

#### 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) Chemico-physical, 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 sulfide.

(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  $\pm 25\%$  by NIOSH's certification program, and many are certified within  $\pm 10\%$ .

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 simultaneous 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.