO PHYSICIAN

VI REACTIVITY DATA

CONDITIONS CONTRIBUTING TO INSTABILITY

INCOMPATIBILITY

HAZARDOUS DECOMPOSITION PRODUCTS

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

VII SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

NEUTRALIZING CHEMICALS

WASTE DISPOSAL METHOD

VIII SPECIAL PROTECTION INFORMATION

VENTILATION REQUIREMENTS

SPECIFIC PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY (SPECIFY IN DETAIL)

EYE

GLOVES

OTHER CLOTHING AND EQUIPMENT

IX SPECIAL PRECAUTIONS

PRECAUTIONARY
STATEMENTS

OTHER HANDLING AND
STORAGE REQUIREMENTS

PREPARED BY

ADDRESS

DATE

▸▸ Note: Appendix V, NIOSH Interim Work Practice Recommendations, of this document is superseded by NIOSH Publication No. 83-127, NIOSH Criteria Document: Comprehensive Safety Recommendations for Land-Based Oil and Gas Well Drilling ◂◂

NIOSH Criteria Documents: Criteria for a Recommended Standard: Occupational Exposure to Hydrogen Sulfide

XIII. APPENDIX V

NIOSH INTERIM WORK PRACTICE RECOMMENDATIONS

In response to a request, the following work practice recommendations were issued by NIOSH for the gas and oil industry.

HYDROGEN SULFIDE IN THE GAS AND OIL INDUSTRY: INTERIM WORK PRACTICE RECOMMENDATIONS

National Institute for Occupational Safety and Health
Division of Criteria Documentation & Standards Development
Office of Extramural Coordination & Special Projects
August 1976

Introduction

Hydrogen sulfide is found in solution in some crude oil. The gas begins to "pass off" as it reaches the surface with the process being greatly accelerated by heat, especially during refining. It is generally believed that excessive exposure can occur at many points in the oil drilling and refining operations. Some of the area/activities in which there might be a potential exposure to hydrogen sulfide are as follows:

1. Drilling operations: Recycled drilling mud, water portion from the sour crude wells, blow outs (infrequent).
2. Tank gauging (the opening of the tank hatch to measure the liquid level in the tank can result in the release of build-up hydrogen sulfide). Includes run-down tanks, storage tanks at pipeline stations, crude oil storage tanks in refineries, storage tanks for intermediate and finished products.
3. Field maintenance of wells (replacement of packing, pulling of pumping rods, etc.).
4. Entry into closed spaces including trenches, pits, process vessels, and tanks.
5. Leaks in pumps or lines (consideration of corrosion and embrittlement). Equipment maintenance.
6. Stripping of hydrogen sulfide and carbon dioxide from crude oil at the oil field and at the refinery.
7. Sulfur recovery during desulferization [sic] of sour crude; and from contaminated molten sulfur.

8. Injection of sour gas back into formation to stimulate oil production.
9. Asphalt storage and associated operations.
10. Acid cleansing of wells and process units.

Because of the extremely serious nature of the rapidly developing effects which may result from exposure to hydrogen sulfide at high concentrations in the oil and gas industry, we recommend that special attention be given to the development and implementation of certain work practices. Work practices related to controlling hydrogen sulfide exposures have been prepared by a number of organizations including the American Petroleum Institute (API), Society of Petroleum Engineers of the American Institute of Mining, Metallurgical and Petroleum Engineers (SPE of AIME), the National Safety Council, and may also be found in several state rules and regulations. If complied with, existing recommendations could provide worker protection, but it appears that they have not been fully implemented. Engineering controls, maintenance of equipment and implementation of work practice procedures are all important in preventing serious "accidents" reulting from exposure to hydrogen sulfide.

Work Practices and Recommendations

General work practices are well covered in the materials referred to above and need not be repeated. However, because of the type of serious accidents and deaths among workers in the gas and oil industry as well as community residents, special emphasis shall be placed on several types of work which have been involved in these accidents. They include entrance into confined spaces, tank gauging, line repair, and the use or lack of use of respirator equipment when working in areas of potentially high hydrogen sulfide concentrations (suspect areas). Automatic monitoring equipment is available in both stationary and portable styles. NIOSH recommends that continuous monitoring, with an automatic audible signal, be required in certain areas where sudden overexposure to hydrogen sulfide is possible.

