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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