1. Confined Spaces
   - (a) Entry into confined spaces such as tanks, pits, process vessels, and trenches shall be controlled by a permit system. Permits signed by an authorized employer representitive [sic] shall certify that preparation of the confined space, precautionary measures, and personal protective equipment are adequate, and that precautions have been taken to ensure that prescribed procedures will be followed. Entry procedures should be maintained in written form and readily available for review by affected employees.
   - (b) Confined spaces which have contained hydrogen sulfide shall be inspected and tested for oxygen

deficiency, hydrogen sulfide, and other contaminants and shall be thoroughly ventilated, cleaned, neutralized or washed, and then retested for hydrogen sulfide and oxygen prior to and during entry.

(c) Possible buildup of hydrogen sulfide into the confined space while work is in progress shall be prevented by positive means. (Example: Forced air ventilation of closed spaces during repair of leaks or equipment maintenance; securing intake valves or disconnecting intake lines.)

(d) Individuals entering confined spaces where they may possibly be exposed to hydrogen sulfide shall wear either a combination type-C supplied-air respirator operated in the continuous-flow mode (positive pressure) or pressure-demand mode (positive pressure) and an auxiliary self-contained breathing air supply, or a self-contained breathing apparatus operated in the pressure-demand mode (positive pressure) equipped with a full facepiece. Each individual shall also wear a suitable harness with lifelines tended by another employee outside the space who shall also be equipped with the necessary protective equipment, including a self-contained breathing apparatus which operates in the pressure-demand mode (positive pressure) and has a full facepiece. Communications (visual, voice, signal line, telephone, radio or other suitable means) shall be maintained by the standby person with the employee inside the enclosed space.

2. Suspect Areas

In such job activities which could be expected to potentially expose the worker to high levels of hydrogen sulfide (not defined in section 1 above), the work practices specified (in Sections 1(a), (b), (c), and (d)) shall be modified to provide adequate monitoring, ventilation, and personal protection. Examples of those job activities are: tank gauging, maintenance operations, and line repair.

3. Monitoring

Because of olfactory nerve fatigue (concentrations of hydrogen sulfide at 100 ppm or more can kill the sense of smell) a worker can enter an area where high concentrations of hydrogen sulfide are present without knowing it. Some means for constant monitoring with an automatic audible warning device shall be used in places where a sudden release of hydrogen sulfide might not be expected and would not be recognized without such continuous monitoring.

4. Training and Education

The effectiveness of any work practice program depends on type and availability of training and education services and materials which are available to employees. It is recommended that employee training be provided prior to initial assignment into a potential hydrogen sulfide exposure work area and that refresher training be conducted at regular intervals to keep all employees alerted to the potential danger which exists. This should include training in first aid and emergency procedures and since the worker will probably be responsible for his own protective gear, he should be instructed in proper inspection, maintenance, and emergency repair of his respiratory equipment [144].

XIV. TABLES AND FIGURE

TABLE XIV-1

PHYSICAL AND CHEMICAL PROPERTIES OF HYDROGEN SULFIDE

Molecular formula	H_2S
Formula weight	34.08
Specific gravity compared to air	1.192
Melting point	-82.9 C
Boiling point	-61.8 C
Solubility in water, 20 C	2.9 volumes gas/volume H_2O
Autoignition temperature	250 C
Explosive range in air	4.5-45.5%
Color	Colorless
Odor threshold	0.02 ppm
Olfactory fatigue level	100 ppm
Vapor pressure, 25 C	19.6 atm
Conversion factors	1 mg/cu m = 0.717 ppm 1 ppm = 1.394 mg/cu m

Adapted from references 1 and 2

TABLE XIV-2

OCCUPATIONS WITH POTENTIAL EXPOSURE TO HYDROGEN SULFIDE

Animal fat and oil processors
Animal manure removers
Artificial-flavor makers
Asphalt storage workers
Barium carbonate makers
Barium salt makers
Blast furnace workers
Brewery workers
Bromide-brine workers
Cable splicers
Caisson workers
Carbon disulfide makers
Cellophane makers
Chemical laboratory workers, teachers, students
Cistern cleaners
Citrus root fumigators
Coal gasification workers
Coke oven workers
Copper-ore sulfidizers
Depilatory makers
Dyemakers
Excavators
Felt makers
Fermentation process workers
Fertilizer makers
Fishing and fish-processing workers
Fur dressers
Geothermal-power drilling and production workers
Gluemakers
Gold-ore workers
Heavy-metal precipitators
Heavy-water manufacturers
Hydrochloric acid purifiers
Hydrogen sulfide production and sales workers
Landfill workers
Lead ore sulfidizers
Lead removers
Lithographers
Lithopone makers
Livestock farmers
Manhole and trench workers
Metallurgists
Miners
Natural gas production and processing workers
Painters using polysulfide caulking compounds
Papermakers
Petroleum production and refinery workers
Phosphate purifiers
Photoengravers
Pipeline maintenance workers
Pyrite burners
Rayon makers
Refrigerant makers
Rubber and plastics processors
Septic tank cleaners
Sewage treatment plant workers
Sewer workers
Sheepdippers
Silk makers
Slaughterhouse workers
Smelting workers
Soapmakers
Sugar beet and cane processors
Sulfur spa workers
Sulfur products processors
Synthetic-fiber makers
Tank gagers
Tannery workers
Textiles printers
Thiophene makers
Tunnel workers
Well diggers and cleaners
Wool pullers

Adapted from references 3-6

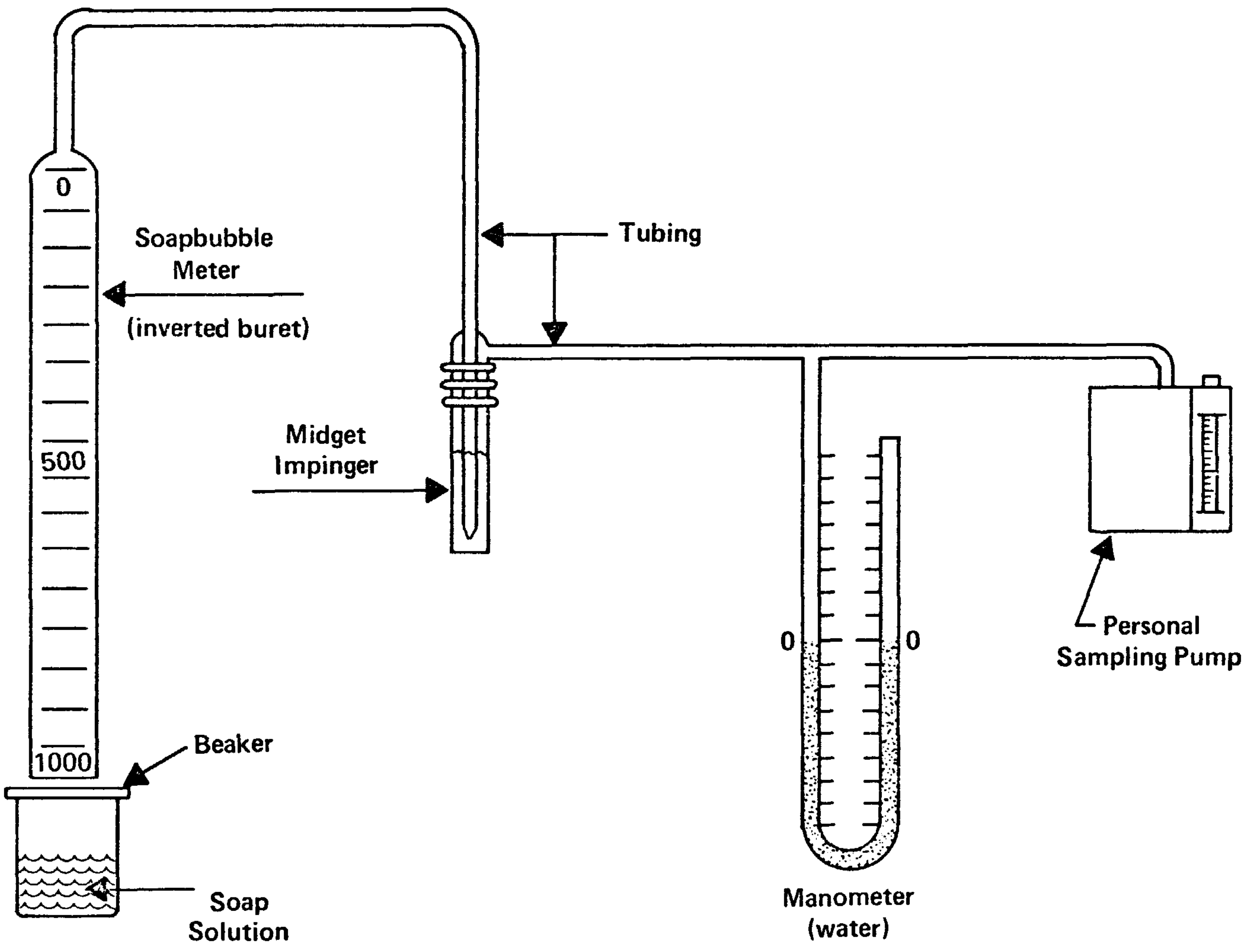

Figure XIV-1

CALIBRATION SETUP FOR PERSONAL SAMPLING PUMP WITH MIDGET IMPINGER

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